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Polymer-Supported Palladacycles: Efficient Reagents for Synthesis of Benzopyrans with Palladium Recovery. Relationship among Resin Loading, Pd:P Ratio, and Reactivity of Immobilized Palladacycles

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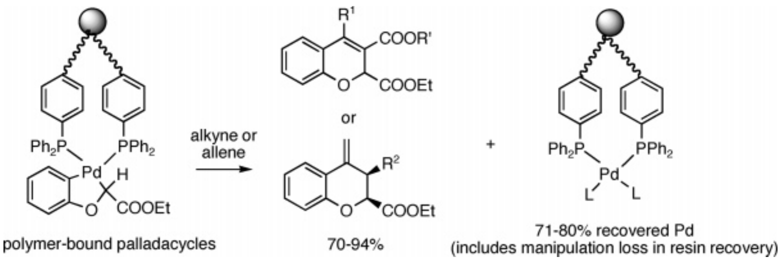

Oxapalladacycles were immobilized on polystyrene−divinylbenzene supports and treated with 3-aryl-2-propynoates or 1-alkyl-1,2-propadienes to afford 2*H*-1-benzopyrans in yields superior to those for solution-phase experiments. Isolation of benzopyrans was facilitated, and 71−80% of the palladium was recovered. Effects of resin loading with phosphorus and palladium were studied, and the optimum immobilized palladacycles featuring a medium loading with P (1.35 mmol P/g) and a high loading with Pd (Pd:P ratio 1:1.7) were identified. Resins with higher swelling capacities were more reactive.

Advances in solid-phase organic synthesis (SPOS)[1] led to the development of new technologies for parallel synthesis of combinatorial libraries.[2] In particular, the immobilization of transition-metal complexes on solid supports, providing catalysts or stoichiometric reagents,[3] has helped to address the associated environmental and economic concerns. The physical and chemical properties of the polymeric supports were shown to affect the outcome of chemical transformations occurring in the swelled polymer gel phase.[4] Although the polymer swelling has been considered the key prerequisite for good reactivity,[5] cases when the reaction kinetics did not correlate with the resin's swelling capacity are known.[6] Furthermore, the economically desirable resins with high functional group loadings (>1.5 mmol/g)[7] may give rise to detrimental microenviromental effects.[8] Surprisingly, studies focusing on fine-tuning of the polymer support structure to achieve optimum reactivities of the immobilized transition-metal complexes have remained limited,[9] and polymer-bound transition-metal catalysts have often been generated in situ by the addition of the metal salt to polymer-bound auxiliary ligands.[10] Our prior studies[11] uncovered a regiocontrolled conversion of palladacycles **I** into diverse 2*H*-

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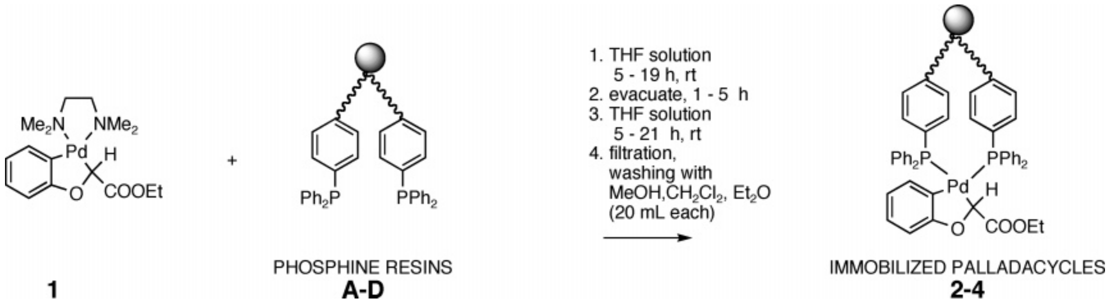
10.1021/jo052105w CCC: $33.50

TABLE 1. Preparation and Properties of the Immobilized Palladacycles



entry	resins with immobilized phosphines			immobilization conditions	immobilized palladacycles **2−4**				
		mmol of P/g[a]	swelling in DCE (mL/g)[b]	Pd:P[c]		Pd (%)[a]	P (%)[a]	Pd:P[d]	swelling in DCE (mL/g)[b]
1	**A**[e]	3.06	4.5	1:2.05	**2a**	10.03	5.73	1:1.9	3.2[f]
2	**A**	3.06		1:2.05	**2b**	9.21	6.12	1:2.3	2.9[f]
3	**B**[e]	3.01	4.5	1:2.02	**2c**	9.15	6.78	1:2.5	3.6
4	**B**	3.01		1:3.04	**2d**	8.41	7.49	1:3.0	3.7[f]
5	**C**[g]	1.35	5.7	1:1.69	**3a**	7.05	3.55	1:1.7	
6	**C**	1.35		1:1.69	**3b**	6.30	3.51	1:1.9	3.6[h]
7	**C**	1.35		1:2.53	**3c**	4.53	2.84	1:2.1	4.2
8	**C**	1.35		1:2.53	**3d**	5.44	3.84	1:2.4	4.1
9	**C**	1.35		1:5.06	**3e**	2.72	4.81	1:6.0	6.9
10	**C**	1.35		1:1.69	**3f**	7.26	3.63	1:1.7	
11	**D**[i]	0.89	5.3	1:1.80	**4a**	3.34	2.54	1:2.6	6.4
12	**D**	0.89		1:1.80	**4b**	3.35	2.54	1:2.6	6.7

[a] Established by commercial ICP analysis. [b] Swelling (volume of swelled resin (mL)/mass of dry polymer (g)) measured by the volumetric method.[15] [c] The mole ratio of palladacycle present in solution to total P present in the resin. [d] Calculated on the basis of the Pd and P analyses. [e] Resins **A** and **B** featured 200−400 mesh size and 2% cross-linking. [f] Resin sank in DCE. [g] Resin **C** featured 100−200 mesh size and 1% cross-linking. [h] Resin partially sank and partially floated in DCE. [i] Resin **D** featured 200−400 mesh size and 1% cross-linking.

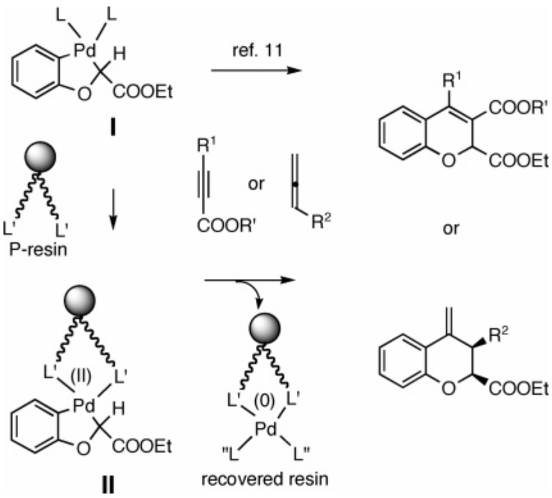


FIGURE 1. The synthetic methodology under investigation.

1-benzopyrans (Figure 1). Aiming to apply this methodology to combinatorial chemistry, we considered immobilization of palladacycles **I** to solid supports (Figure 1). Herein we report the preparation of polystyrene−divinylbenzene (PS-DVB)-supported oxapalladacycles **II** and a survey of the effects of the phosphine group[6] and palladium loading on the resin and of swelling capacities of the resins on the reactivity of the immobilized complexes. Preparations of diverse benzopyrans demonstrating the benefits of immobilized palladacycles **II** for product isolation and purification, as well as an efficient recovery of palladium (71−80%), are also described.

The attachment of palladacycles to solid supports was envisioned to occur through the substitution of a weak ligand *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (L−L = TMEDA) in soluble palladacycles **I** with monodentate phosphines (L′ = $RC_6H_4PPh_2$)[12] covalently bonded to polymeric supports (Figure 1).[13] In addition to commercially available polystyrene−divinylbenzene (PS-DVB)-bonded triphenylphosphine with phosphorus loading of 3.0 mmol of P/g (resins **A** and **B**) and 1.4 mmol of P/g (resin **C**), a resin with reduced loading (resin **D**, 0.89 mmol of P/g) was obtained by coupling of (*p*-diphenylphosphino)benzoic acid[14] to commercially available PS-DVB Wang resin (1.21 mmol of OH/g), thereby incorporating a benzyl ester linker[14] (Table 1). Swelling capacities of resins **A**−**D** in 1,2-dichloroethane (DCE) were measured by the volumetric method[15] (Table 1). Resins **A**−**D** were treated with solutions of oxapalladacycle **1** (THF, room temperature) for an initial reaction period followed by removal of the volatiles

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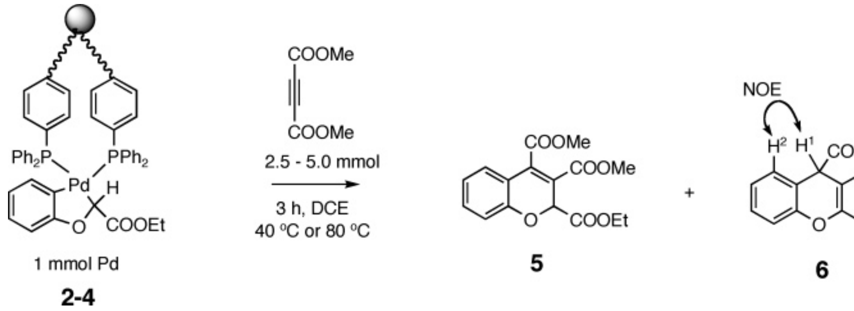
[12] Palladacycle **I** (L = PPh_3) reacted with dimethyl acetylenedicarboxylate (3.0 equiv) at 40 °C (1 h) to afford the corresponding 2*H*-1-benzopyran **5** in 95% yield. Palladacycle **I** (L = dppb, DIOP) afforded only <40% yield of benzopyran **5**.[11d,e]

[13] Leadbeater, N. E. *Curr. Med. Chem.* **2002**, *9*, 2147.

[14] Dahan, A.; Portnoy, M. *Org. Lett.* **2003**, *5*, 1197.

[15] Herein, the swelling capacity is represented as the volume of the swollen polymer per 1 g of dry resin; see: (a) Adams, J. H.; Cook, R. M.; Hudson, D.; Jammalamadaka, V.; Lyttle, M. H.; Songster, M. F. *J. Org. Chem.* **1998**, *63*, 3706. For volumetric methods, see: (b) Wilson, M. E.; Paech, K.; Zhou, W.-J.; Kurth, M. J. *J. Org. Chem.* **1998**, *63*, 5094.

TABLE 2. Alkyne Insertion Reactions of the Immobilized Palladacycles 2−4



	resin	P loading (mmol of P/g)^a	swelling range (mL/g)^b	Pd:P^c	range of Pd:P ratios^d	conditions time (h)/ temp (°C)	yield^e **5** + **6** (%)	**5**:**6** mole ratio^f	av yield (%)^g
1	**2a**	high (3.0)	3.2	1:1.9	1:(1.7−2.6)	3/40	17	5:1	17
2	**3a**	medium (1.4)	NA^h	1:1.7			35	22:1	35
3	**4a**	low (0.9)	6.4	1:2.6			87	20:1	84
4	**4a**			1:2.6			81	1:0	
5	**2a**	high (3.0)	2.9−3.6	1:1.9	1:(1.9−2.5)	3/80	49	1:0	55
6	**2b**			1:2.3			64	1:0	
7	**2c**			1:2.5			57	2:1	
8	**2c**			1:2.5			50	1:0	
9	**3a**	medium (1.4)	3.6 − 4.2	1:1.7	1:(1.7−2.4)	3/80	86	4:1	74
10	**3b**			1:1.9			84	3:1	
11	**3c**			1:2.1			69	3:1	
12	**3c**			1:2.1			72	3:1	
13	**3d**			1:2.4			59	2:1	
14	**4a**	low (0.9)	6.4	1:2.6	1:2.6	3/80	78	12:1	79
15	**4a**			1:2.6			80	12:1	
16	**2d**	high (3.0)	3.7	1:3.0	1:(3.0−6.0)	3/80	28	1:0	34
17	**2d**			1:3.0			39	1:0	
18	**3e**	medium (1.4)	6.9	1:6.0			0	-	0

[a] The loading of source resins **A**−**D**. [b] The range of the swelling capacities for multiple entries. [c] Pd:P molar ratio. [d] The range of Pd:P molar ratios in the immobilized palladacycles used. [e] Combined yield. [f] Molar ratio of the benzopyran products. [g] Average combined yield of **5** + **6** calculated from the indicated entries. [h] Not measured.

(TMEDA) under reduced pressure, fresh solvent addition, and a continued treatment for a second time period to favorably shift the equilibrium of the ligand exchange process.[16] Immobilized palladacycles **2**−**4** were isolated as air-stable yellow powders.[16] As expected, swelling capacities of resins **2**−**4** increased with decreasing loading with P and Pd, which is known to cause additional cross-linking.[4,5] In immobilized palladacycles **2a**−**d** and **3a**−**f** the Pd:P molar ratios (1:1.7−6.0) determined by ICP analyses[17] reflected satisfactorily within the experimental error the ratios of substrates **1** and **A**−**C** (P content) in the reaction mixtures (entries 1−10, Table 1). These data, along with ^{1}H NMR analyses of the material in the combined filtrate and resin extracts, suggested that, in most cases, the loading of palladium to the solid support was at least 90% complete.[18] In a sharp contrast, the ligand exchange reactions of resin **D** did not reach completion, and significant quantities (30%) of unreacted palladacycles **1** were recovered, even when prolonged reaction times and repeated cycles of ligand exchange−evacuation were employed.[19] Thus, the highest loading of resin **D** with palladium that could be achieved was Pd:P = 1:2.6 (entries 11 and 12, Table 1), and reproducibility of this protocol was compromised.[19] Due to economic concerns[7] immobilization of palladacycles on resin **D** with further decreased loading of Pd was not pursued.

The reactivity of palladacycles **2**−**4** was assessed by investigating the insertion of activated dimethyl acetylenedicarboxylate (DMAD).[11,12] Suspensions of immobilized palladacycles **2**−**4** in DCE were treated with DMAD for a standard time (3 h) at low (40 °C) or elevated (80 °C) temperatures to afford the 2*H*-1-benzopyran **5**,[11e] accompanied in some cases by smaller quantities of the chromatographically inseparable 4*H*-1-benzopyran **6** (Table 2).[20] The benzopyran **6** originated from an in situ isomerization of benzopyran **5** caused by high local concentrations of the phosphine and the palladacycle at elevated temperatures.[21] The isomerization was not expected to be problematic with alkynes other than DMAD (vide infra). For palladacycles with high and medium loading levels, e.g. resins

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[16] A quantitative exchange of the TMEDA ligand in palladacycle **I** (L−L = TMEDA) with PPh_3 occurred in a solution-phase experiment.[11e] Gel-phase ^{31}P NMR on resins **2**−**4** did not yield spectra with sufficiently narrow lines to provide useful characterization data. IR spectra of resins **2**−**4** did not change upon storage.

[17] The standard deviation of the ICP analysis of Pd or P was ±0.2−0.3%, translating into a precision of calculated Pd:P ratios of ±0.3 units, e.g. 1:(2.0 ± 0.3).

[18] The filtrates and resin extracts from experiments described in entries 1 and 4−10 (Table 1) contained either no palladacycle **1**, or only traces of palladacycle **1**, and in three cases 4−12% of the total balance of palladacycle **1**. The residues from experiments described in entries 2, 3, 11, and 12 (Table 1) contained 20−30% of residual palladacycle **I**.

[19] The lower *concentration* of phosphine groups in resin **D**, as well as the presence of electron-deficient phosphine ligands bearing COOR, may account for this observation. A partial oxidation of phosphine groups in resin **D** during its preparation was not ruled out.

[20] A ^{1}H NMR NOE experiment recorded on mixtures of benzopyrans **5** and **6** indicated the NOE correlation between protons H^1 and H^2 in benzopyran **6** (see Table 2).

2a−**d** and **3a**−**e**, several experiments utilizing resins with different Pd:P ratios were performed (entries 5−13, Table 2). Considering the precision of the measured Pd:P ratios,[17] the combined yields of products **5** and **6** arising from resins with Pd:P ratios in the range of 1:1.7−1:2.5 were averaged to provide statistically meaningful pieces of data (entries 5−8 and 9−13, Table 2). The reactivity of the high- and medium-loading resins **2** and **3** at 40 °C was limited (17−35% yields of **5** + **6**) in comparison to that of the solution-phase reaction (entries 1 and 2, Table 2).[12] Furthermore, the high-loading resins **2a**−**c** showed diminished reactivity even in reactions performed at 80 °C, providing a 55% average yield of **5** + **6** (entries 5−8, Table 2). Better yields of benzopyrans were obtained with resins featuring a minimal excess of phosphine: e.g., Pd:P ratios of 1:1.9−2.5 (compare entries 5−8 to entries 16 and 17, Table 2). Synthetically practical yields of the benzopyrans **5** and **6** (74%) could be obtained with medium-loading resins **3a**−**d** at elevated temperatures, with Pd:P ratios in the range 1:1.7−2.4 (entries 9−13, Table 2). Resin **3e** with an excess of free phosphine (Pd:P = 1:6) failed to afford any heterocyclic products (entry 18, Table 2), indicating that the alkyne insertion reaction was strongly inhibited by the excess of phosphine.[22] Further extension of the arbitrarily chosen reaction time (3 h), which may cause undesirable product isomerization,[21] would likely be needed to achieve yields comparable to those obtained from solution-phase experiments.[11,12] The improved reactivity profile of the medium-loading palladacycles **3a**−**d**, in comparison to that of the high-loading palladacycles **2a**−**c**, might reflect the increased swelling capacities of the medium-loading resins with lower cross-linking (Tables 1 and 2).[5] Seeking resins with excellent swelling capacities, and a higher chain flexibility,[4−8] we made unsuccessful attempts to immobilize palladacycles on poly(ethylene glycol)-grafted Tentagel resins.[23] As a replacement, palladacycle **4a** (0.89 mmol/g, mole ratio Pd:P = 1:2.6) derived from PS-DVB Wang resins was employed, although the range of accessible Pd:P mole ratios remained limited to Pd:P = 1:2.6 (vide supra) (Tables 1 and 2). Indeed, the yields of benzopyrans **5** and **6** isolated from reactions with palladacycle **4a**, at both low (84%) and elevated temperatures (79%) (entries 3−4 and 14−15, Table 2), exceeded the average yields obtained with resins **2** and **3**. The dramatic increase in reactivity at 40 °C achieved with resin **4a** is especially notable (compare entries 1 and 2 and entries 3 and 4, Table 2) and suggests that the microenvironment in the resin closely resembles the solution phase, resulting in only minimal isomerization of benzopyran **5** into **6**.[12,24] As indicated by the average combined yields of benzopyrans **5** and **6** obtained from reactions of immobilized palladacycles with different P-loading levels and comparable Pd:P ratios (1:1.7−2.6), the reactivity of resins **2**−**4** increased with decreasing loading with P, for reactions both at 40 °C (entries 1−4, Table 2) and at 80 °C (entries 5−15, Table 2). This trend parallels the increase in swelling capacities of the resins.[5] Additional factors, including the electronic properties of the ligand, or the effects of the polymer support structure on the chelate size and flexibility of the ligand sphere of immobilized palladium(II) complexes, may be responsible for the observed reactivities of resins **2**−**4**.[24] On the basis of the data in Table 2 the medium-loading immobilized palladacycle with the molar ratio Pd:P = 1:1.7 was selected as a resin with the optimum balance between reactivity and process economy (e.g. mass of polymer per 1 mol of Pd). Resin **4a**, despite its promising reactivity, proved impractical to synthesize and use on a larger scale. The described results highlight the importance of considering a precise loading of the polymer with the transition metal and the auxiliary ligand when developing reagents for SPOS.

The resins were recovered as orange-colored powders, likely bearing complexes of palladium(0) with phosphine and DMAD ligands (Figure 1).[25] Considering our failed attempts at palladium recovery via scavenging resins,[26] the potential of immobilized palladacycles **II** as tools for palladium recovery was explored. To evaluate this technology, reactions with alkynes and allenes less activated than DMAD,[27a] which may compromise the retention of palladium(0) on the solid support, were studied (Table 3). The medium-loading immobilized palladacycle **3** (resin **3f**, Pd:P = 1:1.7, entry 10, Table 1) was treated for an extended time (24 h) with aromatic alkynyl esters and aliphatic allenes at elevated temperatures in DCE or in THF[11] (Table 3). The resins **E**−**I** were recovered by filtration, and the heterocycles were isolated from the combined filtrates and resin extracts. The immobilized oxapalladacycle **3f** afforded excellent yields of benzopyrans **7a**−**c** (70−94%) as single regioisomers (entries 1−3, Table 3). The yields of benzopyrans **7a** (94%), **7b** (70%), and **7c** (79%) compared favorably with those for solution-phase reactions of palladacycle **I** (L = PPh_3), providing the benzopyrans in 76%,[11e] 62%, and 65% yields, respectively. Insertion of allenes afforded benzopyrans **8** and **9** in yields higher, 90% and 76%, than those achieved in solution, e.g. 84% and 64%, respectively, with equally high ratios of regioisomers **8a**:**9a** and **8b**:**9b** (entries 4 and 5, Table 3).[11b] The improved yields of the solid-phase syntheses demonstrate the ease of purification of the crude mixtures, which contained only the heterocycles[28] and the alkynes or allene dimers,[29] permitting high-yielding separations. Resins **E**−**G** were isolated from reactions with alkynes as reddish brown powders.[27b] In contrast, resins **H** and **I**, arising from reactions with allenes, were black powders, clearly containing encapsulated palladium as anticipated due to the relatively weaker bonding of allenes to

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[21] Isomerization of benzopyran **5** into **6** at elevated temperatures in solution required the presence of free phosphine and/or palladacycle (see the Supporting Information).

[22] Control reactions of palladacycle **I** (L = PPh_3) with dimethyl acetylenedicarboxylate (3.0 equiv) in solution were inhibited by an excess of phosphine (see the Supporting Information).

[23] Palladacycles immobilized on Tentagel resins could only be obtained as spongelike materials retaining solvent, undergoing oxidation, and rapidly releasing palladium(0).

[24] The lower concentration of the phosphine and the additional linker in palladacycle **4a** may increase the conformational flexibility of the ligand sphere, thus generating complexes with reactivity similar to that of palladacycle **I** (L = PPh_3). For effects of the conformational flexibility of immobilized ligands, see: Nozaki, K.; Itoi, Y.; Shibahara, F.; Shirakawa, E.; Ohta, T.; Takaya, H.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 4051.

[25] IR spectra recorded on the resin recovered from the experiment in Table 2, entry 13, featured strong absorptions for $\nu_{C\equiv C}$ at 1843 and 1830 cm^{-1}, corresponding to the IR data reported for the isolated $(PPh_3)_2Pd(DMAD)$ complex (1845 and 1830 cm^{-1}); see: Greaves, E. O.; Lock, C. J. L.; Maitlis, P. L. M. *Can. J. Chem.* **1968**, *46*, 3879.

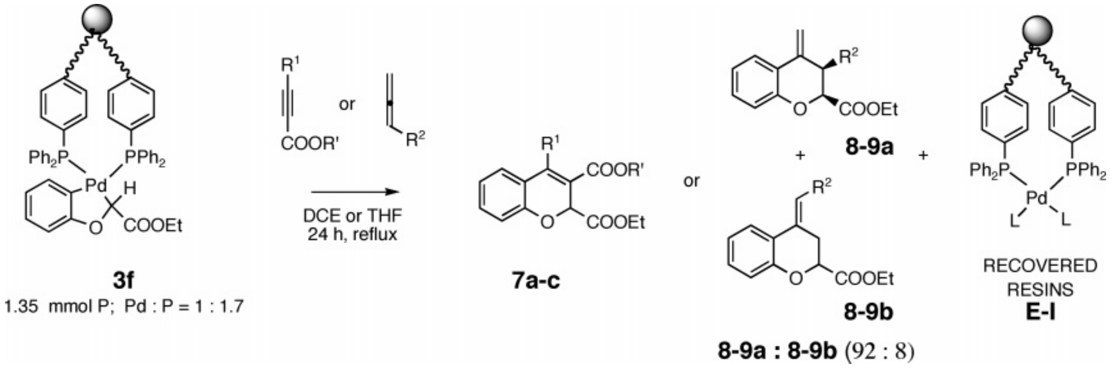
[26] Palladium(0) from solution-phase reactions could not be efficiently removed by the use of 3-mercaptopropyl-functionalized silica gel. For Pd scavenging see: Crudden, C. M.; Sateesh, M.; Lewis, R. *J. Am. Chem. Soc.* **2005**, *127*, 10045.

[27] (a) Ahlquist, M.; Fabrizi, G.; Cacchi, C.; Norrby, P.-O. *Chem. Commun.* **2005**, 4196. (b) IR data recorded on resins **E**−**G** are provided and discussed in the Supporting Information.

[28] Ziegert, R. E.; Torang, Knepper, K.; Brase, S. *J. Comb. Chem.* **2005**, *7*, 147.

[29] For palladium(0)-catalyzed dimerization of allenes, see: Arisawa, M.; Sugihara, T.; Yamaguchi, M. *Chem. Commun.* **1998**, 2615.

TABLE 3. Solid-Phase Synthesis of 2*H*-1-Benzopyrans



	alkyne/allene	conditions solv/ time (h)/temp (°C)	product	yield (%)	solution yield (%)[a]	recovered resin	Pd (%)[b]	recovered Pd (%)[c]
1	$R^1 = Ph$; $R' = Et$	DCE/24/80	**7a**	94	76	**E**	5.53	78
2	$R^1 = p$-FC_6H_4; $R' = Me$	DCE/24/80	**7b**	70	62	**F**	5.69	72
3	$R^1 = p$-$MeOC_6H_4$; $R' = Me$	DCE/24/80	**7c**	79	65	**G**	6.00	80
4	$R^2 =$ *n*-hexyl	THF/24/65	**8a**:**8b** (92:8)[d]	90	84	**H**	5.98	71
5	$R^2 =$ (2-ethyl)hexyl	THF/24/65	**9a**:**9b** (92:8)[d]	76	64	**I**	6.03	77

[a] Yields of solution-phase reactions with palladacycle **I** ($L = PPh_3$). [b] Pd content (mass %) established by commercial ICP analyses. [c] The mol % of Pd (based on mol of Pd present in the immobilized palladacycle **3f**) recovered in resins **E**−**I**. [d] The ratio of the regioisomeric products.

palladium(0).[27] The content of palladium (5.53−6.03% Pd by weight) and the mass of the dry isolated resins **E**−**I** indicated that 71−80% of the Pd originally present in resin **3f** was recovered from these experiments (Table 3). The good levels (70−80%) of Pd recovery, including a manipulation loss, demonstrate the environmental and economic benefits of the solid-phase technology and motivate our studies aimed at designing methods for the reuse of recovered resins **E**−**G** in these reaction systems.

In summary, immobilized oxapalladacycles were synthesized. Resins featuring a medium loading with phosphorus (1.4 mmol of P/g) and a high loading with palladium (Pd:P = 1:2.0) provided the most practical reagents. The reactivity of polymer-bound oxapalladacycles correlated with the swelling capacities of the resins. 4-Aryl- or 2-alkyl-substituted 2*H*-1-benzopyrans were prepared from the polymer-supported oxapalladacycle in better yields (70−94%) than from analogous solution-phase experiments. This new technology facilitated product isolation and purification and allowed for the recovery of 71−80% of the palladium metal. The protocol is currently being applied to parallel synthesis of combinatorial libraries.

Experimental Section

Preparation of Immobilized Palladacycles 2−4. A suspension of the phosphine resins **A**−**D** (equivalent to 1.7−3.3 mmol of P) in the solution of the palladacycle **1** (1 mmol) in THF (10−33 mL/1 mmol of Pd) was stirred for the initial time period (5−19 h) at room temperature under argon. Volatile components were removed under reduced pressure (1 mmHg, 1−5 h). Fresh THF (10−15 mL/1 mmol of Pd) was added, and the resulting suspension was stirred for the second time period (5−21 h). In some cases, the cycle of stirring and evacuation was repeated. The suspension was filtered, and the resin was washed with methanol (20 mL), methylene chloride (20 mL), methanol (20 mL), methylene chloride (20 mL), and diethyl ether (20 mL) and dried under reduced pressure to afford immobilized palladacycles **2**−**4** as yellow powdery solids. The filtrates were evaporated, and the crude extracts were analyzed by ^1H NMR spectroscopy. Data for the preparation of the individual resins **2**−**4** are provided in the Supporting Information.

Synthesis of 2*H*-1-Benzopyrans 7a−c, 8, and 9 from Immobilized Palladacycle 3f. To a suspension of the immobilized palladacycle **3f** (7.26% mass Pd, Pd:P mol ratio 1:1.7; 0.100 mmol of Pd) in 1,2-dichloroethane (3.0 mL for the reaction with alkynes) or THF (3.0 mL for the reaction with allenes) at room temperature under argon was added either the alkyne (0.3 mmol) or allene (0.4 mmol). The resulting suspension was refluxed for 24 h under argon. The suspension was filtered, and the resin was washed with methanol (20 mL), methylene chloride (20 mL), and diethyl ether (20 mL), and dried under vacuum to afford the recovered resins as yellow to dark orange powders or black solids. The filtrate and resin washes were combined, solvents were removed under reduced pressure, and the crude product was purified by flash chromatography over silica, with ethyl acetate/hexane mixtures as eluent to afford benzopyrans **7a**−**c**, **8,** and **9** as colorless oils. Data for the preparations of heterocycles **5**−**9** are given in the Supporting Information.

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Supporting Information Available: Text and figures giving methods for synthesis of resin **D**, immobilized palladacycles **2**−**4**, and benzopyrans **7**−**9**, procedures for experiments in Table 2, and solution-phase controls, including ^1H and ^{13}C NMR spectra for new compounds and measurements of the resin swelling. This material is available free of charge via the Internet at http://pubs.acs.org.

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