Simple Palladacyclic and Platinacyclic Catalysts for the 1,4-Conjugate Addition of Arylboronic Acids and Arylsiloxanes to Enones

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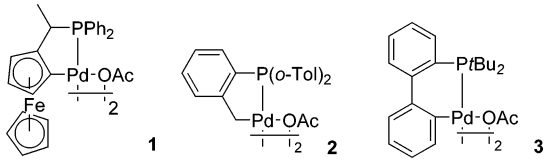
Received July 19, 2007

A range of palladacyclic, platinacyclic, and pincer-based catalysts have been tested for activity in 1,4-conjugate addition reactions. π-Acidic palladacycles show excellent activity at room temperature in the reaction of enones with arylboronic acids and reasonable activity when the arylboronic acids are replaced by arylsiloxanes. The X-ray structures of three new palladium κ^3-"*PCP*"-pincer complexes are presented; surprisingly, these complexes show no activity, despite the fact that notionally related phosphine and carbene adducts of palladacycles do.

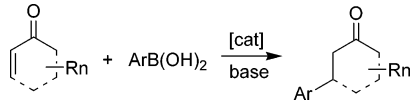
Introduction

The 1,4-addition of arylboronic acids to enones (Scheme 1) and related substrates is a versatile method for the formation of new C−C bonds. To date, the catalysis of these reactions has been dominated by rhodium-based complexes.[1]

By contrast, the use of palladium-based systems remains less well developed, despite the lower cost associated with palladium catalysis.[2−5] This is in part due to the propensity of palladium catalysts to promote the competitive formation of Heck coupling products via β-elimination pathways.[3] Very recently, Hu and co-workers demonstrated that electron-rich palladacycles, in particular complex **1**, show excellent activity in the conjugate additions of arylboronic acids.[4] They reasoned that the superior activity that palladacycle **1** showed over complexes **2** and **3** was due to a combination of the smaller size of the substituents on the P donor and the higher electron density on the metalated aromatic ring; factors that should lead to **1** showing a reduced propensity to undergo reductive elimination in the presence of an aryl nucleophile, a process that would generate inactive palladium(0) species.



Scheme 1. 1,4-Conjugate Addition of Arylboronic Acids to Enones



It may be anticipated that lowering the net electron density on the palladium center would lead to a further increase in activity in Lewis acid catalysis. Indeed, several of the most efficient catalysts based on Pd(II) are cationic.[5] The lowering of electron density of a neutral palladacyclic catalyst could be achieved if the electron-donating orthometalated phosphine moieties in complexes **1** are replaced by more π-acidic orthometalated aryl phosphite or phosphinite groups. In this regard, it is worth noting that the activity of "*PCP*"-bis(phosphite) pincer complexes in the nucleophilic allylation of benzaldehyde with allyltributyltin is markedly enhanced as compared to that of more electron-rich bis(phosphinite) complexes.[6]

If the rate of catalysis is significantly faster than the rate of reductive elimination to inactive Pd(0) species, then palladacycles with π-acidic ligands may be expected to be very active catalysts. For this reason, we decided to compare the activity of a range of phosphite- and phosphinite-based palladacycles, pincer complexes, and platinacycles with varying steric and electronic properties in the 1,4-conjugate addition reactions of arylboronic acids and arylsiloxanes, and the results from this study are reported below.

Results and Discussion

The P-based palladacycles, pincer complexes, and platinacycle investigated in this study are shown in Chart 1. In addition, we examined the use of the new palladium bis(phosphinite) κ^3-

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(1) For recent reviews on Rh(I)-catalyzed addition reactions of arylboronic acids with carbonyl-containing compounds, see: (a) Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3364. (b) Hayashi, T.; Yamasaki, K. *Chem.Rev.* **2003**, *103*, 2829. (c) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169−196 and references cited therein.

(2) For recent examples of Pd catalysis, see: (a) Yamamoto, T.; Iizuka, M.; Ohta, T.; Ito, Y. *Chem. Lett.* **2006**, *35*, 198. (b) Gini, F.; Hessen, B.; Minnaard, A. J. *Org. Lett.* **2005**, *23*, 5309. (c) Lu, X.; Lin, S. *J. Org. Chem.* **2005**, *70*, 9651.

(3) (a) Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S.; Shim, S. C. *J. Org. Chem.* **1995**, *60*, 883. (b) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317.

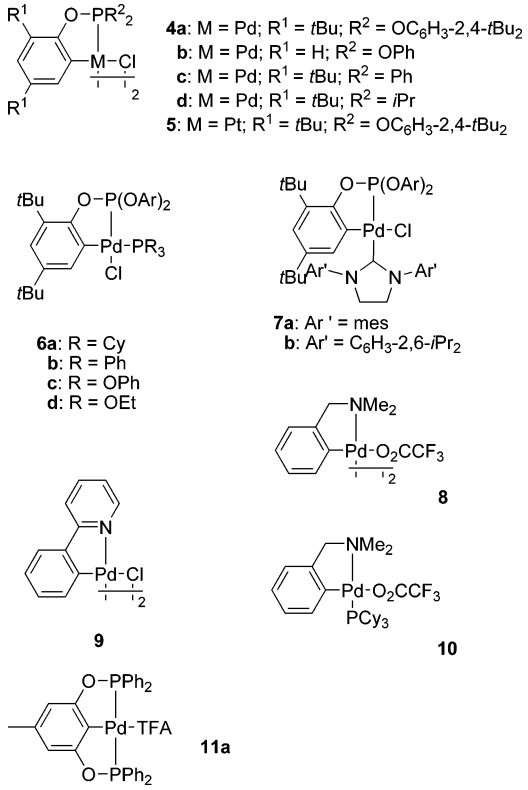
(4) He, P.; Lu, Y.; Dong, C.-G.; Hu, Q.-S. *Org. Lett.* **2007**, *9*, 343.

(5) For examples of cationic palladium catalysts, see: Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Chem. Lett*. **2003**, *32*, 752. Also see ref 3b.

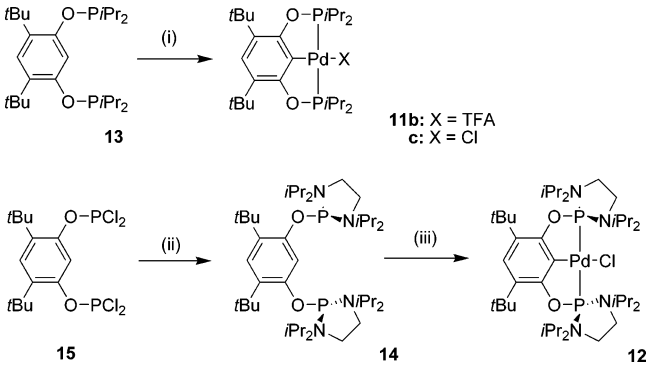
(6) Baber, R. A.; Bedford, R. B.; Betham, M.; Blake, M. E.; Coles, S. J.; Haddow, M. F.; Hursthouse, M. B.; Orpen, A. G.; Pilarski, L. T.; Pringle, P. G.; Wingad, R. L. *Chem. Commun.* **2006**, 3880.

10.1021/om700724c CCC: $37.00
Publication on Web 11/07/2007

Chart 1



Scheme 2. Synthesis of Pincer Complexes[a]



[a] Conditions: (i) $Pd(TFA)_2$, THF, rt, 2 h or $[PdCl_2(NCMe)_2]$, 1,2-dichloroethane, reflux, 18 h. (ii) *N*,*N*′-Diisopropylethylene diamine, Et_3N, toluene, 90 °C, 18 h. (iii) 1,2-Dichloroethane, reflux, 18 h.

"*PCP*"-pincer complexes **11b** and **c** and the related pincer complex **12**, which were prepared by reaction of appropriate Pd(II) precursors with the free pincer ligands **13** and **14** (Scheme 2).

The bis(diamidophosphinite)pincer ligand **14** was prepared from the resorcinol bis(dichlorophosphite) **15** in situ and used without purification in the synthesis of complex **12**. The ^{31}P NMR spectra of complexes **11b** and **c** show singlets at 186.4 and 185.9 ppm respectively, close to that reported for the analogous complex $[PdCl\{\kappa^3\text{-}P,C,P\text{-}C_6H_3\text{-}2,6\text{-}(P^iPr_2)_2\}]$ (187.7 ppm).[7] The ^{31}P NMR spectrum of complex **12** shows a singlet at 132.6 ppm.

The structures of complexes **11b**,**c** and **12** were confirmed by single-crystal X-ray analysis and the molecules are shown in Figures 1−3.[8] The lengths of the Pd−C bonds in complexes

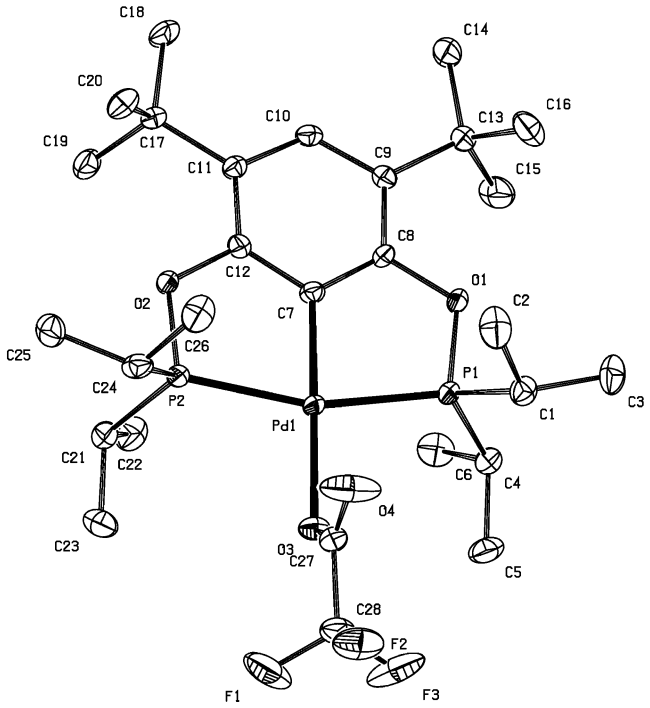


Figure 1. The molecular structure of complex **11b**. Thermal ellipsoids set at 50% probability.

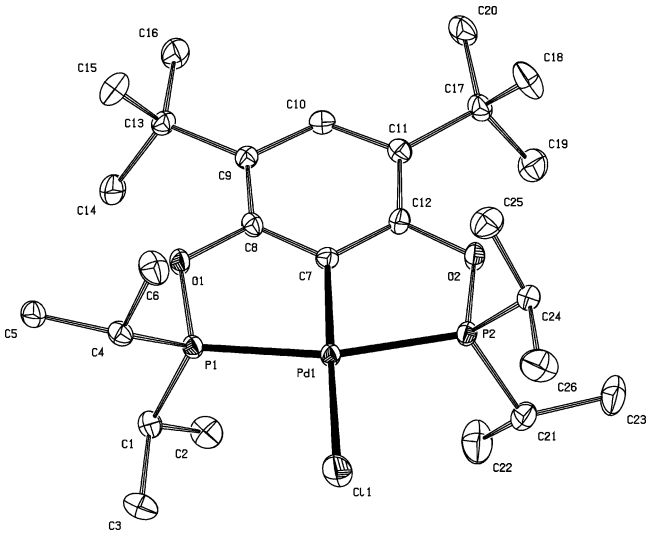


Figure 2. The molecular structure of complex **11c**. Thermal ellipsoids set at 50% probability.

11b and **c** are essentially identical to each other and that in $[Pd(O_2CCF_3)\{\kappa^3\text{-}P,C,P\text{-}C_6H_3\text{-}2,6\text{-}(P^iPr_2)_2\}]$,[7] while the Pd−C bond in complex **12** (1.974(3) Å) is about 0.15 Å longer.

(7) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redón, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*−*2*, 958.

(8) For full crystallographic data, see Supporting Information. Crystal data: **11b**, $C_{28}H_{47}F_3O_4P_2Pd$, $M = 673.00$, monoclinic, $a = 14.7332(4)$, $b = 10.3695(7)$, $c = 23.1394(14)$ Å, $\beta = 96.308(4)°$, $V = 3513.7(3)$ Å^3, $T = 120(2)$ K, space group $P2_1/c$, $Z = 4$, $\mu = 0.662$ mm^{-1}, $R_{int} = 0.0334$ (for 35 909 measured reflections), $R_1 = 0.0326$ [for 6494 unique reflections with $>2\sigma(I)$], w$R_2 = 0.1047$ (for all 8037 unique reflections); **11c**, $C_{26}H_{47}ClO_2P_2Pd$, $M = 595.43$, monoclinic, $a = 10.4540(13)$, $b = 13.929(3)$, $c = 20.714(6)$ Å, $\beta = 100.759(19)°$, $V = 2963.2(11)$ Å^3, $T = 120(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu = 0.844$ mm^{-1}, $R_{int} = 0.0334$ (for 35 376 measured reflections), $R_1 = 0.0245$ [for 5827 unique reflections with $>2\sigma(I)$], w$R_2 = 0.0661$ (for all 6776 unique reflections); **12**, $C_{30}H_{55}ClN_4O_2P_2Pd$, $M = 707.57$, triclinic, $a = 13.335(3)$, $b = 15.403(3)$, $c = 18.835(4)$ Å, $\alpha = 85.42(3)°$, $\beta = 89.33(3)°$, $\gamma = 65.45(3)°$, $V = 3506.8(15)$ Å^3, $T = 100(2)$ K, space group $P\bar{1}$, $Z = 4$, $\mu = 0.728$ mm^{-1}, $R_{int} = 0.0395$ (for 39 545 measured reflections), $R_1 = 0.0433$ [for 12 756 unique reflections with $>2\sigma(I)$], w$R_2 = 0.1116$ (for all 16 023 unique reflections).

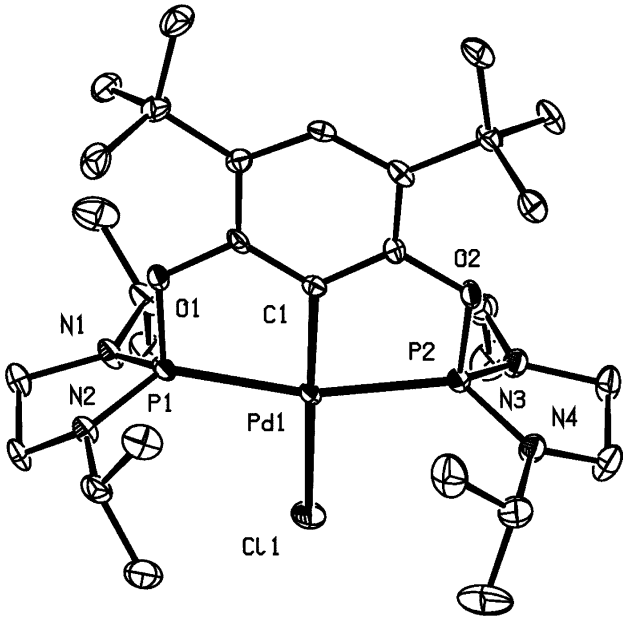


Figure 3. The molecular structure of complex **12**. Thermal ellipsoids set at 50% probability.

In the first instance, we screened the catalysts **4**−**12** in the addition of phenylboronic acid to chalcone, and the results of this study are summarized in Table 1. As can be seen, all of the N-based palladacycles and their phosphine adducts tested show no activity (entries 1−3), and rapid catalyst deactivation is observed on addition of the boronic acid. This is in accord with Hu and co-workers observation that an *N,C*-palladacycle based on 2-phenyl-4,4-dimethyloxazoline is inactive.[4] In sharp contrast, all of the P-based palladacycles and platinacycles tested show moderate to excellent activity.

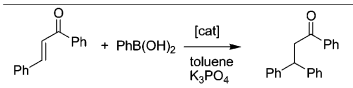
The phosphite-based palladacyclic complex **4a** efficiently catalyzes the coupling of phenylboronic acid with chalcone at room temperature, with essentially quantitative conversion to product being obtained in less than 30 min at 1 mol % Pd loading in toluene. On changing the solvent (entries 6−10), it was found that both dichloromethane and THF give satisfactory performance, although the results are not quite as good as those obtained in toluene. Gratifyingly, the reaction proceeds well under aerobic conditions (entry 11).

At 0.1 mol % loading of **4a**, 43% conversion to the desired product is seen within 6 h; increasing the reaction time further does not lead to improved results (entries 12 and 13). Comparing entries 4 and 14, it can be seen that reducing the size of the orthometalated triarylphosphite leads to a reduction in performance. Similarly a comparison of entries 5, 15, and 16 shows that the catalyst performance is sensitive to changes in the electronic properties of the orthometalated ligands, with the less π-acid diisopropyl phosphinite-based palladacycle **4d** showing reduced activity compared with **4a**. This is in agreement with the suggestion that more π-acidic ligands should render the metal center more electron-deficient, thus facilitating Lewis acid catalysis. The π-acidity of the diphenylphosphinite ligand in complex **4c** is intermediate between the ligands in **4a** and **4d** and so is the activity, although it is closer to that observed for the more electron-deficient complex **4a** with a significant diminution only apparent at 0.1 mol % Pd loading (compare entries 12 and 17).

The platinum analogue of **4a**, complex **5**, shows moderately good activity (entry 18), comparable to that shown by the palladacyclic complex **4d**, but is not as efficient as **4a**; Zhang and co-workers have shown a similar ordering of activity in platinum and palladium *PCP*-pincer complexes in Lewis acid catalysis.[9] The use of phosphine, phosphite, and carbene adducts of the phosphite palladacycle **4a**, complexes **6** and **7**, gives variable results, but in all cases the activity obtained is lower than that for the parent palladacycle irrespective of size, electronic factors, or isomerism (entries 19−24).

The pincer complexes **11** and **12** showed no activity regardless of electronic and steric variation of the pincer ligand or the nucleofugicity of the "X" group (Cl or TFA) on palladium. This is perhaps surprising considering that they are notionally

Table 1. Screening of Metallacycles (Pd, Pt) and Pincer Complexes in the Coupling of Phenylboronic Acid with Chalcone[a]



Entry	Catalysts [mol% Pd]	Solvent	Time (h)	Conversion, %[b]
1	**8** [5]	Toluene	1	0
2	**9** [5]			0
3	**10** [5]			0
4	**4a** [5]			>99
5	**4a** [1]		0.5	> 99
6	**4a** [5]	Hexane		29
7		CH_2Cl_2		90
8		1,4-dioxane		37
9		THF		97
10		Et_2O		16
11		Toluene		> 99[c]
12	**4a** [0.1]		6	43
13	**4a** [0.1]		18	44
14	**4b** [5]		1	79
15	**4d** [1]		1	78
16	**4c** [1]		1	98
17	**4c** [0.1]		6	22
18	**5** [5]		1	71
19	**6a** [1]		1	77
20	**6b** [1]			23
21	**6c** [1]			56
22	**6d** [1]			24
23	**7a** [5]			44
24	**7b** [5]			70
25	**11a** [5]			0
26	**11b** [5]			0
27	**11c** [5]			0
28	**11c** [5] + $AgBF_4$ (4 equiv.)			0
29	**12** [5]			0

[a] Conditions: $PhB(OH)_2$ (1.0 mmol), chalcone (0.5 mmol), K_3PO_4 (0.5 mmol), solvent (2 mL), rt. [b] Conversion to 1,3,3-triphenylpropanone determined by ^1H NMR spectroscopy (1,3,5-$(MeO)_3C_6H_3$, internal standard), average of two runs. [c] Under air.

(9) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374.

related to the phosphine, phosphite, and carbene adducts **6** and **7** and that palladium *PCP*-bis(phosphinite) and related bis(phosphite) pincer complexes have been successfully used in a range of catalytic nucleophilic additions.[6,10] Presumably, the lack of activity in these cases is due either to the structural rigidity or a lack of lability associated with the pincer motif at lower reaction temperatures. The addition of $Ag[BF_4]$, which should lead to the in situ formation of a cationic complex with a vacant coordination site, proved ineffective.

In all of the successful reactions, the ^1H NMR spectrum of the product mixture indicated no Heck coupling byproducts, suggesting that competitive β-elimination is not a problem with palladacyclic catalysts. The results of this screen show the best catalyst system to be the phosphite-based complex **4a**; furthermore, the commercial availability of both the parent triarylphosphite ligand and the palladacycle **4a** renders this the catalyst of choice, and it was therefore exploited in the remainder of the catalytic studies. The results of the use of **4a** in the coupling of various arylboronic acids with α,β-unsaturated ketones and related Michael acceptors are summarized in Table 2.

As can be seen, very high activity is observed in most cases at room temperature and 5 mol % Pd catalyst loading, irrespective of whether the arylboronic acid used is electron-rich or electron-deficient. The introduction of steric hindrance into the arylboronic acid leads to a lowering in activity with 2-tolylboronic acid, giving only 37% conversion to the desired product in the coupling with chalcone at room temperature (entry 5); however, when the reaction is repeated for 6 h at 50 °C, then conversion increases to 96% (88% isolated yield, entry 6). Changing the enone to (*E*)-4-phenylbut-3-en-2-one, cyclohexenone, 5,6-dihydro-*2H*-pyran-2-one, or cyclopentenone again leads to between very high and essentially quantitative conversion to the desired products (entries 7−11). Lower activity is observed with the open-chain alkyl-substituted enone pent-3-ene-2-one. Replacing enones with β-nitrostyrene leads to unsatisfactory performance, even when the temperature and reaction time are increased, in which case only 47% conversion to product is obtained (entry 13). Again, in all cases, ^1H NMR spectroscopy showed no Heck products derived from competitive β-elimination; indeed, the spectra show only product and residual staring materials.

We next investigated the possibility of replacing the arylboronic acids with arylsiloxanes. While such substrates have been exploited as the nucleophile in rhodium-catalyzed reactions,[11] much less attention has been focused on their use in palladium-catalyzed addition reactions.[3b,5,12,13] The results from this study are summarized in Table 3. In the first instance, we performed a brief optimization study. Compared with the use of anhydrous toluene as solvent, aqueous dioxane proved to be deleterious in the reaction of phenyl trimethoxysilane with chalcone, using 20 mol % $Ag[BF_4]$ as an activator. This is perhaps a little surprising when it is considered that in analogous rhodium-catalyzed reactions the active nucleophile is suggested to be the hydrolyzed arylsilanol.[11e] Increasing the loading of $PhSi(OMe)_3$ proved beneficial until a maximum was encountered at 3 equiv, which gives 76% spectroscopic yield. The mostly likely function of the $Ag[BF_4]$ additive is that it generates a cationic palladacyclic species in situ, which further increases the electron deficiency of the palladium center, increasing the propensity of a coordinated substrate to react with nucleophiles. By contrast, activation of the siloxane seems to work less well; the addition of fluoride or phosphate anions gives no activity (entries 6 and 7).

Having established the best conditions for the reaction of $PhSi(OMe)_3$ with chalcone (entry 4), these conditions were used for the rest of the studies. In general, the results are noticeably poorer than when the arylboronic acids are used as substrates. The introduction of either electron-withdrawing or, more surprisingly, electron-donating groups into the *para*-position of the arylsiloxane is deleterious to performance (compare entries 4, 8, and 9). Interestingly, the use of β-nitrostyrene as the Michael acceptor does not give a substantial reduction in yield (entry 16) compared with enone substrates, which is in contrast with results obtained with phenylboronic acid (Table 2, entry 14).

In terms of catalyst stability, it is interesting to note that in the absence of an unsaturated substrate, the palladacycle **4a** undergoes rapid (seconds) decomposition in the presence of phenylboronic acid and K_3PO_4, liberating palladium black. GC/MS analysis of the product mixture after acid hydrolysis indicates the presence of the coupled phenol **16**,[14] formed by the reductive elimination of the orthometalated ligand and the phenyl group introduced by the arylboronic acid (Scheme 3).

Similar reduction processes have been observed previously with arylphosphinite-based palladacycles.[15] By contrast, all of the successful catalytic reactions remain yellow at completion with no obvious precipitation of palladium metal; this is despite the fact that the boronic acid substrates are used in excess. This suggests that both the starting enone and the product ketone are able to stabilize the palladium with respect to decomposition in the presence of arylboronic acids. The ^{31}P NMR spectrum recorded at 50 min of a catalytic reaction between 2-tolylboronic acid and chalcone catalyzed by **4a**[16] shows the presence of the starting complex **4a** as by far the most significant component. In addition, there are smaller peaks observed further downfield at 126.7, 129.8, and 132.3 ppm, consistent with intermediates containing orthopalladated triarylphosphite ligands.

The use of adducts of palladacycles not only seems to slow down catalysis, but also leads to a considerable increase in the stability of the arylated intermediates with respect to reductive elimination. Thus, the reaction of complex **6b** with $MeOC_6H_4B(OH)_2$

(10) (a) Johansson, R.; Wendt, O. F. *Dalton Trans.* **2007**, 488. (b) Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabó, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767. (c) Wallner, O. A.; Szabó, K. J. *Chem.-Eur. J.* **2006**, *12*, 6976. (d) Solin, N.; Wallner, O. A.; Szabó, K. J. *Org. Lett.* **2005**, *7*, 689. (e) Solin, N.; Kjellgren, J.; Szabó, K. J. *J. Am. Chem. Soc.* **2004**, *126*, 7026. (f) Wallner, O. A.; Szabó, K. J. *Org. Lett.* **2004**, *6*, 1829.

(11) (a) Huang T.-S.; Li, C.-J. *Chem. Commun.* **2001**, 2348. (b) Murata, M.; Shimazaki, R.; Ishikura, M.; Watanabe, S.; Masuda, Y. *Synthesis* **2002**, 717. (c) Koike, T.; Du, X.; Mori, A.; Osakada, K. *Synlett* **2002**, 301. (d) Mori, A.; Danda, Y.; Fujii, T.; Hirabayashi, K.; Osakada, K. *J. Am. Chem. Soc.* **2001**, *123*, 10774. (e) Oi, S.; Honma, Y.; Inoue, Y. *Org. Lett.* **2002**, *4*, 667. (f) Hargrave, J. D.; Herbert, J.; Bish, G.; Frost, C. G. *Org. Biomol. Chem.* **2006**, *4*, 3235. (g) Oi, S.; Taira, A.; Honma, Y.; Inoue, Y. *Org. Lett.* **2003**, *5*, 97. (h) Oi, S.; Taira, A.; Honma, Y.; Sato, T.; Inoue, Y. *Tetrahedron: Asymmetry* **2006**, *17*, 598.

(12) (a) Gini, F.; Hessen, B.; Feringa, B. L.; Minnaard, A. J. *Chem. Commun.* **2007**, 710. (b) Denmark, S. E.; Amishiro, N. *J. Org. Chem.* **2003**, *68*, 6997.

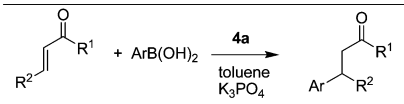
(13) For the use of aryltifluorosilanes as substrates in palladium-catalyzed reactions, see: Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *24*, 5025.

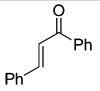
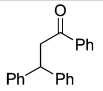
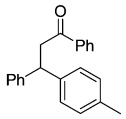
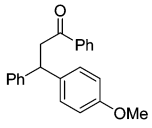
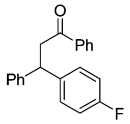
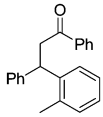
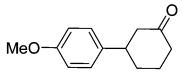
(14) Identical retention time and fragmentation pattern as compared to a genuine sample of **16** prepared according to a literature method: Bedford, R. B.; Limmert, M. E. *J. Org. Chem.* **2003**, *68*, 8669.

(15) Bedford, R. B.; Hazelwood, S. L.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, 4164.

(16) Conditions: 2-tolyl-$B(OH)_2$ (0.6 mmol), chalcone (0.3 mmol), K_3PO_4 (0.3 mmol), **4a** (0.011 mmol), $C_6D_5CD_3$ (0.6 mL), rt.

Table 2. Coupling of $ArB(OH)_2$ with α,β-Unsaturated Ketones and Related Substrates Catalyzed by 4a[a]

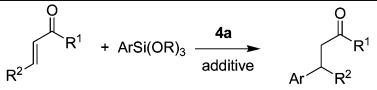


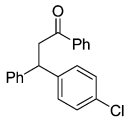
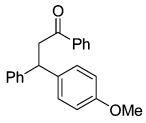
Entry	Acceptor	Aryl	Product	Time (h)	Conversion, % [b]
1		Ph		0.5	> 99 (93) [c]
2		4-MeC_6H_4		1	> 99 (90) [c]
3		4-$MeOC_6H_4$			> 99 (89) [c]
4		4-FC_6H_4			> 99
5		2-MeC_6H_4			37
6				6 [d]	96 (88) [c]
7		Ph		1	94
8		Ph		1	96 (89) [c]
9		4-$MeOC_6H_4$			> 99
10		Ph			> 99
11					> 99
12				24	70
13				24	47 [d]

[a] Conditions: $ArB(OH)_2$ (1.0 mmol), unsaturated substrate (0.5 mmol), K_3PO_4 (0.5 mmol), **4a** (0.025 mmol), toluene (2 mL), rt. [b] Conversion to coupled product determined by ^1H NMR spectroscopy (1,3,5-$(MeO)_3C_6H_3$ internal standard), average of two runs. [c] Isolated yield. [d] Reaction temperature = 50 °C.

and K_3PO_4 in $C_6D_5CD_3$ at room temperature shows the slow formation (96 h) of two isomers of a new complex tentatively assigned as the arylated Pd(II) palladacyclic complex **17** on the basis of the similarity of the ^{31}P data obtained compared with

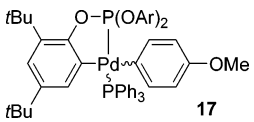
Table 3. Coupling of Aryl Siloxanes with α,β-Unsaturated Ketones and Related Substrates Catalyzed by 4a[a]



Entry	Additive [mmol]	Acceptor	Siloxane [equivs.]	Product	Solvent [Temp. (°C)] {Time (h)}	Conv. % [b]
1	$AgBF_4$ [20]		$PhSi(OMe)_3$ [2]		Dioxane/H_2O [c]	7 [d]
2	$AgBF_4$ [20]				Toluene [75] {16}	63
3					Toluene [90] {16}	50
4			[3]		Toluene [75] {21}	76
5			[4]		Toluene [75] {16}	66
6	KF [150]		[3]		Toluene [75] {21}	0
7	K_3PO_4 [150]					0
8			4-$ClC_6H_4Si(OMe)_3$			52
9			4-$MeOC_6H_4Si(OMe)_3$			35
10						44
11						0
12						56
13						0
14						53

[a] Conditions: $ArSi(OR)_3$ (1.5 mmol), unsaturated substrate (0.5 mmol), $AgBF_4$ (20 mol %), **4a** (0.025 mmol), toluene (2 mL), 75 °C. [b] Conversion to coupled product determined by ^1H NMR spectroscopy (1,3,5-$(MeO)_3C_6H_3$, internal standard), average of two runs. [c] 1,4-Dioxane:water 2:1, 9 mL, 1 mol % Pd catalyst loading.

6b,[17] as well as the observation of characteristic peaks, for instance for the methoxy groups, in the ^1H NMR spectrum.



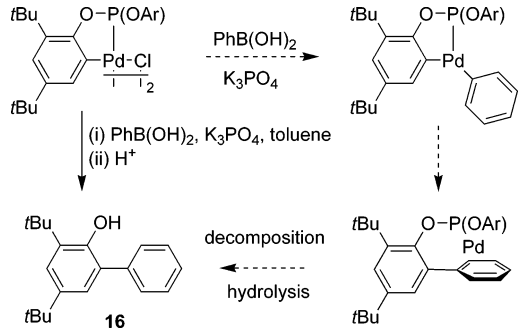
17

A substantial amount of starting complex **6b** is also seen in the ^{31}P NMR spectrum (ratio of **17**:**6b** ≈ 60:40). In addition, small amounts of palladium species containing PPh_3 ligands as the sole P-donors are seen at 24.4 and 24.3 ppm, and a small singlet is seen at 132.6 ppm, which is in the range for a non-coordinated triarylphosphite ligand.

In conclusion, the palladacyclic phosphite-based catalyst **4a** shows excellent activity in the coupling of aryl boronic acids with a range of Michael acceptors, and the ease of synthesis

(17) ^{31}P NMR of **17** ($C_6D_5CD_3$): major isomer, doublets at 137.2 and 36.6 ppm ($^2J_{PP}$ = 575.4 Hz); minor isomer, 155.1 and 22.5 ppm ($^2J_{PP}$ = 26.7 Hz). By contrast, the ^{31}P spectrum in toluene of **6b** shows doublets at 133.8 (phosphite) and 18.9 (phosphine) with a mutual coupling of 39.1 Hz.

Scheme 3. Synthesis of 16 and Probable Mechanism of Formation



and commercial availability of complex **4a**[18] makes it particularly attractive for such reactions. More modest activity is observed when arylsiloxanes are used as the nucleophilic coupling partners. Phosphine, phosphite, and carbene adducts of **4a** show variable activity, but they demonstrate that the coordination sphere of the catalysts can be easily modified while retaining moderate to good levels of activity; this should allow for the facile introduction of chirality into the catalysts, and we are currently exploring the application of such complexes in asymmetric versions of the reactions.

Experimental Section

General. All reactions and preparations were carried out under a nitrogen atmosphere either in a glovebox or using standard Schlenk techniques. Unless specified otherwise, all solvents were anhydrous. Complexes **4**−**11a**[15,19−22] and compounds **13**[23] and **15**[6] were prepared according to literature methods.

Preparation of Complex 11b. Ligand **13** (0.310 g, 0.68 mmol) and $Pd(TFA)_2$ (0.226 g, 0.68 mmol) were dissolved in THF (10 mL), and the resultant solution was stirred at rt for 2 h. After this time, the solvent was removed under reduced pressure, and the crude product was redissolved in CH_2Cl_2 (20 mL) and then filtered through Celite. The solvent was removed under reduced pressure to give a gray powder, which was then recrystallized from CH_2Cl_2:hexane. Yield: 0.317 g (69%). Crystals of **11b** suitable for X-ray analysis were grown by slow diffusion of hexane into a concentrated CH_2Cl_2 solution. Anal. Calcd for $C_{28}H_{47}F_3O_4P_2Pd$: C, 49.96; H, 7.04. Found: C, 49.32; H, 7.37. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 298 K): δ 186.4 (s). ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 1.15−1.32 (m, 42H, $C(CH_3)_3$ and $CH(CH_3)_2$), 2.43 (heptet, J = 7.5 Hz, 4H $CH(CH_3)_2$), 6.89 (br s, 1H, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298 K): δ 17.05 (br s, CH_3), 17.13 (apparent t, J_{CP} = 4.0 Hz, CH_3), 29.26 (apparent t, J_{CP} = 12.0 Hz, CH), 30.08 (s, CH_3), 34.64 (s, C), 116.43 (q, J_{CF} = 216.8 Hz, CF_3), 123.59 (s, CH), 127.58 (apparent t, J_{CP} = 6.0 Hz, C), 128.09 (t, J_{CP} = 4.0 Hz, Pd−C), 161.54 (q, J_{CF} = 18.8 Hz, CO_2), 162.16 (apparent t, J_{CP} = 6.0 Hz, C−O). HRMS (+ESI) calcd for $C_{26}H_{47}O_2P_2Pd$ ($M^+ - C_2F_3O_2$) 559.208063, found 559.209431.

Preparation of Complex 11c. Ligand **13** (0.268 g, 0.59 mmol) and $[PdCl_2(NCMe)_2]$ (0.153 g, 0.59 mmol) were dissolved in 1,2-dichloroethane (10 mL), and the resultant solution was heated at reflux for 18 h. The solution was allowed to cool, and the solvent was removed under reduced pressure. The crude product was redissolved in CH_2Cl_2 (20 mL), filtered through Celite, and then the solvent was removed under reduced pressure to give a yellow powder, which was then recrystallized from CH_2Cl_2:ethanol. Yield: 0.201 g (57%). Crystals of **11c** suitable for X-ray analysis were grown by slow diffusion of ethanol into a concentrated CH_2Cl_2 solution. Anal. Calcd for $C_{26}H_{47}ClO_2P_2Pd$: C, 52.44; H, 7.96. Found: C, 51.95; H, 8.21. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 298 K): δ 185.9 (s). ^1H NMR ($CDCl_3$, 300 MHz, 298 K): 1.14−1.35 (m, 42H, $C(CH_3)_3$ and $CH(CH_3)_2$), 2.41 (heptet, J = 7.5 Hz, 4H, $CH(CH_3)_2$), 6.88 (br s, 1H, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298 K): δ 16.77 (br s, CH_3), 17.18 (apparent t, J_{CP} = 4.0 Hz, CH_3), 28.65 (apparent t, J_{CP} = 12 Hz, CH), 29.85 (s, CH_3), 34.42 (s, C), 123.01 (s, CH), 127.40 (apparent t, J_{CP} = 6.0 Hz, C), 127.99 (s, C), 133.43 (t, J_{CP} = 4.0 Hz, Pd−C), 161.76 (apparent t, J_{CP} = 6.0 Hz, C−O). HRMS (+ESI) calcd for $C_{26}H_{47}O_2P_2Pd$ (M^+ − Cl) 559.208063, found 559.209451.

Preparation of Ligand 14. A solution of *N*,*N*′-diisopropylethylenediamine (0.460 g, 3.20 mmol) in toluene (20 mL) was added to a stirred solution of **15** (0.660 g, 1.56 mmol) and Et_3N (1 mL, 7.18 mmol) in toluene (20 mL). The resultant mixture was stirred overnight at 90 °C. It was then cooled to room temperature, filtered through Celite to remove the $[Et_3NH]Cl$ precipitate, and reduced in vacuo to give ligand **14** as a pale yellow oil (0.796 g, 90%), which was used without further purification. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 298 K): δ 112.2 (s). ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 1.02 (d, J = 6.0 Hz, 24H, $CH(CH_3)_2$), 1.26 (s, 18H, $C(CH)_3$), 2.76 (hept., J = 6.0 Hz, 4H, $CH(CH_3)_2$), 3.07−3.27 (m, 8H, CH_2), 7.03 (s, 1H, Ar*H*), 7.48 (t, J = 4.5 Hz, 1H, Ar*H*).

Preparation of Complex 12. Ligand **14** (0.455 g, 0.839 mmol) and $[PdCl_2(NCMe)_2]$ (0.173 g, 0.671 mmol) were dissolved in 1,2-dichloroethane (30 mL), and the resultant solution was heated at reflux for 18 h. The solution was cooled, filtered through Celite, and reduced under pressure to give a pale yellow powder, which was subsequently washed with Et_2O (10 mL). The washings were concentrated under reduced pressure to give a pale cream-colored powder. Yield: 0.278 g (47%). Crystals of **12** suitable for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution under air. Anal. Calcd for $C_{34}H_{65}ClN_4O_3P_2Pd\cdot(Et_2O)$: C, 52.24; H, 8.38; N, 7.17. Found: C, 52.14; H, 7.98; N, 7.98. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 298 K): δ 132.6 (s). ^1H NMR ($CDCl_3$, 300 MHz, 298 K): 1.10−1.41 (m, 42H, $C(CH_3)_3$ and $CH(CH_3)_2$, 3.19−3.36 (m, 8H, CH_2), 3.61 (heptet, 4H, J = 6.41 Hz $NCH(CH_3)_2$), 6.91 (br s, 1H, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298 K): δ 21.94 (t, J = 2.25 Hz, $CH(CH_3)_2$), 21.97 (t, J = 2.25 Hz, $CH(CH_3)_2$), 30.11 (s, $C(CH_3)_3$), 34.67 (s, $C(CH_3)_3$), 43.27 (s, CH_2), 47.36 (t, J = 7.5 Hz, $CH(CH_3)_2$), 123.46 (s, CH), 127.30 (apparent t, J = 7.5 Hz, $CC(CH_3)_3$), 135.74 (t, J = 3.75 Hz, C−Pd), 153.41 (apparent t, J = 8.25, C−OP). HRMS (+ESI) calcd for $C_{30}H_{55}ClN_4O_2P_2Pd$ (M^+ − Cl) 559.208063, found 559.209451.

General Method for the Reaction of Arylboronic Acids with Catalyst Loading of 1−5 mol % Pd (Tables 1 and 2). To a stirred solution of $ArB(OH)_2$ (1.0 mmol) in the appropriate solvent (1 mL) were added the appropriate unsaturated substrate (0.5 mmol), K_3PO_4 (0.106 g, 0.5 mmol), the required amount of appropriate catalyst, and then extra solvent (1 mL) to ensure all reagents were washed down the side of the reaction vessel. The resulting mixture was stirred for the required time at the temperature indicated, quenched with water (50 mL), extracted with dichloromethane (3 × 50 mL), and dried ($MgSO_4$). The filtrate was concentrated under reduced pressure, and 1,3,5-trimethoxybenzene (28 mg, 0.166 mmol, internal NMR standard) was added. The conversion to the coupled product was determined by ^1H NMR spectroscopy ($CDCl_3$). The data obtained were comparable with literature values, and

(18) Sigma-Aldrich.
(19) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E.; Albisson, D. A.; Draper, S. M.; Scully, P. N.; Coles, S. J.; Hursthouse, M. B. *Chem.-Eur. J.* **2003**, *9*, 3216.
(20) Bedford, R. B.; Betham, M.; Blake, M. E.; Frost, R. M.; Horton, P. N.; Hursthouse, M. B.; López-Nicolás, R.-M. *Dalton Trans.* **2005**, 2774.
(21) Bedford, R. B.; Cazin, C. S. J.; Coles, S. J.; Gelbrich, T.; Horton, P. N.; Hursthouse, M. B.; Light, M. E. *Organometallics* **2003**, *22*, 987.
(22) Bedford, R. B.; Draper, S. M.; Scully, P. N.; Welch, S. L. *New J. Chem.* **2000**, 745.
(23) Bedford, R. B.; Betham, M.; Blake, M. E.; Coles, S. J.; Draper, S. M.; Hursthouse, M. B.; Scully, P. N. *Inorg. Chim. Acta* **2006**, *359*, 1870.

representative examples of the products were isolated by column chromatography (silica gel).

General Method for the Reaction of Arylboronic Acids with Chalcone at 0.1 mol % Pd Catalyst Loading (Table 1, Entries 12, 13, and 17). To a mixture of $ArB(OH)_2$ (1.0 mmol), chalcone (0.104 g, 0.5 mmol), and K_3PO_4 (0.106 g, 0.5 mmol) was added the appropriate catalyst as a 0.1 M solution in toluene (1.00 mL), and then extra toluene (1 mL) was added to ensure all reagents were washed down the side of the reaction vessel. The reaction was then stirred for the time indicated in Table 1 and was quenched and worked up as described above.

Isolated Products. 1,3,3-Triphenylpropan-1-one (Table 2, Entry 1).[12c] Colorless solid, 93% isolated yield. $R_f = 0.45$ (Et_2O/hex 1:10), mp = 94−96 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 3.68 (d, J = 7.3 Hz, 2H, CHC*H*$_2$), 4.76 (t, J = 7.3 Hz, 1H, C*H*CH$_2$), 7.04−7.15 (m, 2H, ArH), 7.15−7.28 (m, 8H, ArH), 7.32−7.42 (m, 2H, ArH), 7.43−7.57 (m, 1H, ArH), 7.82−7.98 (m, 2H, ArH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 44.8, 46.0, 88.3, 103.3, 127.9, 128.2, 128.7, 128.7, 133.2, 144.2, 197.0. IR (neat): ν = 3063, 3026, 1676, 1594, 1494, 1448, 1262, 1184, 1034, 746, 694 cm^{-1}. *m*/*z* (EI): 286 (M$^+$), 167, 165, 152, 105, 103, 77.

3-(4-Methylphenyl)-1,3-diphenylpropan-1-one (Table 2, Entry 2).[24] Colorless solid, 90% isolated yield. $R_f = 0.6$ (CH_2Cl_2), mp = 97−98 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.28 (s, 3H, ArC*H*$_3$), 3.72 (d, 2H, J = 8.0 Hz, CHC*H*$_2$), 4.79 (t, 1H, J = 8.0 Hz, C*H*CH$_2$), 7.04−7.11 (m, 2H, ArH), 7.11−7.20 (m, 3H, ArH), 7.21−7.31 (m, 4H, ArH), 7.39−7.47 (m, 2H), 7.50−7.57 (m, 1H), 8.00−7.89 (m, 2H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 20.9, 44.7, 45.5, 126.2, 127.6, 127.7, 128.0, 128.5, 128.5, 129.2, 133.0, 135.8, 137.0, 141.1, 144.3, 198.0. IR (neat): ν = 3059, 3027, 2159, 1674, 1514, 1255, 1212, 1077, 1037, 746 cm^{-1}. *m*/*z* (EI): 300 (M$^+$), 285, 181, 105, 91, 77.

3-(4-Methoxyphenyl)-1,3-diphenylpropan-1-one (Table 2, Entry 3).[25] Colorless solid, 89% isolated yield. $R_f = 0.30$ (Et_2O/hexane 1:5), mp = 93.1−94.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 3.70 (d, J = 7.2 Hz, 2H, CHC*H*$_2$), 3.73 (s, 3H, OC*H*$_3$), 4.78 (t, J = 7.3 Hz, 1H, C*H*CH$_2$), 6.80 (dt, J = 9.1 and 2.0 Hz, 2H, ArH), 7.05−7.35 (m, 7H, ArH), 7.42 (tt, J = 6.6 and 1.7 Hz, 2H, ArH), 7.53 (tt, J = 7.3 and 1.3 Hz, 1H, ArH), 7.92 (dd, J = 8.6 and 1.7 Hz, 2H, ArH). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$, 298 K): δ 44.8, 45.0, 55.1, 113.8, 126.2, 127.6, 127.9, 128.4, 128.5, 128.6, 132.9, 136.1, 136.9, 144.4, 157.9, 198.0. IR (neat): ν = 3086, 3028, 2987, 2925, 1687, 1598, 1513, 1494, 1448, 1363, 1203, 1113, 1077, 759 cm^{-1}. *m*/*z* (EI): 316 (M$^+$), 300, 181, 165, 105, 91, 77.

3-(2-Methylphenyl)-1,3-diphenyl-1-propanone (Table 2, Entry 5).[26] Colorless solid, 88% isolated yield. $R_f = 0.83$ (CH_2Cl_2), mp = 81.2−83.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.32 (s, 3H, ArC*H*$_3$), 3.72 (dd, J = 8.1 and 5.4 Hz, 2H, C*H*$_2$CH), 5.01 (t, 1H, J = 8.1 Hz, CH$_2$C*H*), 7.01−7.38 (m, 14H, ArH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 20.1, 42.0, 45.1, 126.1, 126.3, 126.4, 126.5, 128.1, 128.2, 128.6, 128.7, 130.9, 133.2, 136.6, 137.2, 141.9, 143.9, 198.2. IR (neat): ν = 3060, 3025, 2962, 2878, 1683, 1595, 772, 685 cm^{-1}. *m*/*z* (EI): 300 (M$^+$), 285, 181, 105, 91, 77.

3-Phenylcyclohexanone (Table 2, Entry 8).[2c] Colorless oil, R_f = 0.2 (CH_2Cl_2), 89% isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.68−1.94 (m, 2H, CH_2), 2.02−2.25 (m, 2H, CH_2), 2.30−2.73 (m, 4H, CH_2), 2.94−3.10 (m, 1H, CHPh), 7.09−7.49 (m, 5H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ 25.6, 32.8, 41.3, 44.8, 49.0, 126.6, 126.7, 128.7, 144.4, 211.2. IR (neat): ν = 2936, 1708, 1450, 1223, 753, 698 cm^{-1}. *m*/*z* (EI): 174 (M$^+$), 131, 104, 91.

Spectroscopically Charaterized Products. 3-(4-Fluorophenyl)-1,3-diphenyl-1-propanone (Table 2, Entry 4).[24] ^{1}H NMR (270 MHz, $CDCl_3$, 298 K): δ 3.64 (d, J = 7.6 Hz, 2H, CHC*H*$_2$), 4.74 (t, J = 7.6 Hz, 1H, C*H*CH$_2$), 6.94−6.82 (m, 2H, ArH), 7.43−7.33 (m, 2H, ArH), 7.54−7.44 (m, 1H, ArH), 7.28−7.01 (m, 7H, ArH), 7.90−7.79 (m, 2H, ArH). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$, 298 K): 44.8, 45.1, 115.2, 115.4, 126.5, 127.6, 128.0, 128.6, 129.2, 129.3, 133.3, 137.0, 139.9, 144.1, 197.9.

4,4-Diphenylbutan-2-one (Table 2, Entry 7).[4] ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.00 (s, 3H, CH_3), 3.11 (d, J = 7.56 Hz, 2H, CH_2), 4.51 (t, J = 7.56 Hz, 1H, C*H*CH$_2$), 7.06−7.28 (m, 8H, ArH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 206.7, 127.7, 127.9, 126.4, 49.6, 55.3, 46.0, 30.8.

3-(4-Methoxyphenyl)cyclohexanone (Table 2, Entry 9).[4] ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.72−1.85 (m, 2H, CH_2), 2.01−2.16 (m, 2H, CH_2), 2.31−2.59 (m, 4H, CH_2), 2.97 (m, 1H, CHAr), 3.80 (s, 3H, OCH_3), 6.87 (d, J = 8.4 Hz, 2H, ArH), 7.14 (d, J = 8.4 Hz, 2H, ArH). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): 25.63, 33.15, 41.32, 44.11, 49.36, 55.39, 114.09, 127.58, 158.36, 161.61, 211.32.

4-Phenyl-tetrahydropyran-2-one (Table 2, Entry 10).[27] ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 1.95−2.24 (m, 2H, CH_2), 2.64−2.70 (m, 1H, CH_2), 2.85−2.98 (m, 1H, CH_2), 3.23 (m, 1H, CHPh), 4.33−4.56 (m, 2H, CH_2), 7.15−7.45 (m, 5H, ArH). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ 29.7, 30.1, 38.3, 68.0, 128.3, 130.2, 144.2, 177.1.

3-Phenylcyclopentanone (Table 2, Entry 11).[28] ^{1}H NMR (270 MHz, $CDCl_3$, 298 K): δ 2.02−1.82 (m, 2H, CH_2), 2.48−2.14 (m, 2H, CH_2), 2.62 (dd, J = 18.9 and 8.1 Hz, $COCH_2$), 3.46−3.26 (m, 1H, CHPh), 7.34−7.12 (m, 5H, ArH). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$, 298 K): δ 31.3, 39.0, 42.3, 45.9, 92.9, 126.8, 128.8, 143.1, 218.1.

4-Phenylpentan-2-one (Table 2, Entry 12) Lit.[3] ^{1}H NMR (270 MHz, $CDCl_3$, 298 K): δ 1.20 (d, J = 8.1 Hz, C*H*$_3$CH), 1.99 (s, $COCH_3$), 2.67−2.48 (m, 2H, CHC*H*$_2$), 3.32−3.14 (m, 1H, C*H*CH$_2$), 7.27−7.03 (m, 5H, ArH). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$, 298 K): δ 21.9, 30.4, 35.4, 51.9, 126.2, 126.7, 128.4, 146.1, 207.6.

1-Nitro-2,2-diphenylethane (Table 2, Entry 13), Lit.[20] ^{1}H NMR (270 MHz, $CDCl_3$, 298 K): δ 4.94−4.79 (m, 3H, $CHCH_2$), 7.40−7.15 (m, 10H). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$, 298 K): δ 49.0, 79.3, 127.7, 127.8, 129.1, 139.3.

Acknowledgment. This work is dedicated in memory of Dr. Anthony Avent. We thank Dr. Christopher Barnard (Johnson Matthey) for useful discussions, the EPSRC (Advanced Research Fellowship to R.B.B., PDRA to M.B., DTA to L.T.P.) and the Royal Society of Chemistry (Sir Edward Frankland Fellowship to RBB) for funding, and Johnson Matthey for funding and the loan of palladium and platinum salts.

Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM700724C

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