


Table 1. Selected Results of the Heck Reaction with Pd(II) Chelate Complexes

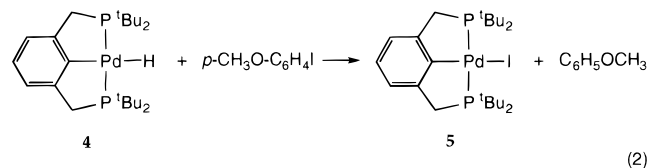
ArX		arene/ olefin (mmol/ mmol)	catalyst (mmol) $\times 10^{-5}$	time/ temp (h)/(°C)	TON	yield (%) ^a	
1	PhI	COOMe	5/6	3.5 1	60/40	142 900	100
2			50/60	17.5 1	253/140	267 600	94
3			50/60	8.75 1	350/140	520 500	91
4			5/6	3.5 2	20/140	142 900	100
5			5/6	1.75 2	40/140	277 700	97
6			50/60	9.0 2	40/140	528 700	95
7			5/6	3.5 3	40/140	142 900	100
8	PhI	COOBu	5/6	3.5 1	40/140	5 650	4
9			5/6	3.5 1	88/160	108 000	77
10			5/6	3.5 2	64/140	142 900	100
11			5/6	3.5 2	14/160	142 900	100
12	PhI	C(O)Me	1.34/1.5	3.5 1	40/140	11 500	30
13	PhI	Ph	5/6	3.5 2	60/140	133 000	93 ^b
14	<i>p</i> -MeOPhI	COOMe	5/6	3.5 2	16/140	142 900	100
15	PhBr	COOMe	5/6	3.5 2	63/140	132 900	93
16	<i>p</i> -OCHPhBr	COOMe	5/6	3.5 2	63/140	113 300	79

^a Determined by GC, based on haloarene and product (PhCHCH-COOMe). ^b Product mixture of two isomers (*E/Z* = 7/1).

is added and the mixture is stirred at 140 °C while the course of the reaction is followed by NMR spectroscopy and gas chromatography. Selected results are listed in Table 1.

With iodobenzene and methyl acrylate, essentially complete conversions are obtained with exceptionally high TONs of up to 500 000. Lower conversions and yields were realized with aryl bromides, although the observed TON of 132 900 with **2** in the case of bromobenzene is among the highest reported. Chlorobenzene was almost inactive. Thus, we believe that this catalyst is among the most active and stable reported so far.

The new catalysts are of interest also from the mechanistic point of view. While the mechanism has not been studied in detail yet, involvement of a Pd(0) complex as the active species seems unlikely. It was shown that a metalated Pd(II) *o*-tolylphosphine complex can be reduced to a Pd(0) complex under conditions of the Heck catalysis via formation of a palladium(II) hydride followed by ring opening by C–H reductive elimination.⁴ The presence of the two strong chelating rings renders opening of the Pd–aryl bond during the reaction unlikely. Nevertheless, to check this possibility, we have studied the reactivity of the hydride complex **4**.¹¹ Significantly, reaction of **4** with *p*-iodoanisole leads exclusively and quantitatively to anisole and to the iodide complex **5** (eq 2),⁹ which was

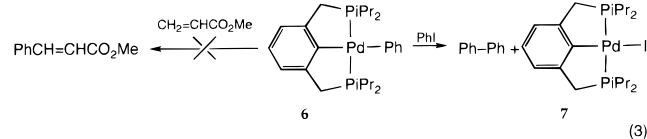


independently prepared by reaction of the corresponding TFA complex with LiI. Since hydrodehalogenation to the arene is

(11) Moulton C. J.; Shaw B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020–1024.

not observed in our catalysis, a route involving a PCP–Pd(II) hydride such as **4** is unlikely.

Generation of an anionic Pd(0) complex without chelate opening (e.g., by deprotonation of a complex such as **4**) is also unlikely. Such a mechanism would involve nucleophilic attack of the anionic complex on iodobenzene to give the Pd–Ph complex **6**.⁹ However, complex **6**, prepared by reaction of **1** with PhLi, does not lead to any coupling products upon heating with methyl acrylate. Moreover, treating **6** with various aryl iodides results in the quantitative formation of the corresponding palladium iodide complex **7** and biaryls (eq 3).¹² Since biaryl



formation is not observed in our catalysis, such a mechanism can be excluded. Thus, we believe that the traditional mechanism involving a Pd(0) complex may not be involved. A Pd(II)/Pd(IV) cycle based on oxidative addition of the aryl halide to **1–3** is a distinct possibility.

A competitive experiment using *p*-BrPhI, PhI, *p*-MePhI, *p*-MeOPhI, and methyl acrylate (in molar ratio of 5:5:5:1) and complex **1** as a catalyst results in a linear correlation with Hammett σ values, yielding $\rho = 1.39$. While this electronic effect is not surprising, since the oxidative addition of the aryl–I bond to the metal is expected to be facilitated by electron-withdrawing substituents on the aromatic ring, the ρ value is too low to fit a rate-determining nucleophilic aromatic substitution.¹³ A subsequent rate-determining step with different electronic requirements, such as olefin insertion, may account for this observation.

The higher efficiency of complex **2** can be attributed to electronic factors, the metal center in **2** being more electron rich than in **1**. Complex **3** is less efficient than **2** due to the higher steric bulk of the phosphine ligands.

In summary, the PCP-type palladium(II) complexes show exceedingly high catalytic activity in the Heck reaction, including reactions of nonactivated aryl bromides. The new catalyst system is very thermally and air stable. Our evidence suggests that this catalysis may not involve the classical Pd(0) cycle. Further investigations aimed at clarification of the scope and mechanism of these novel catalysts are in progress.

Acknowledgment. We thank Dr. L. J. W. Shimon for the X-ray analysis of complex **3**. This work was supported by The Israel Science Foundation, Jerusalem, Israel. M.O. thanks the Deutsche Forschungsgemeinschaft for a fellowship. A.O. thanks the Minerva Foundation, Munich, Germany, for a fellowship. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry.

Supporting Information Available: Spectroscopic characterization of complexes **1–3**, **5**, and **6**, text describing X-ray crystal structure analysis, and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complex **3** (9 pages). See any current masthead page for ordering and Internet access instructions.

JA9729692

(12) H.-B. Kraatz, M. E. van der Boom, Y. Ben-David, and D. Milstein, unpublished results.

(13) Portnoy, M.; Milstein, D. *Organometallics* **1993**, 12, 1665–1673.