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Highly Efficient Alkyne Hydroarylation with Chelating Dicarbene Palladium(II) and Platinum(II) Complexes[1]

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Abstract: We report on a novel reaction protocol for the coupling of arenes with alkynes (the Fujiwara reaction), yielding products of formal *trans*-hydroarylation of the triple bond. The protocol makes use of a chelating N-heterocyclic dicarbene palladium(II) complex as catalyst and allows us to perform the reaction in a few hours with only 0.1 mol% catalyst yielding the *trans*-hydroarylation product in high yields and with excellent selectivity. We discuss the applicability of this reaction protocol, which appears at present quite general with respect to the alkyne, albeit limited to electron-rich arenes. We also present the results of catalyst optimisation with respect to the nature of the nitrogen substituents in the carbene units, of the bridging group between the carbene units and of the coordinated anionic ligands. Finally, we also discuss the catalytic performance of a related chelating dicarbene complex of platinum(II).

Keywords: alkynes; C–H activation; hydroarylation; N-heterocyclic carbenes; palladium; platinum

Introduction

Transition metal-catalysed C–C coupling reactions have undoubtedly become one of the most important reaction classes in chemical synthesis.[2] In particular, Pd-catalysed coupling reactions, most notably the Heck and Suzuki reactions, have been developed up to a very high degree of synthetic utility.[3] Such reactions allow the transformation of aryl and vinyl halides into more complex organic compounds, through the substitution of the halide with an organic moiety. However, their applicability to chemical processes is often limited by the need to use aryl bromides or iodides as reagents, which are more reactive but also more costly and less widely available than the corresponding chlorides; furthermore, salt waste is usually formed as coproduct of the reaction. A process that effects the same transformations upon direct functionalisation of an aromatic C–H bond would be obviously preferable from the point of view of both reagent cost and process cleanness, but has yet to be developed, although there are considerable literature precedents for reactions of this kind.[4,5]

Simple palladium(II) compounds such as $Pd(OAc)_2$ in an acidic environment are, for example, known to promote the coupling reaction of arenes with alkynes (the Fujiwara reaction).[6] In this case, products of formal hydroarylation of the triple bond are formed. The reaction is characterised by a high and quite unusual stereoselectivity: in fact, *cis*-arylalkenes (i.e., the thermodynamically less favoured alkenes) are the major products. The reaction mechanism was initially thought to involve electrophilic arene metallation as the key reaction step;[6b] however, in recent years valuable experimental work carried out by Tunge and Foresee as well as theoretical calculations by Soriano and Marco-Contelles have brought evidence in favour of a mechanism going through a Friedel–Crafts-type alkenylation.[7]

From the technological point of view, the Fujiwara reaction is arguably one of the most promising C–C coupling reactions *via* C–H activation/functionalisation, since it involves cheap, commercially available reagents and it requires neither directing groups on the arene nor oxidising agents to regenerate the catalyst. However, its possible industrial utilisation cannot leave apart a thorough optimisation of the catalyst and of the reaction conditions. In particular, the original Fujiwara reaction protocol implies using 1–5 mol% palladium, which heavily affects the cost of the process. Other metal centres such as platinum(II),[8] gold(I) and gold(III)[9] have been successfully employed as alternative catalysts, but their efficiency appears to be lower than that of palladium(II). Furthermore, use of less-noble, electrophilic metal centres has been also reported; however, their applicability appears to be currently limited to arylacetylenes.[10]

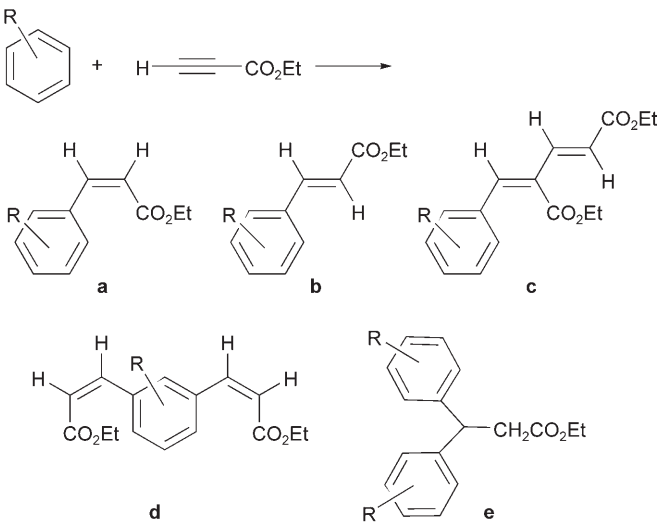
A viable solution could be the use of palladium(II) complexes with suitable ligands, which should increase the stability of the catalyst under reaction conditions without negatively affecting its reactivity. N-heterocyclic carbene ligands[11] appear particularly suited to this purpose since it is known that their palladium(II) complexes possess a high thermal and hydrolytic stability, even under strongly acidic conditions.[12] Not surprisingly, therefore, monocarbene palladium(II) complexes are the only complexes which have been reported to be active in the Fujiwara reaction in the absence of other promoters, though their activity is only slightly superior to that of simple $Pd(OAc)_2$.[13]

Our research group has been interested for some time in the synthesis and catalytic application of transition metal complexes with N-heterocyclic carbene ligands in technologically relevant reactions like, for example, Heck reaction or C–N and C–O couplings.[14] In particular, we have recently started a systematic study aimed at critically evaluating the reactivity of chelating dicarbene palladium(II) complexes, by tuning the properties of the dicarbene ligand, acting on the substituents at the imidazole ring and on the nature of the bridging group.[14b] In this contribution, we investigate the catalytic efficiency of complexes of this kind in the Fujiwara reaction.

Results and Discussion

We decided to begin our evaluation of the catalytic efficiency of chelating dicarbene palladium(II) complexes in the Fujiwara hydroarylation by testing complex **1** (Figure 1), whose preparation and characterisation is reported for the first time herein,[15] in a standard test reaction between pentamethylbenzene and ethyl propiolate.

At first, we adopted the reaction conditions usually employed by Fujiwara (1 equiv. alkyne, 2 equivs. arene, 0.01 equiv. catalyst, solvent CF_3COOH:CH_2Cl_2 4:1, room temperature, 20 h).[6b] However, under these conditions the conversion amounted to only a few percent (albeit with complete selectivity for the *Z* product). While attempting to improve the reactivity of the catalytic system, we chose to increase the reaction temperature to 80 °C and to replace dichloromethane with 1,2-dichloroethane. Remarkably, under these conditions, the reaction gave complete conversion and 88 % selectivity to the *Z* product (other products being the *E* isomer **b** and the product of double alkyne insertion **c**, see Scheme 1). We repeated the experiment using only 0.1 mol % catalyst and again we obtained a very high conversion (96 %) with 86 % selectivity to the *Z* product. Finally, determination of the conversion curve (Figure 2) made it clear that the reaction proceeded rapidly during the first five hours, reaching 89 % conversion with 92 % selectivity; after this time, the concentration of the *Z* product remained almost constant, eventually decreasing at longer reaction times, while there was a slow but continuous increase in the concentration of the *E* product, due to a background acid-catalysed isomerisation process.



Scheme 1. Possible reaction products of the Fujiwara hydroarylation.

We also found out that use of excess arene was not necessary in order to achieve good results, although the reaction rate was somewhat slower: 68 % conversion with 94 % selectivity for the *Z* product were obtained after 7 h using catalyst **1** with only 1 equiv. of pentamethylbenzene. On the other hand, excess trifluoroacetic acid was indeed fundamental, as in Fujiwara's case. Using as solvent CF_3COOH:1,2-dichloroethane 1:4 the conversion was halved, while the selectivity remained high (94 %). In conclusion, at the end of this preliminary study we found ourselves able to perform the reaction in high yields at 80 °C with stoichiometric reagents and using only 0.1 mol % catalyst.

On the basis of the above, the catalytic efficiency of complex **1** appears superior to both $Pd(OAc)_2$[6b] and monocarbene palladium(II) complexes[13] which, however, were tested at lower temperature. Therefore, we performed some additional experiments to compare more directly the efficiency of the various catalysts.

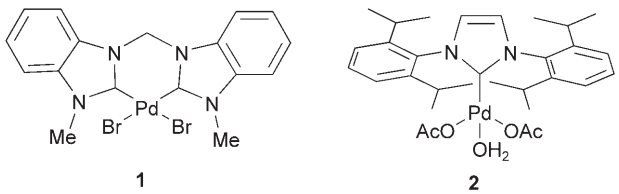


Figure 1. Complexes **1** and **2**.

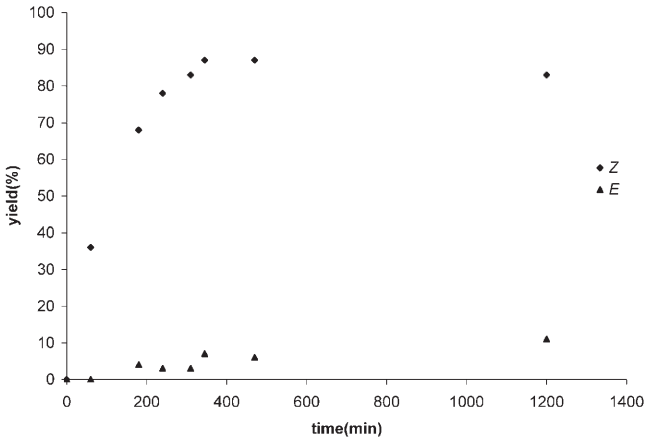


Figure 2. Yield (%) *vs.* time diagram for the reaction of pentamethylbenzene and ethyl propiolate catalysed by complex **1**.

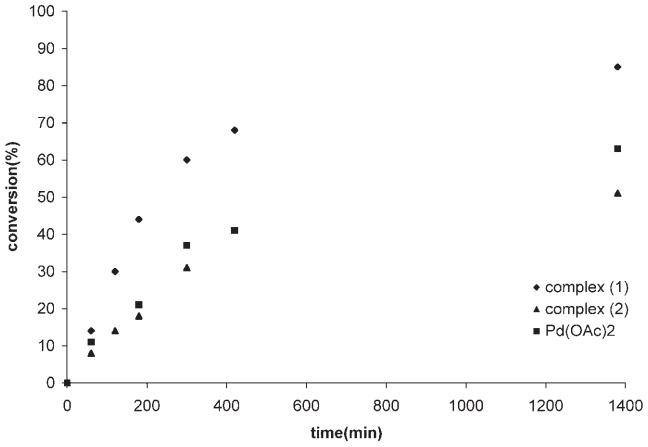


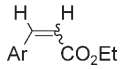
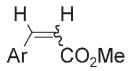
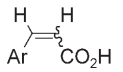
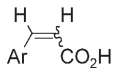
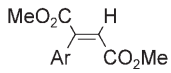
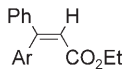
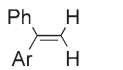
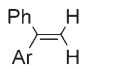
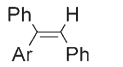
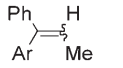
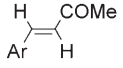
Figure 3. Conversion (%) *vs.* time diagram for the reaction of pentamethylbenzene and ethyl propiolate catalysed by complex **1**, complex **2** and $Pd(OAc)_2$.

Determination of the conversion curves under our reaction conditions (Figure 3) revealed that complex **1** was indeed the most efficient catalyst for this reaction, with an initial activity almost two times higher than that of both $Pd(OAc)_2$ and monocarbene palladium complex **2**,[16] which expectedly forms Nolan's bis(trifluoroacetate) complex *in situ*. After five hours of reaction, $Pd(OAc)_2$ gave only 37% conversion with 92% selectivity for the *Z* product, while complex **2** gave 31% conversion with 94% selectivity.

With this result at hand, we set out to evaluate the generality of our catalytic system, with respect to both the alkyne and the arene. The results are reported in Table 1 and Table 2, respectively.

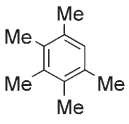
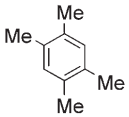
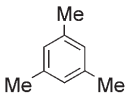
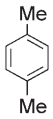
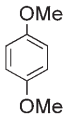
Differently substituted alkynes were reacted with pentamethylbenzene under our standard conditions; the reaction time was not optimised for any of the alkynes employed. It is apparent from the results reported in Table 1 that our catalytic system displays higher activities and selectivities than Fujiwara's one, which invariably requires larger amounts of catalysts and/or longer reaction times.[6b] Electron-poor terminal alkynes are very reactive, though internal alkynes substituted with two electron-withdrawing groups are converted more sluggishly. 3-Butyn-2-one (Table 1, entry 9) gives the *E*-product exclusively, and phenylacetylene (Table 1, entry 6) the α-arylated product, as it is invariably the case with metal-catalysed hydroarylations;[6–10,13] with the latter substrate the yield is quite low, but it has to be remarked that in this case alkyne polymerisation and hydration by traces of water are found to be serious competitive reactions. Clearly, the reaction conditions need in this case to be further optimised in order to suppress or at least to limit the side reactions. 1-Phenyl-1-propyne, diphenylacetylene and ethyl phenylpropiolate are also hydrated to a small extent under the employed reaction conditions, thus explaining the moderate yields observed (Table 1, entries 8, 7 and 5, respectively).

Table 1. Alkyne screening for the Fujiwara hydroarylation with pentamethylbenzene catalysed by complex **1**.

Entry	Alkyne	Time [h]	Product	Yield [%][a] (*Z*:*E*)
1	H–≡–CO_2Et	5		58 (57:1)
2	H–≡–CO_2Me	5		56 (18:1)
				11 (10:1)
3	H–≡–CO_2H	5		79 (25:1)
4	MeO_2C–≡–CO_2Me	48		28
5	Ph–≡–CO_2Et	24		23
				25
6	Ph–≡–H	5		20
7	Ph–≡–Ph	5		35
8	Ph–≡–Me	5		39 (7:1)
9	H–≡–COMe	5		87

[a] Yield [%] determined by GC-MS and/or ^1H NMR. *Reaction conditions:* see Experimental Section.

Table 2. Arene screening for the Fujiwara hydroarylation with ethyl propiolate catalysed by complex **1**.

Arene	Time [h]	Conversion[a]	Yield [%][a]				
			a[b]	**b**	**c**	**d**	**e**
	5	73	64 (5)	1 (1)	2	-	-
	24	87	50 (25)	7 (3)	2	-	-
	5	58	47 (4)	-	3	4	-
	24	81	62 (11)	1	3	4	-
	5	74	58 (4)	1	3	8	-
	24	81	34 (25)	5 (3)	4	10	-
	5	10	5 (1)	2	2	-	-
	24	30	7 (14)	6	3	-	-
	5	20	4	-	-	-	8

[a] Yield [%] determined by GC-MS and/or ^{1}H NMR.
[b] In parentheses the yield in the hydrolysed product. *Reaction conditions:* see Experimental Section.

Traces of water may also hydrolyse ester functions under the conditions of the Fujiwara reaction:[6b] limited hydrolysis of the reaction product was indeed observed, most notably with methyl propiolate (Table 1, entry 2), while in the case of ethyl phenylpropiolate (Table 1, entry 5) the reaction product was a mixture of the expected ester and of the corresponding decarboxylated compound, presumably deriving from ester hydrolysis with subsequent rapid decarboxylation.

The screening of arene substrates was performed upon reacting ethyl propiolate with differently substitued arenes, both in terms of the numbers of substituents and of their nature. The results reported in Table 2 show that most methyl-substituted benzenes are competent substrates irrespective of the number of substituents, although the yield recorded with *p*-xylene was unexpectedly low. Hydroarylation yields could be improved by prolonging the reaction time. However, this also resulted in the extensive hydrolysis of the ester function of the product (Table 2). We are currently further optimising the reaction conditions in order to suppress hydrolysis as well as the other side reactions observed with different alkynes (see above).

The distribution of side products (see Scheme 1) also changes significantly upon going from 1,2,4,5-tetramethylbenzene to *p*-xylene. While in the former case the double hydroarylation product is the main side product, in the latter case it is the *E*-monoarylated product. This is evidently the consequence of the decreased reactivity of the aromatic ring towards hydroarylation as well as of the possible greater incidence of thermal isomerisation through the dipolar mechanism already proposed by Fujiwara and by Alper.[6b,17]

A slow reaction was observed with *p*-dimethoxybenzene as well, as reported also by Fujiwara and Nolan;[6b,13] however, in our case the arene:alkyne 2:1 adduct **e** was the main reaction product (Scheme 1). Prolonging the reaction time led to an increase in conversion but also to the formation of oligomeric products presumably deriving from further electrophilic substitution reactions (attack of another product molecule on the arene rings of the 2:1 adduct). Finally, the presence of halide substituents had a deleterious effect on the reaction, *p*-bromotoluene being almost inactive and *p*-bromoanisole being only slowly converted with poor selectivity. However, it has to be remarked that arenes substituted with electron-withdrawing groups are usually inactive for this reaction: the only aryl bromide that is known to be converted is mesityl bromide.[6–10,13]

Having established the high catalytic efficiency in the Fujiwara reaction of complex **1**, we then tested and compared the efficiency of a series of chelating dicarbene palladium(II) complexes, already known in literature,[15,18–22] and characterised by different sets of dicarbene and anionic ligands (Figure 4). The Fujiwara reaction between pentamethylbenzene and ethyl propiolate was employed as a standard test reaction to probe the reactivity of these palladium(II) complexes.

First of all, we evaluated the influence of the nature of the anionic ligand on the reactivity of our complexes. Determination of the conversion curves for complexes **1** and **3** (Figure 5) and for complexes **4**–**6** (Figure 6) revealed that this influence is very small. Indeed, the catalytic activity of the complexes is the same within the margin of experimental error, irrespective of the nature of the halid. These results strongly support the hypothesis that the actual catalytically active species does not contain halide ligands, which are probably removed through exchange with trifluoroacetate anions. Remarkably, DFT calculations, performed by Strassner et al., have predicted that replacement of the two halides by trifluoroacetate anions takes place at high temperatures, like in our reaction conditions, and that the binding energy difference between the various halides and the metal is not large enough to produce effects on the kinetic outcome of the reaction.[23]

On the other hand, the nature of the dicarbene ligand has an effect on catalytic activity. This effect can be appreciated by comparing the performance of a series of complexes with the same anionic ligand but different dicarbene ligands (**3** and **6**–**9**). Analysis

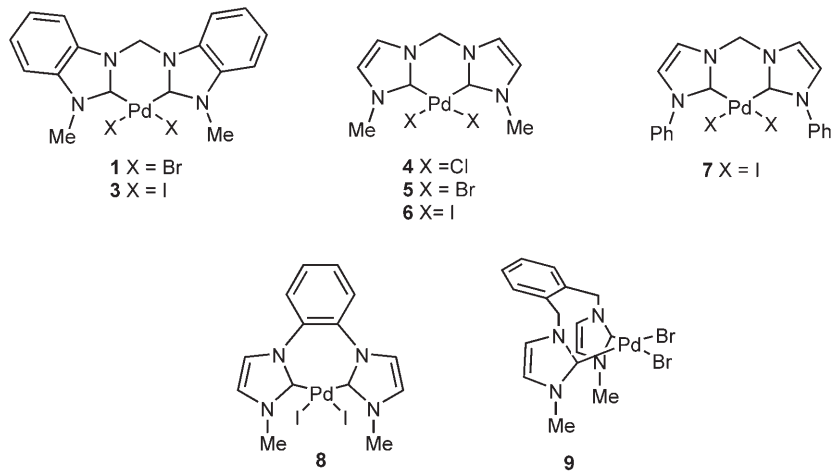


Figure 4. Palladium(II) dicarbene complexes employed as catalysts in this study.

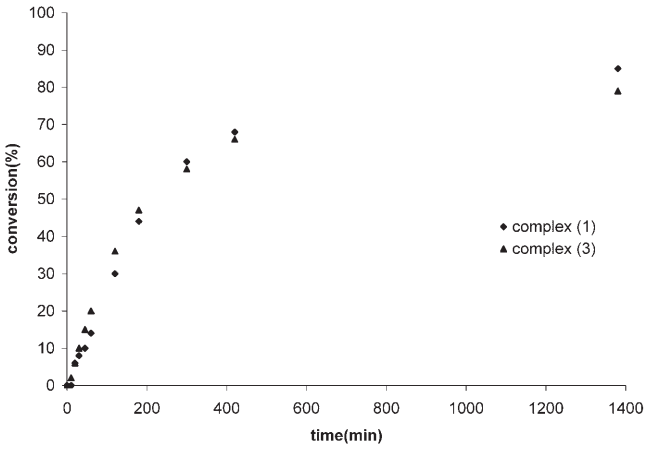


Figure 5. Conversion (%) *vs.* time diagram for the reaction of pentamethylbenzene and ethyl propiolate catalysed by complexes **1** and **3**.

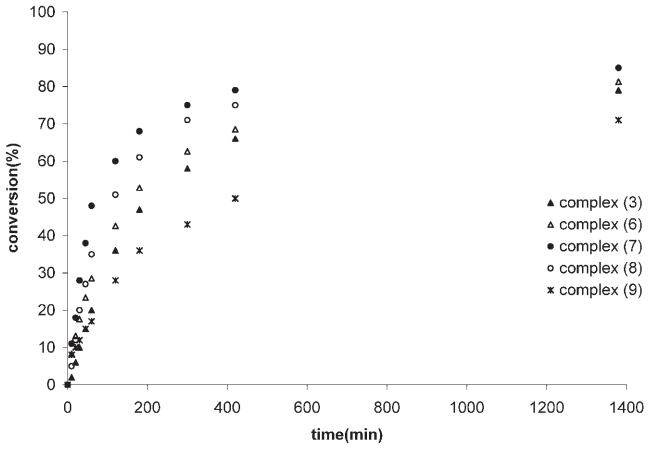


Figure 7. Conversion (%) *vs.* time diagram for the reaction of pentamethylbenzene and ethyl propiolate catalysed by complex **3** and complexes **6–9**.

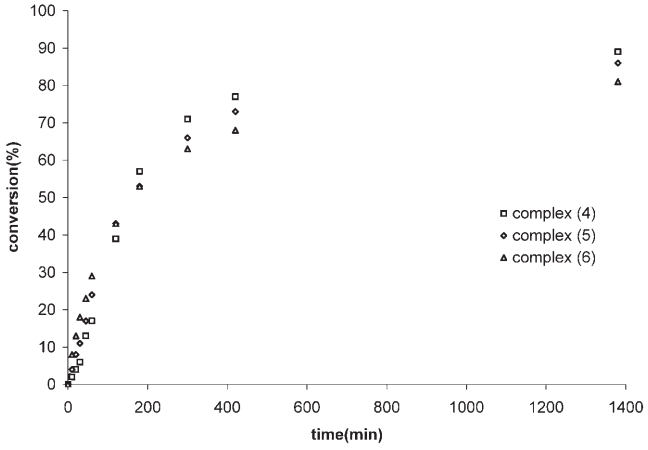
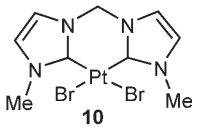


Figure 6. Conversion (%) *vs.* time diagram for the reaction of pentamethylbenzene and ethyl propiolate catalysed by complexes **4–6**.

of the conversion curves (Figure 7) revealed that all complexes perform in a similar manner over long reaction times (23 h), reaching comparable conversions. However during the first 5 h of reaction the catalytic performances are quite different and, in particular, it turns out that complexes with the more hindering NHC ligands **7** and **8** show higher activity. The methylbenzimidazolin-2-ylidene complex **3** and the corresponding imidazolin-2-ylidene complex **6** also perform quite well in this reaction, while the reactivity of complex **9** is significantly lower. These results suggest that the actual catalytically active species still contains the dicarbene ligand, and that the steric hindrance of the dicarbene ligand is an important factor in determining the reactivity of the catalyst. We are now extending this study in order to further optimise the structure of the dicarbene ligand as well as to fully identify the



10

Figure 8. Platinum(II) complex **10**.

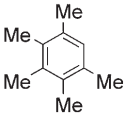
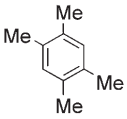
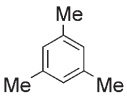
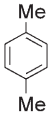
real catalytically active species involved in the reaction.

Finally, we have also started a preliminary evaluation of the catalytic performance of dicarbene platinum(II) complex **10** (Figure 8), which has been synthesised following an already reported strategy.[24] Simple platinum(II) salts such as $PtCl_2$ were already tested as catalysts by Fujiwara et al., and found to be less active but sometimes more selective than palladium(II) compounds, provided they are activated upon halide removal by a proper silver(I) salt of a non-coordinating anion.[6,8] The results in the arene and alkyne screening are reported in Table 3 and Table 4, respectively.

The screening of arene and alkyne substrates was performed following the protocol used for the palladium complexes, that is, upon reacting ethyl propiolate with differently substitued arenes or upon reacting pentamethylbenzene with various alkynes. In general, our catalytic system using complex **10** displays slightly lower productivities than Fujiwara's systems ($PtCl_2$/2 AgOAc or $PtCl_2$/2 AgOTf) which, however, require higher catalyst loadings (2.5–5 mol%), longer reaction times (15–24 h), and most notably an Ag salt as cocatalyst.[6b,8b] Moreover, comparing the results obtained with platinum complex **10** with those of palladium complex **1**, it is evident that conversions and selectivities are quite similar.

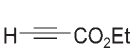
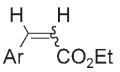
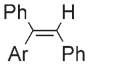
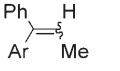
Therefore, the results of this preliminary study highlight the fact that Pt-dicarbene complexes can represent an alternative to Pd complexes in this reaction. Consequently, we are currently investigating also these complexes in more detail.

Table 3. Arene screening for the Fujiwara hydroarylation with ethyl propiolate catalysed by complex **10**.

Arene	Time [h]	Conversion[a]	Yield [%][a]				
			a[b]	**b**	**c**	**d**	**e**
	5	72	63 (6)	1 (1)	-	-	-
	5	56	47 (4)	-	1	4	-
	5	63	45 (4)	1 (1)	-	12	-
	5	4	3 (1)	-	-	-	-

[a] Yield [%] determined by GC-MS and/or ^{1}H NMR.
[b] In parentheses the yield in the hydrolysed product. *Reaction conditions:* see Experimental Section.

Table 4. Alkyne screening for the Fujiwara hydroarylation with pentamethylbenzene catalysed by complex **10**.

Alkyne	Time [h]	Product	Yield [%][a] (*Z*:*E*)
	5		72 (35:1)
	5		51
	5		45 (7:2)

[a] Yield [%] determined by GC-MS and/or ^{1}H NMR.
[b] In parentheses the yield in the hydrolysed product. *Reaction conditions:* see Experimental Section.

Conclusions

In conclusion, we have developed a novel reaction protocol for the Fujiwara hydroarylation employing chelating dicarbene palladium(II) and platinum(II) complexes as catalyst. The protocol allows us to perform the reaction with good to excellent yields and with high chemo- and stereoselectivity in short times, with stoichiometric reagents and with only 0.1 mol% catalyst. The reaction protocol appears to be quite general with respect to the alkyne, while its applicability to arene substrates is at present limited to electron-rich molecules. Work currently in progress aims at expanding the applicability of this reaction to electron-poor arenes (a class of compounds for which there is at present no viable catalyst), at running the reaction under milder conditions (lower temperature, less acidic environment) as well as at understanding the reaction mechanism in greater detail.

Experimental Section

General Remarks

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or dinitrogen. The reagents were purchased by Aldrich as high-purity products and generally used as received. Complexes **2**,[16] **4**,[18] **5**,[19]

6,[20] **7**,[21] **8**,[14b] **9**,[22] **10**[24] and 1,1′-dibenzimidazolylmethane[25] were prepared according to literature procedures. Complex **3** was prepared in the same manner as **1** (see below) using KI instead of KBr and its spectroscopic characterisation was identical to that reported in the literature.[15] 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.

Synthesis of 1,1′-Dimethyl-3,3′-methylenebis(benzimidazolinium) Tetrafluoborate (1a)

A solution of 1,1′-dibenzimidazolylmethane (1.0 g, 4.0 mmol) in dichloromethane (15 mL) was added in small portions to a suspension of Me_3OBF_4 (1.43 g, 9.7 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at room temperature for 24 h and then filtered. The obtained white solid was recrystallised from MeOH/H_2O (95/5); yield: 50%; anal. calcd. for $C_{17}H_{18}B_2F_8N_4{\cdot}2H_2O$ (M = 487.99): C 41.84, H 4.54, N 11.48; found: C 41.60, H 3.74, N 11.25%; ^{1}H NMR (DMSO-d_6, 25 °C): δ = 4.13 (s, 3H, CH_3), 7.39 (s, 1H, CH_2), 7.5–8.5 (m, 4H, Ar), 10.10 (s, 1H, NC*H*N); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 25 °C): δ = 33.7 (CH_3), 54.9 (CH_2), 113.5, 114.1, 127.2, 127.5, 130.3, 131.8 (C Ar), 144.3 (N*C*HN).

Synthesis of (1,1′-Dimethyl-3,3′-methylenedibenzimidazolin-2,2′-diylidene)palladium(II) Dibromide (1)

A solution of $Pd(OAc)_2$ (0.12 g, 0.49 mmol), diimidazolium salt (**1a**) (0.25 g, 0.50 mmol) and KBr (0.12 g, 1.00 mmol) in DMSO (10 mL) was heated at 60 °C for 2 h, 80 °C for 1 h, 120 °C for 1 h; the solvent was removed under vacuum and the orange residue was washed with acetonitrile (3 × 5 mL), filtered and dried under vacuum; yield: 58%; anal. calcd. for $C_{17}H_{16}Br_2N_4Pd{\cdot}2KBF_4$ (M = 794.2): C 25.71, H 2.01, N 7.05; found: C 25.65, H 1.92, N 7.14%; ^{1}H NMR (DMSO-d_6, 25 °C): δ = 4.10 (s, 3H, CH_3), 6.75 e 7.40 (2d, 1H, CH_2), 7.40–7.50 (m, 4H, Ar), 7.67 (d, 1H, C*H*=CH), 8.19 (d, 1H, C*H*=CH); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 25 °C): δ = 35.9 (CH_3), 57.4 (CH_2), 110.9, 111.8, 124.1, 124.3, 132.4, 134.0 (C Ar), 171.4 (N*C*N).

General Procedure for the Catalytic Tests

This is a general procedure for the catalytic tests reported in Table 1 and for the determination of conversion curves. The arene (2.65 mmol, if solid) and the palladium(II) complex (0.00265 mmol) were placed in a 50-mL round-bottomed flask, previously evacuated and filled with argon. Trifluoroacetic acid (4 mL), 1,2-dichloroethane (1 mL) and the arene (if liquid) were then added and the resulting solution was stirred at room temperature for 5 min. Finally the alkyne (2.65 mmol) was added and the reaction mixture was heated at 80 °C and further stirred for 5 h, unless otherwise noted. Portions of the solution (0.2 mL) were drawn off from the reaction mixture and analysed by ^{1}H NMR or GC-MS. For the catalytic tests reported in Table 2 the molar amounts of the various reagents were slightly changed as follows: arene (4.3 mmol), alkyne (4.3 mmol), catalyst (0.0043 mmol), TFA (4 mL) and 1,2-dichloroethane (1 mL). For the catalytic tests reported in Table 3 and Table 4 the molar amounts of the various reagents were as follows: arene (7.9 mmol), alkyne (7.9 mmol), catalyst (0.0079 mmol), TFA (4 mL) and 1,2-dichloroethane (1 mL).

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