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# NC-palladacycles as highly effective cheap precursors for the phosphine-free Heck reactions

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**Abstract**

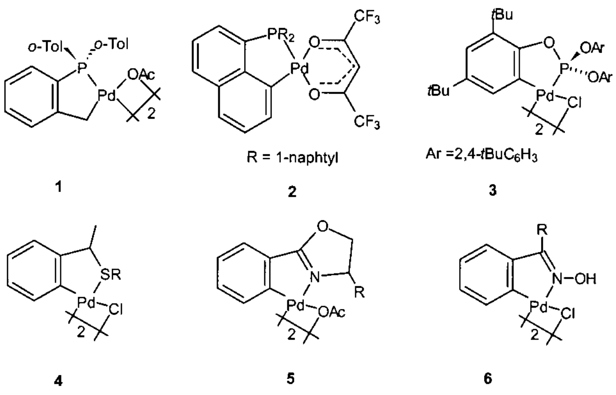
Eight cyclopalladated complexes of the formula $[Pd_2(\mu\text{-}L)_2(N\text{–}C)_2]$ (L = OAc, Cl; N–C = cyclometalled N donor: *o*-(2-pyridyl)phenyl, *o*-(2-pyridyloxy)phenyl, *o*-(2-pyridylmethyl)phenyl, *o*-(*N*,*N*-dimethylaminomethyl)phenyl, 8-quinolylmethyl and others) and a six-membered palladacycle with OC coordination (ligand related to 2-acetoamido-4-nitrophenyl), are highly efficient catalysts for the Heck arylation of olefins (styrene, ethyl acrylate) by aryl halides (iodobenzene, bromobenzene, 4-bromoacetophenone). These catalysts are air stable, easy to obtain from a vast number of readily available nitrogen containing molecules, are generally much cheaper than phosphine-ligated palladacycles, but as or more efficient than the latter. Turnover numbers (*ton*) of up to 4 100 000 and turnover frequencies (*tof*) up to 530 000 are achieved in the reaction of iodobenzene with ethyl acrylate. Bromobenzene undergoes the Heck reaction (*ton* = 400–700; *tof* = 5–30) in the presence of the promoter additive $Bu_4NBr$. The palladacycles are likely to operate in a common phosphine-free Pd(0)/Pd(II) catalytic cycle, while the differences between various types of palladacycle precursors are accounted for by the kinetics of the catalyst preactivation step. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Aryl halides; Catalysis; Heck reaction; Metallacycles; Palladium

## 1. Introduction

In recent years the arylation of olefins with aryl halides (Mizoroki–Heck reaction [1]) became not only one of the most important ways to form $C_{sp^2}$–$C_{sp^2}$ bond but also a benchmark to estimate the efficiency of a catalytic system. Palladacycles with PC coordination (complexes **1**–**3**, Scheme 1) were found to be among the most active precatalysts for the Heck reaction [2–4]. Complex **1** (Herrmann's catalyst) is most extensively studied and used in different types of Pd-catalyzed reactions including the Heck reactions [2], the cross-coupling reactions (Suzuki and Stille coupling) and the arylation of amines. The use of nitrogen-based ligands is very rare [5] though some of them were recently demostrated to possess very high activity [5b,c]. The SC-palladacycles are able to catalyze the reactions with a wide selection of aryl halides, as well as vinyl halides [6].

The palladacycles with «pincer» ligands of PCP and SCS type (complexes **7**–**12**, Scheme 2) turned out to be also very efficient in the Heck reaction [7–11].



Scheme 1.

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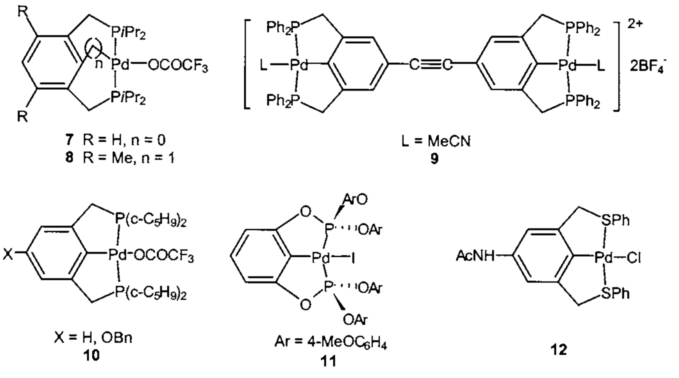
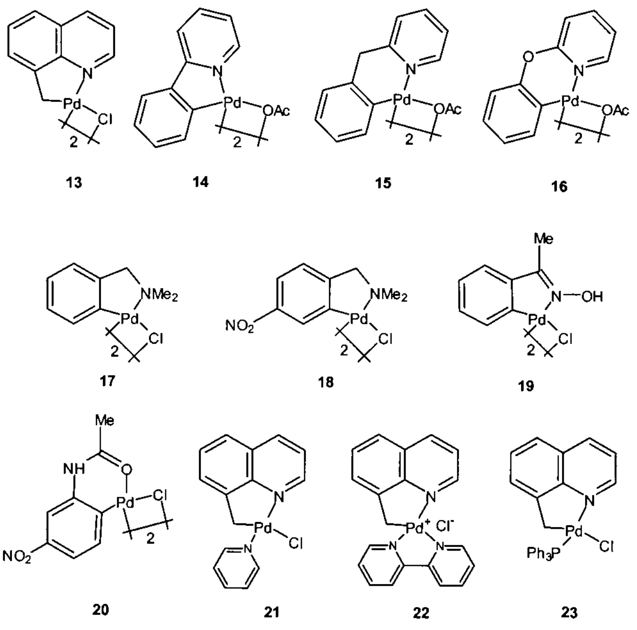


Scheme 2.



Scheme 3.

A characteristic feature of the palladacycles is the thermostability, which makes it possible to perform the reactions at temperatures above 100°C needed for less reactive substrates (e.g. non-activated aryl bromides). The highest turnover numbers (*ton*, mol product per mol palladium) equal to $5.75 \cdot 10^6$ (180°C, 69 h, the yield of 4-acetoxystilbene is 57.5%) [4] and $8.9 \cdot 10^6$ (180°C, 22 h, the yield of butyl cinnamate is 89%) [10] were recorded so far for catalyst **3** in the reaction of 4-bromoacetophenone with styrene, and for catalyst **11** with «pincer» PCP ligand in the reaction of iodobenzene with butyl acrylate, respectively.

Here we report that many palladacycles with NC coordination (complexes **13**–**19** and **21**, Scheme 3), and the complex with OC coordination **20**, derived from readily avalable and very inexpensive ligands can also be used as catalyst precursors for the Heck reaction, and some of them are very efficient allowing to carry out the reactions under mild conditions [8].

## 2. Results and discussion

The comparison of catalytic activity of the palladacycles was made in the reaction of iodobenzene with ethyl acrylate in *N*,*N*-dimetylformamide (DMF) or dimethylacetamide (DMAA) at 85°C (Table 1). This reaction is largely selective and proceeds without formating biphenyl. All mentioned complexes were found to be able to catalyze the reaction to give high yields of ethyl cinnamate (Scheme 4).

Under these conditions (0.1 mol% catalyst) the values of *ton* are similar for the whole series of dimeric complexes **13**–**20** to be practically equal to the value of *ton* for catalyst **1** (entry 20, Table 1). However, the values of turnover frequency (*tof*, mol product per mol palladium $h^{-1}$) vary strongly and show that complex **1** is the most efficient one, while complexes **13**, **15**, **16**, **20** follow it closely.

It is worth noting that for complex **15** *tof* value determined at half life time of the reaction is even higher than that of complex **1** (entries 5 and 20, Table 1).

A similar catalytic activity of the palladacycles has been observed in the Heck reaction with styrene; though, the values of *tof* are consistently lower (by about three times) than for the reaction of ethyl acrylate (entries 3, 9, 11, 13, 15, Table 1). The ratio of diphenylethylene isomers determined by GLC is similar to that observed for other catalyst systems [12]. The conversion and sum of yields of the isomers agree within experimental error limits (Scheme 5).

So far, we considered only the dimeric palladacycle complexes. The monomeric complex **21** with pyridine ligand showed similar catalytic activity as compared to that of the respective dimeric complex **13** (entry 16 vs. entry 1, Table 1). However, the presence of a $Ph_3P$ ligand in complex **23** decreases the activity very strongly (entry 19, Table 1; the reaction requires 22 h for completion instead of 1.8 h for complex **1** or 3 h for complex **13**). The monomeric complex **22** with 2,2′-dipyridyl ligand is inefficient in this reaction (entry 18, Table 1). The addition of 2,2′-dipyridyl to the reaction mixture in the presence of complex **21** also suppressed the reaction (entry 17, Table 1).

Some of the palladacycles introduced above were studied in the reaction with bromobenzenes. It was shown that the reaction of 4-bromoacetophenone with ethyl acrylate or styrene runs smoothly to give high yields of the respective products though requiring a prolonged heating at high temperature (140°C, Table 2) (Scheme 6).

Though we have not attempted to search for lowest possible loads of the precatalyst in the reactions with bromoarenes, the data already available show that the activity of palladacycles under study is among the highest reported so far. Thus, at a low load of pallada-

Table 1
Heck arylation of olefins with iodobenzene in the presence of palladacycles [a]

| Entry | Palladacycle | Olefin | *t* (h) | Conversion of PhI (%) [b] | *ton* [c] | *tof* [d] | $tof_{1/2}$ [g] |
|---|---|---|---|---|---|---|---|
| 1 | 13 | Ethyl acrylate | 3.3 | 63 (58) | 630 | 191 | 300 |
| 2 | 13 | Ethyl acrylate | 3 | 100 (93) [e] | 1000 | 333 | 430 [e] |
| 3 | 13 | Styrene | 7.5 | 100 (95) [e] | 1000 | 133 | 120 [e] |
| 4 | 14 | Ethyl acrylate | 2.3 | 48 | 480 | 209 | 220 |
| | | | 5.5 | 95 (89) | 950 | 173 | |
| 5 | 15 | Ethyl acrylate | 3 | 89 (82) | 890 | 297 | 1000 |
| 6 | 16 | Ethyl acrylate | 1.4 | 58 | 580 | 414 | 400 |
| | | | 6 | 98 | 980 | 163 | |
| 7 | 17 | Ethyl acrylate | 12.8 | 83 | 830 | 65 | 86 |
| 8 | 17 | Ethyl acrylate | 18 | 100 (96) [e] | 1000 | 55 | |
| 9 | 17 | Styrene | 35 | 72 (69) [e] | 720 | 21 | |
| 10 | 18 | Ethyl acrylate | 4.5 | 100 [e] | 1000 | 222 | 330 |
| 11 | 18 | Styrene | 9 | 55 [e] | 550 | 61 | 67 [e] |
| 12 | 19 | Ethyl acrylate | 17 | 97 | 970 | 57 | 53 [e] |
| 13 | 19 | Styrene | 30 | 91 [e] | 910 | 30 | |
| 14 | 20 | Ethyl acrylate | 2.7 | 93 [e] | 930 | 340 | 700 [e] |
| 15 | 20 | Styrene | 15 | 100 (97) | 1000 | 66 | 42 |
| 16 | 21 | Ethyl acrylate | 6.5 | 87 | 870 | 134 | 120 |
| 17 | 21 | Ethyl acrylate | 2 | 1 [f] | | | |
| 18 | 22 | Ethyl acrylate | 16 | 5 | | | |
| 19 | 23 | Ethyl acrylate | 22 | 88 | 880 | 40 | 35 |
| 20 | 1 | Ethyl acrylate | 1.8 | 95 (90) | 950 | 528 | 860 |

[a] Iodobenzene (0.1 mmol), olefin (0.12 mmol), tri-*n*-butylamine (0.1 mmol), catalyst (0.1 mol%), *N*,*N*-dimethylacetamide (20 ml), 85°C.

[b] Determined by titration of liberated iodide ions, see Section 4; data in parentheses refer to GLC yield of the olefinated product.

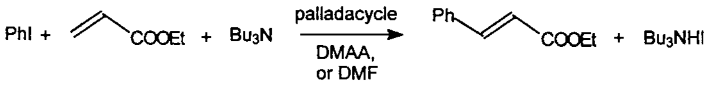
[c] *ton*-turnover number (mol product per mol catalyst).

[d] *tof*-turnover frequency (mol product per mol catalyst $h^{-1}$).

[e] In *N*,*N*-dimethylformamide.

[f] In the presence of 2,2′-dipyridyl (0.1 mol% related to iodobenzene).

[g] *tof* in the range of 50% conversion of PhI.



Scheme 4.

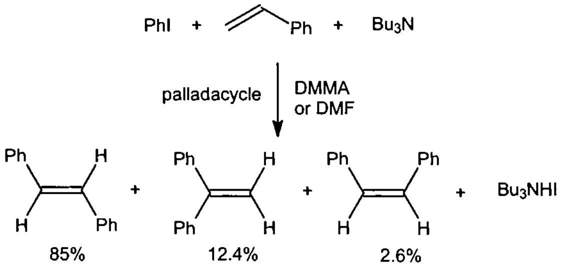
cycle **13** at 0.002 mol% (entry 3, Table 2) the conversion and yield of the cinnamate in the reaction of 4-bromoacetophenone with ethyl acrylate were high, and *tof* reached 43500, a value comparable to that reported for the reaction with complex **1** [2c].

The reaction of bromobenzene with ethyl acrylate or styrene in the presence of the catalyst **13** is too slow (entry 4, Table 2) but the addition of 20 mol% of tetrabutylammonium bromide allowed one to achieve 72% and 38% conversion of bromobenzene after 24 h or 72 h, respectively (entries 5 and 7, Table 2) (Scheme 7).

In the case of the Heck reaction catalyzed by palladacycles, a positive effect of tetrabutylammonium bromide was observed by Herrmann et al. [2a,c]. The efficiency of complex **13** under the conditions studied is close to that of catalyst **1** in the reaction of bromobenzene with butyl acrylate (NaOAc, 140°C) [2c].

To test the higher limits of activity of the palladacycles, we performed the reaction of iodobenzene with ethyl acrylate with very low loads of complex **13** (Table 3).

A huge *ton* value of about $1\cdot10^5$ can be achieved at 85°C with 0.001 mol% of the catalyst (entry 5, Table 3). The highest values of *ton* $(2–4)\cdot10^6$ comparable with the record figures obtained previously [4,10] were observed for this reaction at 140°C in DMAA using $(1–3)\cdot10^{-5}$ mol% of catalyst **13** (entries 7–9, Table 3).



Scheme 5.

Table 2
Heck arylation of olefins with aryl bromides in the presence of palladacycles[a]

| Entry | Pallada-cycle | mol% | Olefin | Aryl bromide | *t* (h) | Conversion of PhI (%)[b] | *ton*[c] | *tof*[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 13 | 0.05 | Ethyl acrylate | 4-Bromoacetophenone | 24 | 100 (95) | 2000 | 83 |
| 2 | | 0.01 | Ethyl acrylate | 4-Bromoacetophenone | 24 | 98 | 9800 | 410 |
| 3 | | 0.002 | Ethyl acrylate | 4-Bromoacetophenone | 24 | 87 | 43500 | 1810 |
| 4 | | 0.1 | Ethyl acrylate | Bromobenzene | 24 | 3 | | |
| 5 | | 0.1 | Ethyl acrylate | Bromobenzene | 24 | 72[e] | 720 | 30 |
| 6 | | 0.1 | Styrene | 4-Bromoacetophenone | 64 | 100 (98) | 1000 | 16 |
| 7 | | 0.1 | Styrene | Bromobenzene | 72 | 38[e] | 380 | 5.3 |
| 8 | 16 | 0.01 | Ethyl acrylate | 4-Bromoacetophenone | 24 | 92 | 9200 | 380 |
| 9 | | 0.1 | Styrene | 4-Bromoacetophenone | 64 | 92 (86) | 920 | 14 |

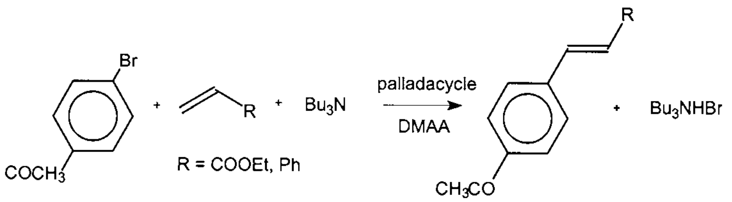
[a] Aryl bromide (0.25 mmol), olefin (0.3 mmol), tri-*n*-butylamine (0.25 mmol), *N*,*N*-dimethylacetamide (0.5 ml), 140°C.

[b] Determined by titration of liberated iodide ions, see Section 4; data in parentheses refer to GLC yield of the olefinated product.

[c] *ton*-turnover number (mol product per mol catalyst).

[d] *tof*-turnover frequency (mol product per mol catalyst $h^{-1}$).

[e] In the presence of *n*-$Bu_4NBr$.



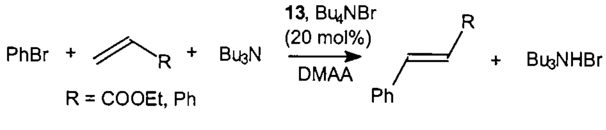
Scheme 6.

Both *ton* and *tof* values (the letter reflects the relative reaction rate) are equally important for a large-scale implementation. The *tof* value for catalyst **13** is equal to 530000 (entry 7, Table 3) and it is a record figure obtained so far for any palladium catalyst in the Heck reaction. This puts the NC-palladacycles in one row with the most active catalysts such as the Herrmann's catalyst.

It is interesting to consider how the values of *ton* and *tof* change in the course of the reaction. The monitoring of the reaction was carried out by potentiometric titration of the formed iodide ions. It was shown that the concentration of iodide ions is in good agreement with the product yield obtained by GLC technique. Moreover the titration method is more exact than GLC in range of small conversion of PhI.The time dependence of the *ton* and *tof* values for the most promising complexes **13** and **15** in comparison with those of catalyst **1** is shown in Table 4 and Fig. 1.

In order to quantify the activity of a given catalytic system, the values of *tof* are routinely used. In most cases, these values are computed by dividing of the cumulative *ton* value by the overall reaction time to give a rough approximation of average activity. It should be noted that the use of such averaged *tof* values can be misleading, if two factors are not explicitly taken into consideration: the induction period and flatness of reaction rate profile at high conversions when the concentration of reagents becomes low. Both these regions of a kinetic curve steal from the averaged *tof* values, thus making the latter an inadequately underestimated measure of the true catalytic activity. Therefore, catalytic activity should be better quantified either by a tangent of a kinetic curve at the point at which the catalytic process starts after the induction period (the initial *tof*), or, if a smooth continuous kinetic curve is not available, by *tof* averaged over shorter period of time corresponding to incomplete conversion (e.g. 50% conversion).

The inadequacy of *tof* values averaged over the whole duration of reaction is clearly seen in the comparison of the behaviour of NC-palladacycles with Herrmann's catalyst. As is seen from Fig. 1 complexes **1**, **13**, and **15** give closely matching averaged *tof* values, while their actual behaviour is different. The reaction in the presence of complex **1** starts immediately after mixing of the reagents without any traceable induction period, and runs to completion within ca. 2 h. The reaction in the presence of complex **15** shows a similar kinetics, though while the initial activity is even somewhat higher than the activity of complex **1**, the conver-



Scheme 7.

Table 3
Heck arylation of ethyl acrylate with iodobenzene with varying initial concentration of palladacycle **13**[a]

| Entry | Solvent | *T* (°C) | mol% of **13** | *t* (h) | Conversion of PhI (%)[b] | *ton*[c] | *tof*[d] |
|---|---|---|---|---|---|---|---|
| 1 | DMF | 85 | 0.1 | 3 | 100 (93) | 1000 | 330 |
| 2 | | – | 0.01 | 10 | 100 | 10 000 | 1000 |
| 3 | | – | 0.001 | 38 | 87 | 87 000 | 2300 |
| 4 | DMAA | 85 | 0.1 | 3.3 | 63 (58) | 630 | 190 |
| 5 | | – | 0.001 | 34 | 100 | 100 000 | 2900 |
| 6 | | 140 | 0.0002 | 20 | 100 | 500 000 | 25 000 |
| 7 | | – | 0.00003 | 4 | 63 | 2 100 000 | 530 000 |
| 8 | | – | – | 7.5 | 78 (72) | 2 600 000 | 350 000 |
| 9 | | – | 0.00001 | 24 | 41 | 4 100 000 | 170 000 |

[a] Iodobenzene (0.1 mmol), ethyl acrylate (0.12 mmol), tri-*n*-butylamine (0.1 mmol), *N*,*N*-dimethylacetamide.
[b] Determined by titration of liberated iodide ions, see Section 4; data in parentheses refer to GLC yield of the olefinated product.
[c] *ton*-turnover number (mol product per mol catalyst).
[d] *tof*-turnover frequency (mol product per mol catalyst $h^{-1}$).

Table 4
Dependence of iodobenzene conversion values and *tof* values on reaction time for Heck arylation of ethyl acrylate with iodobenzene in presence of palladacycles[a]

| Entry | Palladacycle | *t* (h) | Conversion of PhI (%)[b] | *tof*[c] | $tof_{1/2}$ |
|---|---|---|---|---|---|
| 1 | 1 | 0.25 | 24 | 960 | 860 |
| | | 0.5 | 43 | 860 | |
| | | 1 | 77 | 770 | |
| | | 1.5 | 90 | 600 | |
| | | 2 | 96 | 480 | |
| | | 3 | 99 | 330 | |
| 2 | 15 | 0.25 | 33 | 1320 | 1000 |
| | | 0.5 | 51 | 1020 | |
| | | 1 | 69 | 690 | |
| | | 1.5 | 76 | 510 | |
| | | 2 | 80 | 400 | |
| | | 3 | 88 | 290 | |
| 3 | 13 | 0.25 | 5 | 200 | 430 |
| | | 0.5 | 14 | 280 | |
| | | 1 | 41 | 410 | |
| | | 1.5 | 75 | 500 | |
| | | 2 | 90 | 450 | |
| | | 3 | 99 | 330 | |

[a] Iodobenzene (0.1 mmol), ethyl acrylate (0.12 mmol), tri-*n*-butylamine (0.1 mmol), catalyst (0.1 mol%), *N*,*N*-dimethylacetamide (20 ml), 85°C.
[b] Determined by titration of liberated iodide ions.
[c] *tof*-turnover frequency (mol product per mol catalyst $h^{-1}$).

sion remains incomplete, as the process is strongly retarded after ca. 70% conversion. Thus, complex **15** gives a more active, but simultaneously less stable catalytic system, which is deactivated due to a fast depletion of the catalytically active palladium species. On the other hand, complex **13**, which gives a catalytic system with an averaged *tof* being identical to that observed for complex **1**, while the kinetic curve displayed a relatively long induction period. Nevertheless, after the induction period it becomes obvious that the complex **13** gives a more reactive catalytic system than complex **1**, as both of the processes run to completion within roughly the same time, in spite of the time wasted for an induction period in the case of complex **13**. If the values of $tof_{1/2}$ are used to quantify the catalytic activity, this parameter is lower for complex **13** than for complexes **1** or **15**. So, we may conclude that the differential initial *tof* values are better for the description of the peak activity of the catalytic system, while the use of $tof_{1/2}$ permits to distinguish between the processes with and without the induction period.

The inductive period in the mentioned reaction can be shortened or even completely eliminated by the addition of an appropriate reductant. Fig. 2 shows the effect of added $NaBH_4$ on the kinetics of the reaction with complex **13**. As we can see that in this case the curve almost loses S-shape character and as a result the conversion of iodobenzene grows by about 40% in the region of 120 min.

The induction period is often observed in the Heck reaction in which palladium is introduced as a palladium(II) derivative. For example, there are short inductive periods in the reaction of 4-bromoacetophenone with butyl acrylate in the presence of the di-*t*-butylphosphino analogue of catalyst **1** [2c], and in the reaction of 4-chlorobromobenzene with α-methylstyrene in the presence of catalyst **1** [13b]. It is eliminated by the addition of appropriate reducing agents, cf., e.g. [14].

It should be noted that the prereduction must be accomplished with proper care, as a fast reduction to Pd(0) in the absence of strong supporting ligands often leads to immediate sedimentation of inactive palladium black. The addition of reductant is therefore not recommended for reactions with high initial loads of palladium precatalyst (roughly more than 0.1 mol%). At lower concentrations, at which the nucleation of palladium clusters is slow due to lower probability of Pd(0) encounters, the prereduction can indeed be helpful for fast triggering of the catalytic process.

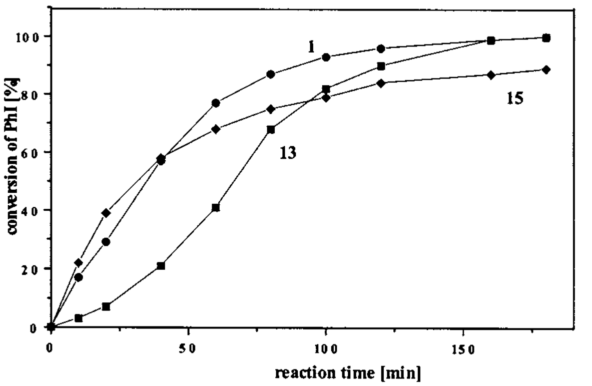


Fig. 1. Comparison of different palladacycles in the Heck reaction: conversion of iodobenzene against time. Reaction conditions: iodobenzene (0.1 mmol), ethyl acrylate (0.12 mmol), tri-*n*-butylamine (0.1 mmol), *N*,*N*-dimethylacetamide (20 ml); $T = 85°C$; catalysts: 0.1 μmol (0.1 mol%) of the palladacycles **1**, **13**, and **15**. The conversion is determined by titration of liberated iodide ions (see Section 4).

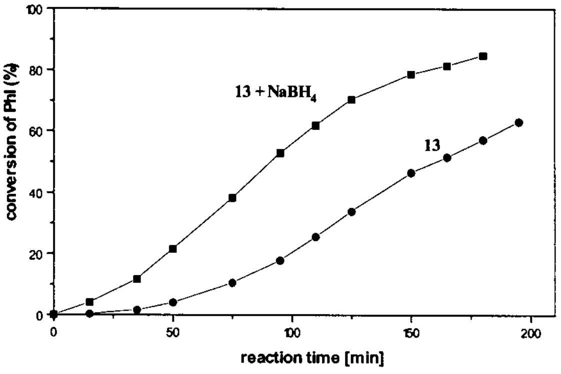
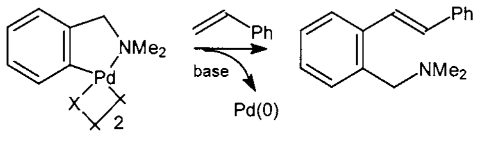


Fig. 2. Conversion/time diagram for the Heck reaction of iodobenzene with ethyl acrylate catalyzed by the complex **9**. Reaction conditions: iodobenzene (0.1 mmol), ethyl acrylate (0.12 mmol), tri-*n*-butylamine (0.1 mmol), *N*,*N*-dimethylacetamide (20 ml); $T = 85°C$; 0.1 μmol (0.1 mol%) of the palladacycle **13**, and in the presence of $NaBH_4$ (0.2 mol%) (upper curve).



Scheme 8.

Both, the S-shaped kinetic curve and the effect of reductant on shortening of the induction period unambiguosly show that the catalytic cycle in the reactions under study is a conventional Pd(0)/Pd(II) Heck cycle [1b,c]. Recently, several researchers put forward a hypothesis that Heck reaction can be driven by Pd(II)/Pd(IV) cycle [3,15], particularly in those cases when palladium is bound to strong multidentate ligands, which are believed not to be capable of full or partial de-ligation, as, for instance, in the reactions catalyzed by complexes with «pincer»-type ligands [7–11].

Still, so far there is no direct experimental evidence in favour of a Pd(II)/Pd(IV) mechanism, while the evidences against are plenty. All data usually cited in favor of this mechanism, such as high thermal stability and post-run recovery of the complexes, the rigidity of the coordination spheres, etc, are not truly convincing. As the reactions with precatalysts suspected for ability to operate through a Pd(II)/Pd(IV) route are usually done under very harsh conditions, the absolute stability of even the most robust complexes is debatable. Moreover, the experiments with recovery are done with higher initial loads of precatalyst than the experiments intended to show a peak activity of a given system. Since 100% recovery cannot be achieved, it is the part of complex which escaped recovery that may indeed be the source of actual catalyst, given the enormous catalytic efficiency of such systems (e.g. for 1 mol% and 99% recovery we lose 0.01 mol% of Pd complex which is well known to be more than enough for the reaction to run at full pace). Thus, we believe that until a more solid proof of a Pd(II)/Pd(IV) mechanism would be available, the conventional Pd(0)/Pd(II) catalytic cycle should be given a preference in the discussion of data for all Heck reactions, except possibly those catalyzed by truly robust «pincer»-type palladacycles with PCP-coordination. All other types of palladacycles in the preactivation stage preceding the entry into the Heck cycle should undergo a full or partial disassembly with a reduction of palladium to the zero-valent state.

The problem of how palladium(0) is generated in a given catalytic system remains open. Some relevant data have been so far obtained only for phosphine-assisted catalytic processes [13,16]. In our case, the prereduction of Pd(II) with a simultaneous disassembly of palladacycle can be effected by the olefin in a non-catalytic Heck reaction [17] (Scheme 8).

Though Herrmann earlier disproved the involvement of olefin insertion into the Pd–C bond of palladacycles with PC-coordination [2c], it can be relevant for NC-palladacycles (by steric reasons the migratory insertion of olefin is impossible without a prior dechelation of N or P arm of the palladacycle, at least for palladacycles with Pd–$C_{sp}2$ bonds). What indeed seems improbable for a PC-system, may readily happen for the less strongly bonded NC-system.

We may hypothesize that the principle mechanism of the involvement of palladacycles in the Heck process is a slow release of low-ligated highly active Pd(0) species. The difference between various palladium precatalysts is most probably accounted for by different rates of Pd(0) release under the given conditions. Too fast a release (which is the case when the precatalyst is a relatively weak complex lacking strongly bonded ligands capable of making Pd(0) state stable) is as ineffective as too slow a release (which is the case when the precatalyst is a robust complex formed by strongly bonded chelating ligands). The former leads to fast accumulation of unstable Pd(0) species liable to aggregation in the absence of excess of supporting phosphine ligands or highly reactive substrates capable of scavenging them via the oxidative addition. Therefore, the first type of precatalysts usually fail in the case of less reactive bromoarenes. On the other hand, too robust precursors (such as PC-palladacycles and particularly «pincer»-type systems) require much higher temperatures to launch the reaction and sustain a reasonable rate.

Thus, the efficiency of a catalytic system utilizing paladacycle precursors (as well as any other strongly bonded complexes, e.g. those with carbene ligands [14]) depends on subtle differences in the kinetics of preactivation. As such factors are practically unpredictable, we believe that the search for highly effective catalytic systems should be done by screening as many available structures as possible. In this respect, NC-palladacycles appear as particularly promising targets for research, as such complexes are readily available from very simple inexpensive nitrogen-containing molecules, the stock of which is practically unlimited.

## 3. Conclusion

Ten palladacycles with NC coordination and one with OC coordination have been studied as precursors of catalysts in the Heck arylation of olefins with aryl halides. Nine of them show an excellent efficiency in the reactions of iodobenzene with styrene and ethyl acrylate. The most active catalysts **13** and **16** were used also in the reaction of styrene or ethyl acrylate with 4-bromoacetophenone and bromobenzene. The reaction with less reactive bromobenzene require the addition of $Bu_4NBr$. Huge *ton* values of up to 4 100 000 have been achieved in the reaction of iodobenzene with ethyl acrylate in the presence of catalyst **13**. The *tof* value for this catalytic system is equal to 530 000 $h^{-1}$, which is a record-making figure for any Heck reaction reported to date.

The palladacycles with NC coordination showed a comparable catalytic activity as the most famous Herrmann's palladacycle.The data obtained can be rationalized within a conventional phosphine-free Pd(0)/Pd(II) cycle. Though the exact mechanism for the release of Pd(0) from the palladacycle carrier remains unknown, the initial disassembly of the palladacycle complex and liberation of highly reactive low ligated Pd(0) species can be suggested to be the principal mode of catalytic activity for the palladacycle and related systems.

## 4. Experimental

### 4.1. General

Commercial chemicals and solvents were distilled or recrystallized prior to use.

The conversion of aryl halide and the yields of products were determined by the two independent methods: (a) the potentiometric titration of halide ions liberated during the reaction; (b) GLC analysis in the significant cases. Quantitative GLC analysis was performed on a Hewlett Packard gas chromatograph 5890 Series II Plus equipped with HP-1701 capillary column (15 m × 0.32 mm, 0.25 μm film) in conjunction with a flame ionization detector (GC/FID); temperature: 35/280°C, 7°C/min. The titration of halide ions with 0.03 M $AgNO_3$/0.1 M $HNO_3$ was carried out on a Radiometer Titrator TTT1c, Titrigraph SBR2c, autoburet ABU1 (0.25 ml) using an indicator electrode Selectrode F1212S.The accuracy of this method is within 2% range. The validity of the potentiometric titration method has been established by blind runs carried out under conditions identical to the conditions of the Heck reaction but in the absence of olefin. The formation of iodide ions in the blind runs does not exceed the instrumental error. The yields determined by GLC and potentiometric titration of halide ions were shown to agree within 7% range.

The reactions were carried out either under positive argon pressure in the reactor equipped with a mercury valve, or in a sealed and evacuated ($10^{-4}$ mmHg) glass ampoule for slower reactions. *N*,*N*-dimethylacetamide and *N*,*N*-dimetylformamide were carefully dried according to known procedures. The solutions of catalysts were prepared for each reaction and used fresh only once.

### 4.2. Preparation of palladacycles

Literature procedures were used for synthesis of complexes **1** [2c], **13** [18], **14** [19], **15** [20], **16** [21], **17** [22], **18** [23], **19** [24], **20** [25], **21** [26], **23** [18].

### 4.3. [8-Quinolylmethyl](2,2′-dipyridyl)palladium(II) chloride (**22**)

Complex **22** was prepared according to a previously described procedure [24b]; Anal. Found: C, 54.21; H, 3.72; N, 9.78. Calc for $C_{20}H_{16}N_3PdCl$ (440.24): C, 54.57; H, 3.66; N, 9.54%.

### 4.4. General procedure for the Heck reaction

Catalyst solution: the appropriate palladacycle (see Scheme 3) was dissolved in 1 ml *N*,*N*-dimethylacetamide. The solution was purged with argon prior to use. Reaction mixture: In a thermostated three-necked flask installed on a magnetic stirrer, aryl halide (0.1 mmol), olefin (0.12 mmol), tri-*n*-butylamine (240 μl, 1 mmol), the solution of 1,4-di-*t*-butylbenzene (GLC internal standard) and *N*,*N*-dimethylacetamide (20 ml) were placed while the flask being continously flushed with argon. The reaction mixture was vigorously stirred for 5 min and heated to 85°C. The catalyst solution (about 10 μl) was injected by syringe into the preheated reaction mixture. For kinetic studies, samples of 20–50 μl were withdrawn from the reaction mixture, mixed with 1.5 ml 0.1 M $HNO_3$ and titrated. To determine the product yields aliquots of the reaction mixture were diluted with 5% hydrochloric acid (1:5) and extracted with methylene chloride (3 × 2 ml). The organic phases were dried with anhydrous magnesium sulfate and analyzed by GLC.

The reactions with minimal loads of the palladium catalyst were carried out in sealed glass ampoules. Aryl halide (0.25 mmol), olefin (0.3 mmol), tri-*n*-butylamine (0.25 mmol), a solution of 1,4-di-*t*-butylbenzene (GC standard), *N*,*N*-dimethylacetamide (0.5 ml) and the catalyst solution (about 10 μl) were placed in an ampoule. The reaction mixture was thoroughly degassed with two freeze-pump-thaw cycles, sealed and placed in a heating bath. The work-up and analysis were performed as specified above.

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