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Reactivity of chelating dicarbene metal complex catalysts, I: An investigation on the Heck reaction

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Abstract

Four chelating di(*N*-heterocyclic carbene) palladium(II) complexes have been prepared and used as catalysts in the Heck reaction of aryl bromides at very low Pd concentration ("omeopathic conditions"). They differ in the nature of the nitrogen substituent, of the bridge between the carbene units or of the heterocyclic system. The obtained results indicate that the catalysts perform well with activated aryl bromides, but less efficiently than simple palladium(II) acetate in the case of deactivated aryl bromides. Such an inhibiting effect of the dicarbene ligands can be correlated with their ability to form inactive dimers and/or bischelate, tetracarbene palladium(II) derivatives in the course of the reaction and appears to depend on their steric features, with catalytic activity increasing with ligand bulkiness.

Keywords: *N*-Heterocyclic carbenes; Palladium; Heck reaction

1. Introduction

Transition metal complexes containing *N*-heterocyclic carbene ligands (NHCs) have gained considerable reputation as homogeneous catalysts in the course of the last 10 years [1]. Since the seminal discovery of stable NHCs by Arduengo et al. [2] and the subsequent pioneering work by the Garching group led by Herrmann et al. on the coordination chemistry of these ligands [1a,3], which took advantage of the previous experience gained by Wanzlick and Öfele on related complexes [4], the reports on highly efficient homogeneous catalysis by NHC–metal complexes have been numerous. The most notable examples include second-generation olefin methatesis catalysts [5], which are now commercially available, catalysts for C–C and C–N coupling reactions [6], for hydrosilylations [7], for telomerizations [8] and for selective alcohol oxidations with molecular oxygen [9]. Remarkably, the vast majority of these highly successful applications involves monocarbene complexes, i.e. complexes containing only one NHC ligand. Biscarbene and especially chelating dicarbene complexes, which have been initially considered as highly promising catalysts for numerous applications and most notably for C–C coupling reactions [10], have not led up to now to outstanding results, as very recently confirmed by a thorough review on the subject [11]. In the light of the above, we have started a research project focused on a systematic evaluation of the catalytic properties of different chelating NHC–metal complexes, with the aim of establishing structure-reactivity correlations, which could enable us to disclose catalytic processes in which these catalysts do indeed exhibit a superior performance. In this first contribution, we have revisited what has arguably become the most popular reaction for testing NHC–palladium complex catalysts, and more generally Pd-containing catalysts, namely the Heck reaction [12]. We have run standard Heck reaction tests at low catalyst loading with a number of palladium(II) complexes with different chelating dicarbene ligands and have critically compared the results obtained with the various complexes and with simple palladium(II) acetate.

2. Experimental

2.1. General comments

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or dinitrogen. The reagents were purchased from Aldrich as high-purity products

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and generally used as received. Complexes (**1**) [10b], (**2**) [13], (**3**) [14] and 1,1′-(1,2-phenylene)bis(imidazole) [15] were prepared according to literature procedures. All solvents were used as received as technical grade solvents. NMR spectra were recorded on a Bruker Avance 300 MHz (300.1 MHz for ^{1}H and 75.5 for ^{13}C); chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals. Elemental analysis were carried out by the microanalytical laboratory of our department with a Fisons EA 1108 CHNS-O apparatus. Gas chromatography was performed on a Shimadzu GC-8A instrument equipped with an OV-1701 capillary column.

2.2. Synthesis of 1,1′-dimethyl-3,3′-(1,2-phenylene)diimidazolium diiodide (*4a*)

MeI (0.240 g, 1.7 mmol) was added to a solution of 1,1′-(1,2-phenylene)bis(imidazole) (0.150 g, 0.7 mmol) in DMSO (2 mL); the reaction mixture was left under stirring for 24 h. Dichloromethane (30 mL) was added to precipitate the product, which was subsequently filtered, washed with dichloromethane (5 mL) and dried in vacuo, giving the product as a white, hygroscopic powder (yield 71%). ^{1}H NMR (DMSO-d_6): δ 3.93 (s, 3H, CH_3), 7.49 (m, 2H, Ar), 7.76 (s, 1H, CH=CH), 7.84 (s, 1H, CH=CH), 9.49 (s, 1H, NCHN). ^{13}C NMR (DMSO-d_6): δ 36.5 (CH_3), 122.8, 124.3, 128.2, 129.6, 132.1 and 138.5 (CH=CH and Ar). Anal. Calcd. for $C_{14}H_{16}I_2N_4$ (M = 493.9): C, 34.04; H, 3.24; N, 11.33. Found: C, 32.36; H, 3.06; N, 10.03.

2.3. Synthesis of (1,1′-dimethyl-3,3′-(1,2-phenylene)diimidazolin-2,2′-diylidene)palladium(II) diiodide (*4*)

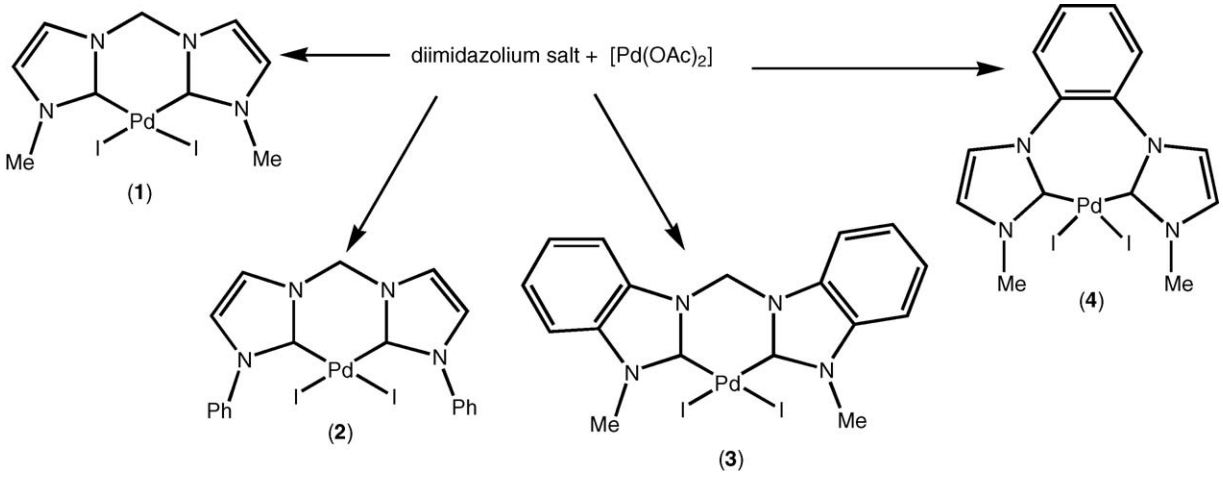
A solution of (**4a**) (0.130 g, 0.26 mmol) and [Pd(OAc)$_2$] (0.06 g, 0.26 mmol) in DMSO (4 mL) was heated at 120 °C for 2 h and then the volatiles were removed in vacuo. The orange residue was washed with MeCN (1 mL) and dried in vacuo, giving (**4**) as a orange powder (yield 70%). ^{1}H NMR (DMSO-d_6): δ 3.93 (s, 3H, CH_3), 7.65 (s, 1H, CH=CH), 7.79 (m, 3H, CH=CH and Ar). ^{13}C NMR (DMSO-d_6): δ 36.1 (CH_3), 123.4, 124.8, 126.6, 130.1 and 132.5 (CH=CH and Ar), 163.8 (NCN). Anal. Calcd. for $C_{14}H_{14}I_2N_4Pd$ (M = 598.3): C, 28.10; H, 2.34; N, 9.36. Found: C, 28.27; H, 2.32; N, 9.35.

2.4. General procedure for Heck coupling reaction

Method A: [10c] The aryl halide (25 mmol), sodium acetate (2.28 g, 27.5 mmol), 25 mL *N*,*N*-dimethylacetamide and 0.5 mL of a freshly prepared 0.5 mM solution of the complex in DMSO (2.5×10^{-4} mmol, 10^{-3} mol%) were placed in a round-bottomed flask, previously evacuated and filled with dinitrogen. The resulting mixture was pre-heated under stirring to 120 °C. Then the olefin (5.0 mL, 35 mmol) was added and heating was continued at 120 °C for 24 h. Yields were determined by GC [16]. *Method B*: [17] The aryl halide (2.0 mmol), sodium acetate (0.22 g, 2.4 mmol) and a solution of the required amount of complex (1.0×10^{-3} mmol, 0.05 mol%) in 4 mL *N*-methylpyrrolidone were placed in a Schlenk tube, previously evacuated and filled with dinitrogen. The resulting mixture was pre-heated under stirring to 120 °C. The olefin (0.35 mL, 2.4 mmol) was then added and the reaction mixture was further heated to 135 °C and stirred for 5 h. Yields were determined by GC [16].

3. Results and discussion

Palladium(II) carbene complexes with a chelating dicarbene ligand can be prepared by reaction of one equivalent of palladium(II) acetate with one equivalent of diimidazolium dihalide in DMSO at 120 °C under vacuum, following a strategy which has already been widely reported [3g,3h,10b,14]. In this reaction, the carbene ligands are generated in situ via deprotonation by the acetate ligands, yielding the corresponding neutral dicarbene-dihalide palladium complexes. We have prepared in this way dicarbene complexes (**1**)–(**4**) (Scheme 1), which differ for the nature of the nitrogen substituent, of the bridge between the carbene units or of the heterocyclic system. Whereas dicarbene complexes (**1**)–(**3**) were already known in literature, [10b,13,14] the preparation and characterization of



Scheme 1. Palladium(II) dicarbene complex catalysts investigated in the present work.

(**4**) is reported for the first time herein. Herrmann et al. have observed decomposition of the starting materials and formation of palladium black during the reaction if the bridge between the imidazolium units is longer than a CH_2 group, i.e. with ethylene or propylene spacers [13]. We have confirmed these findings in the former case. The success of the synthesis of the *o*-phenylenic-bridged complex (**4**) is probably due to the steric and conformational constraints imposed by the rigid spacer, which disfavour the occurrence of the side reactions observed with the more flexible bridges. Indeed, very recently the synthesis of palladium complexes of this kind with ethylene bridges has been reported; bulky aryl groups are, however needed as nitrogen substituents in the imidazolium salt precursors, probably for the same reason reported above [18].

The products are obtained as yellow to orange solids, which can be safely handled in air and are stable for long periods also in solution. They exhibit poor solubility in all solvents, except hot acetonitrile, *N*,*N*-dialkylamides and DMSO (the latter being used for their NMR characterization).

The ^{1}H NMR spectra of complex (**4**) exhibits signals slightly upfield in comparison with the parent diazolium salt; as expected, the C_2–H signal is absent. Correspondingly, the ^{13}C NMR spectrum shows the characteristic coordinated C_2 signal at δ ca. 163.8 ppm, well downfield from δ 138.5 ppm in the diazolium salt. Furthermore, there is only a single set of signals for the imidazolin-2-ylidene rings in both the ^{1}H and ^{13}C NMR spectra, which indicates a highly symmetric structure and therefore a bidentate chelating binding mode of the carbene ligand.

The obtained complexes have been employed as catalysts for the arylation of olefins with aryl halides (Heck reaction) [12]. The Heck reaction has become in the last years a widespread mean to assess the reactivity of palladium complexes; in particular, some Pd-carbene complexes are among the most active catalysts for this reaction [1b,6a,10,19]. Some dicarbene complexes, among which complex (**1**), have also been tested as catalysts [10]. However, in most cases catalytic tests were performed quite unsystematically, with relatively large amounts of catalyst and with strongly activated aryl bromide and iodide substrates. On the other hand, recent reports by de Vries et al. [17] and by Yao et al. [20] have highlighted that simple Pd salts in low concentration are already highly effective in catalyzing the Heck reaction of aryl bromides. The key feature is the dilution that apparently limits the formation of palladium nanoclusters and eventually of palladium black. This prevents the deactivation of the catalyst in that a relatively high proportion of palladium is always present as highly active molecular species. In the light of these findings, it is apparent that, in order to have a proper assessment of the reactivity of a novel Pd complex in the Heck reaction, such assessment should be done at low catalyst loading and preferably with non-activated or deactivated substrates. Catalytic tests at low palladium concentration are also called for by the need of high TON catalysts, which are the most interesting ones in view of practical application of the Heck reaction as highlighted recently by Farina [12b]. In this perspective, catalytic tests with Pd/ArX higher than 10^{-3} are of little use. Furthermore, simple Pd salts such as palladium(II) acetate should be used as benchmark catalysts under the same reaction conditions in order to have a reference value against which to measure the efficiency of the novel catalyst.

Thus, the complexes (**1**)–(**4**) have been tested in two standard Heck reactions, namely the reaction of an activated aryl bromide such as 4-bromoacetophenone or of a deactivated one such as 4-bromoanisole with *n*-butyl acryllate using two different reaction protocols. To the best of our knowledge, complexes (**2**)–(**4**) have never been previously tested as catalysts for this reaction. The protocol for the reactions with 4-bromoacetophenone (Method A) was derived from a work of Cavell and co-workers 10c] on related dicarbene complexes in order to compare the results obtained therein. The protocol for the reaction with 4-bromoanisole (Method B) was instead taken from the recent work of de Vries et al. [17]. Indeed, although we were unable to fully reproduce the results reported by de Vries et al., we have confirmed that the reaction conditions developed by him, and in particular the use of low Pd concentrations (10^{-4} to 10^{-5} M) and of Schlenk tubes as reaction vessels instead of the more traditional apparatus (round bottomed flask and reflux condenser), lead to significantly improved yields with deactivated aryl bromides.

The results of these catalytic tests are reported in Table 1. Initial tests were run with 4-bromoacetophenone (BrAcPh) as the reagent (entries 1–5). It can be appreciated that the majority of the carbene complexes show comparable or slightly supe-

Table 1
Heck reactions catalyzed by complexes (**1**)–(**4**)

Entry	Catalyst	Aryl halide[a]	Mol% of catalyst	Time (h)	Yield (%)	TON
1	(**1**)[b]	BrAcPh	0.001	24	13	13000
2	(**2**)[b]	BrAcPh	0.001	24	88	88000
3	(**3**)[b]	BrAcPh	0.001	24	63	63000
4	(**4**)[b]	BrAcPh	0.001	24	77	77000
5	[Pd(OAc)$_2$][b]	BrAcPh	0.001	24	68	68000
6	(**1**)[c]	BrAn	0.05	5	7	148
7	(**2**)[c]	BrAn	0.05	5	31	424
8	(**3**)[c]	BrAn	0.05	5	19	384
9	(**4**)[c]	BrAn	0.05	5	36	712
10	[Pd(OAc)$_2$][c]	BrAn	0.05	5	66	1320

[a] Reaction conditions: BrAcPh = 4-bromoacetophenone, BrAn = 4-bromoanisole.
[b] Reaction conditions: see Method A in Section 2.
[c] Reaction conditions: see Method B in Section 2.

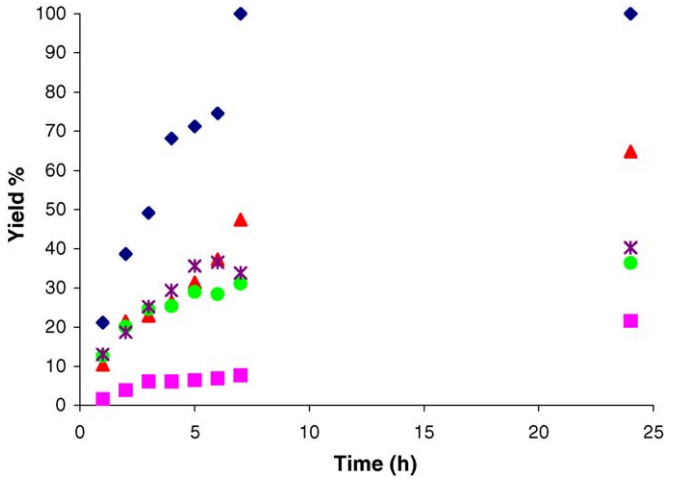


Fig. 1. Yield (%) vs. time diagram for the Heck reaction of 4-bromoanisole with *n*-butyl acrylate with different catalysts: $Pd(OAc)_2$ (♦), complex (**1**) (■), complex (**2**) (▲), complex (**3**) (●) and complex (**4**) (✱). For reaction conditions, see Method B in Section 2.

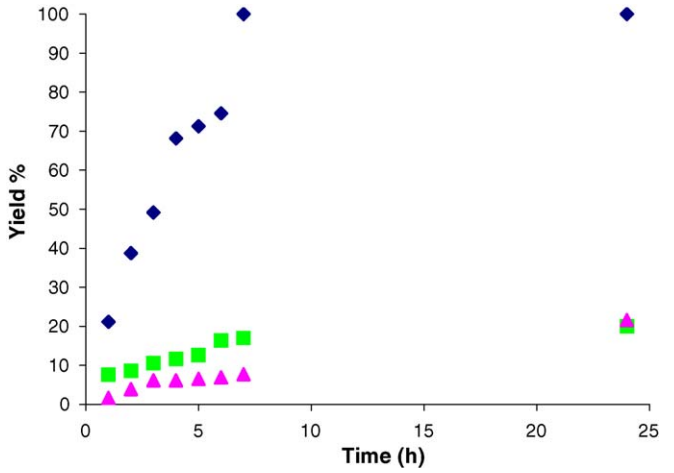


Fig. 2. Yield (%) vs. time diagram for the Heck reaction of 4-bromoanisole with *n*-butyl acrylate with different catalysts: $Pd(OAc)_2$ (♦), complex (**1**) (▲), $Pd(OAc)_2$ in presence of one equivalent of the azolium salt (**1a**) (■). For reaction conditions, see Method B in Section 2.

rior reactivity as compared to palladium(II) acetate, with the only exception of Herrmann's catalyst (**1**). The achieved yields in coupling product are fully comparable to the best results reported by Cavell and co-workers with *ortho*- and *meta*-xilylene bridged complexes, even in the absence of any promoter such as hydrazine hydrate or tetraalkylammonium salts [10c].

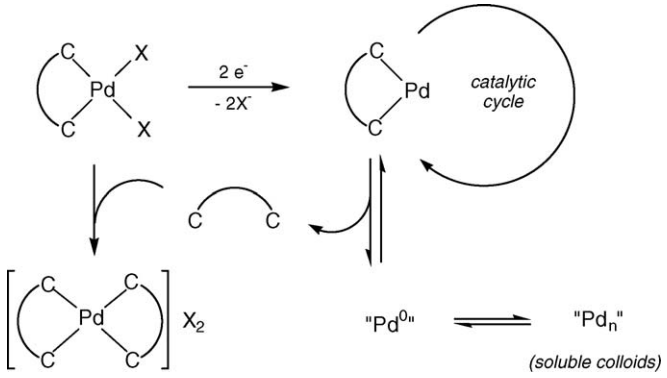
We were initially quite surprised by the low reactivity exhibited by Herrmann's catalyst (**1**) under our reaction conditions. However, the catalytic results proved to be fully reproducible. Moreover, exactly the same order of reactivity was observed in the subsequent tests with 4-bromoanisole (BrAn). In these tests, simple palladium(II) acetate proved to be the best catalyst, and catalyst (**1**) to be the worst, followed by catalyst (**3**). We later found out that very similar observations on the unexpectedly low reactivity of Herrmann's catalyst were reported in a very recent paper under somewhat different reaction conditions (0.5 mol% catalyst, 165–175 °C) [18]. In yet another recent paper on pincer dicarbene complexes as catalysts for the Suzuki reaction, *N*-methyl substituted ligands proved again to be the least effective [21]. In these papers, "steric effects" were claimed as responsible for the unsatisfactory performance of such Herrmann-type catalysts. However, no mention was made about the way in which such putative steric effects could influence the catalytic activity.

We became interested in finding a rational explanation for these experimental observations. First of all, we obtained kinetic plots for the Heck reaction of BrAn (Fig. 1) in order to determine if the different catalytic performances observed could be explained in terms of the existence of different induction times, if any, for the investigated catalysts. As can be clearly seen from Fig. 1, no induction period was however observed for any of them. Whereas palladium(II) acetate proved indeed to have the highest initial rate of reaction, catalysts (**2**)–(**4**) displayed comparable initial rates whereas catalyst (**1**) was clearly inferior.

We then tried to gain more insight into the underlying chemistry by running tests with catalyst (**1**) generated in situ. We found out that $[Pd(OAc)_2]$ in the presence of one equivalent of the parent azolium salt (**1a**) was only slightly more reactive than complex (**1**) and that the final yield at 24 h was the same (Fig. 2). Furthermore, the addition of (**1a**) in a 10-fold excess to $[Pd(OAc)_2]$ fully quenched the catalytic reaction. Thus, the azolium salt (**1a**) effectively acts as *apoison* towards the catalytically active species generated in situ from $[Pd(OAc)_2]$ under these conditions.

The experimental results reported above can be interpreted in the following terms. First of all, the palladium species which enters the catalytic cycle appears to be a dicarbene palladium(0) derivative, ensuing from the in situ reduction of the corresponding dicarbene palladium(II) precursors. This is supported by the fact that the initial reaction rates observed with all dicarbene palladium complex catalysts are significantly different from the one obtained with $[Pd(OAc)_2]$ alone. In principle, one could not rule out that the dicarbene ligand is released from the palladium center giving rise to the same active species formed in the case of a pure ligandless system. In fact, in several instances it was shown that allegedly very stable and robust palladium complexes did not withstand the reaction conditions and that they were only precursors to ligandless systems [17,22]. However, the kinetic reaction profile should in this case exhibit an induction period, after which it should resemble that obtained with a ligandless system (e.g. with simple $[Pd(OAc)_2]$) as shown by de Vries et al. in the case of palladacyclic catalyst precursors [17]. Since this is not the case in our systems, it can be assumed that the catalytically active species involve a coordinated dicarbene ligand.

Such catalytically active species appear to be less active that simple Pd species generated from $[Pd(OAc)_2]$. This aspect and the different initial rates of complex (**1**) and complexes (**2**)–(**4**) are more difficult to rationalize. A possible explanation is that such dicarbene complexes undergo dimerization in solution, leading to catalytically inactive dimers, either before reduction to the catalytically active palladium(0) species or after oxidative addition of the aryl halide (for a discussion about the existence of similar dimerization equilibria under Heck reaction conditions and their effect on the coupling rate, see ref. [23]). Experimen-



Scheme 2. A possible mechanism of deactivation of dicarbene palladium complex catalysts.

tal support for this possibility is offered by literature evidence that trans-binuclear palladium(II) complexes with two bridging dicarbene ligands can be formed in alternative to chelating mononuclear complexes [10a,b], and that the latter can indeed be transformed into binuclear complexes at high temperature [24]. Such a monomer–dimer conversion could also explain the lower initial reaction rate of complex (**1**) as the less sterically demanding ligand is expected to form the dimer more readily. We are currently engaged in finding experimental evidence for this transformation under Heck reaction conditions.

The poisoning effect of (**1a**) is most likely related to its deprotonation under reaction conditions (which are definitely basic) which yields the corresponding dicarbene (1,1′-dimethyl-3,3′-methylene-diimidazolin-2,2′-diylidene, **1b**). Such a free dicarbene ligand can potentially interact with catalytically active palladium(II) or palladium(0) species in solution forming bischelate tetracarbene complex. Although there are apparently no reports on tetracarbene palladium(0) complexes, the corresponding palladium(II) species are well-known [25]; remarkably, they were also reported to be formed during Heck couplings in 1,3-dialkylimidazolium ionic liquids and shown to be catalytically inactive [26]. Incidentally, this is also the reason why Pd-catalyzed reactions in such ionic liquids often occur much more efficiently in 2-alkylated derivatives, where the transformation into cyclic diaminocarbenes is impossible [27].

The rationalization of the poisoning effect of (**1a**) may also help explaining the apparent deactivation of the dicarbene complex catalysts, which was observed after a few hours of reaction (Fig. 1). In the course of the reaction, some degree of catalyst decomposition is invariably observed, as highlighted by the darkening of the reaction solution, which is indicative of the formation of Pd colloids. Remarkably, this does not prevent the catalytic system based on simple [$Pd(OAc)_2$] from reaching reaction completion. On the other hand, in the case of the dicarbene complex catalysts such a decomposition would lead to the buildup of free dicarbene in solution, which then acts as a poison, as discussed above (Scheme 2).

All the dicarbene palladium(II) complex catalysts investigated herein may be expected to behave in a similar way as (**1**). However, for complexes (**2**)–(**4**) the inhibiting effect of the dicarbene ligand is not as strong as for complex (**1**) and intermediate

Table 2
Heck reactions catalyzed by complexes (**1**) and (**2**) in presence of the azolium salts (**1a**) and (**2a**) (five-fold molar excess to palladium)

Catalyst	Diimidazolium salt	Yield (%)	Yield (%) without azolium salt
(**1**)	(**1a**)	14	21
(**1**)	(**2a**)	21	21
(**2**)	(**2a**)	73	65
(**2**)	(**1a**)	0	65

Reaction conditions: see Method B in Section 2.

initial reaction rates and final yields are observed. This implies that the postulated monomer–dimer equilibrium lies more to the side of the monomer in these cases, as well as that the parent dicarbenes (**2b**–**4b**) do coordinate to the corresponding catalytically active palladium(II) and/or palladium(0) dicarbene complexes less strongly than **1b**. The latter conclusion was confirmed by some cross-tests (Table 2), where palladium(II) precatalysts (**1**) and (**2**) were used in the presence of a five-fold excess of either their own parent azolium salt or of the other complex (**1a** and **2a**). Whereas **1a** exhibited a clear poisoning effect on both complexes (quite surprisingly, much more pronounced on complex (**2**) than on complex (**1**) itself), the azolium salt **2b** did not change significantly the catalytic performances of both (**1**) and (**2**). According to the interpretation given above, this means that on one hand the dicarbene **2b** is not able to interfere with the palladium species derived from (**1**). This is in line with recently reported results on a dicarbene ligand with *n*-butyl substituents, with which it was indeed possible to run the Heck reaction in an ionic liquid made out of the diimidazolium salt [28]. On the other hand, **1b** is apparently able to interact with the palladium complexes derived from dicarbenes **1b** or **2b**, so that their catalytic activity is severely compromised.

In summary, the catalytic activity of the dicarbene complexes (**1**)–(**4**) in the Heck coupling of 4-bromoanisole with *n*-butyl acryllate is likely to be dependent on the coordinating ability of the corresponding dicarbene: the higher this ability, the lower the catalytic activity. In fact, the dicarbene ligand appears to have an inhibiting effect, which can be correlated to its ability to form inactive dimers and/or bischelate, tetracarbene palladium(II) derivatives. From the kinetic plots of Fig. 1, we can conclude that the coordinating ability of the dicarbenes (**1b**)–(**4b**) should decrease in the order $\mathbf{1b} > \mathbf{3b} \approx \mathbf{4b} > \mathbf{2b}$, which is roughly the order of increasing steric bulkiness. In this connection, the substitution of the small methyl groups in the 1,1′ positions of the dicarbene moiety with phenyl groups is apparently much more effective in improving the catalytic activity than the replacement of either imidazole rings with benzimidazole ones or of the methylene bridge with the phenylene one.

4. Conclusions

The dicarbene complexes (**1**)–(**4**) are active in the Heck coupling of 4-bromoacetophenone and 4-bromoanisole with *n*-butylacrylate under "omeopathic" conditions. The more reactive 4-bromoacetophenone tends to level off the catalytic performance and with this substrate the dicarbene precatalysts perform

almost equally well as palladium acetate. With the deactivated aryl bromide 4-bromoanisole the dicarbene complexes exhibit lower activity with respect to the ligandless system based on palladium acetate alone. The inhibiting effect of the dicarbene could be associated to its ability to form inactive dimers and/or bischelate, tetracarbene palladium(II) derivatives. In this connection, the coordinating ability of the dicarbenes is likely to depend on its steric features, with catalytic activity increasing with ligand bulkiness.

The results of the present study illustrate once more the importance of making critical comparisons with suitable benchmark catalysts (such as conventional [$Pd(OAc)_2$] under omeopathic conditions) while testing new catalytic systems. Only through comparisons of this kind will the catalytic performance of the new catalysts be properly assessed.

References

[1] (a) W.A. Herrmann, T. Weskamp, V.P.W. Böhm, Adv. Organomet. Chem. 48 (2001) 1;
(b) L. Jafarpour, S.P. Nolan, Adv. Organomet. Chem. 46 (2000) 181;
(c) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.

[2] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[3] (a) W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290;
(b) W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. 36 (1997) 2162 (and references cited therein).

[4] (a) H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. 72 (1960) 494;
(b) H.-W. Wanzlick, H.-J. Klemer, Angew. Chem. 73 (1961) 493;
(c) H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. 80 (1968) 154;
(d) K. Öfele, J. Organomet. Chem. 12 (1968) C42.

[5] A. Fürstner, Angew. Chem. Int. Ed. 39 (2000) 3012.

[6] (a) W.A. Herrmann, K. Öfele, D.V. Preysing, S. Schneider, J. Organomet. Chem. 687 (2003) 229;
(b) C. Yang, H.M. Lee, S.P. Nolan, Org. Lett. 3 (2001) 1511;
(c) S.R. Stauffer, S. Lee, J.P. Stambuli, S.I. Hauck, J.F. Hartwig, Org. Lett. 2 (2000) 1423.

[7] I.E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, Science 298 (2002) 204.

[8] (a) R. Jackstell, S. Harkal, H.J. Jiao, A. Spannenberg, C. Borgmann, D. Rottger, F. Nierlich, M. Elliot, S. Niven, K.J. Cavell, O. Navarro, M.S. Viciu, S.P. Nolan, M. Beller, Chem. Eur. J. 10 (2004) 3891;
(b) R. Jackstell, M.G. Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Rottger, O. Briel, R. Karch, M. Beller, Angew. Chem. Int. Ed. 41 (2002) 986.

[9] D.R. Jensen, M.J. Schultz, J.A. Mueller, M.S. Sigman, Angew. Chem. Int. Ed. 42 (2003) 3810.

[10] (a) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. Int. Ed. 34 (1995) 2371;
(b) W.A. Herrmann, C.-P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93;
(c) M.A. Magill, D.S. McGuinness, K.J. Cavell, G.J.P. Britovsek, V.C. Gibson, A.J.P. White, D.J. Williams, A.H. White, B.W. Skelton, J. Organomet. Chem. 617–618 (2001) 546;
(d) S. Gründemann, M. Albrecht, J.A. Loch, J.W. Faller, R.H. Crabtree, Organometallics 20 (2001) 5485;
(e) J.A. Loch, M. Albrecht, E. Peris, J. Mata, J.W. Faller, R.H. Crabtree, Organometallics 21 (2002) 700.

[11] E. Peris, R.H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239.

[12] For recent reviews, see;
(a) A. Zapf, M. Beller, Chem. Commun. (2005) 431;
(b) V. Farina, Adv. Synth. Catal. 346 (2004) 1553;
(c) A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176;
(d) A. Biffis, M. Zecca, M. Basato, J. Mol. Catal. A: Chem. 173 (2001) 249;
(e) N.J. Whitcombe, K.K. Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449;
(f) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.

[13] W.A. Herrmann, J. Schwarz, M. Gardiner, Organometallics 18 (1999) 4082.

[14] F.E. Hahn, M. Foth, J. Organomet. Chem. 585 (1999) 241.

[15] Y.-H. So, Macromolecules 25 (1992) 516.

[16] C. Tubaro, A. Biffis, M. Basato, F. Benetollo, K.J. Cavell, L.-l. Ooi, Organometallics 24 (2005) 4153.

[17] A.H.M. de Vries, J.M.C. Mulders, J.H.M. Mommers, H.J.W. Hendrickx, J.G. de Vries, Org. Lett. 5 (2003) 3285.

[18] H.M. Lee, C.Y. Lu, C.Y. Chen, W.L. Chen, H.C. Lin, P.L. Chiu, P.Y. Cheng, Tetrahedron 60 (2004) 5807.

[19] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69.

[20] Q. Yao, E.P. Kinney, Z. Yang, J. Org. Chem. 68 (2003) 7528.

[21] V.C. Vargas, R.J. Rubio, K. Hollis, M.E. Salcido, Org. Lett. 5 (2003) 4847.

[22] M. Nowotny, U. Hanefeld, H. van Konigsveld, T. Maschmeyer, Chem. Commun. (2000) 1877.

[23] T. Rosner, J. Le Bars, A. Pfaltz, D.G. Blackmond, J. Am. Chem. Soc. 123 (2001) 1848.

[24] G. Bertrand, E. Diez-Barra, J. Fernandez-Baeza, H. Gornitzka, A. Moreno, A. Otero, R.I. Rodriguez-Curiel, J. Tejeda, Eur. J. Inorg. Chem. (1999) 1965.

[25] (a) W.P. Fehlhammer, T. Bliss, U. Kernbach, I. Brüdgam, J. Organomet. Chem. 490 (1995) 149;
(b) C.A. Quezada, J.C. Garrison, C.A. Tessier, W.J. Youngs, J. Organomet. Chem. 671 (2003) 183;
(c) M.V. Baker, B.W. Skelton, A.H. White, C.C. Williams, J. Chem. Soc., Dalton Trans. (2001) 111;
(d) R.E. Douthwaite, D. Haüssinger, M.L.H. Green, P.J. Silcock, Organometallics 18 (1999) 4584;
(e) R. Fränkel, J. Kniczeck, W. Ponikwar, H. Nöth, K. Polborn, W.P. Fehlhammer, Inorg. Chim. Acta 312 (2001) 23.

[26] L. Xu, W. Chen, J. Xiao, Organometallics 19 (2000) 1123.

[27] See for example L. Magna, Y. Chauvin, G.P. Niccolai, J.-M. Basset, Organometallics 22 (2003) 4418.

[28] C.-M. Jin, B. Twamley, J.M. Shreeve, Organometallics 24 (2005) 3020.