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C–H bond functionalization of aromatic heterocycles with chelating dicarbene palladium(II) and platinum(II) complexes[†]

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Chelating dicarbene complexes of palladium(II) and platinum(II) catalyse at room temperature with 1% catalyst loading the reaction of ethyl phenylpropiolate with aromatic heterocycles to yield synthetically useful intermediates for fine chemicals without the need to use prefunctionalized substrates. The reaction outcome was found to be strongly dependent on the nature of the anionic ligands at the metal complex. Addition of silver salts to replace halide ligands with more weakly coordinating anions improves the reaction yield and changes the product distributions: heterocycle–alkyne 2:1 adducts are obtained together with the usual hydroarylation products, which potentially broadens the scope of the reaction. The nature of the employed heterocycle, in particular its steric characteristics, is also found to strongly influence the outcome of the reaction. Copyright © 2009 John Wiley & Sons, Ltd.

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Keywords: hydroarylation; heterocycle; palladium; platinum; N-heterocyclic carbene

Introduction

The functionalization of heteroaromatic moieties is a highly effective synthetic tool for the chemical industry, heterocycles being readily accessible building blocks for the synthesis of a wide range of biologically active compounds, natural products and pharmaceuticals. The classical synthetic methodologies employed for heterocycle functionalization usually involve crosscoupling reactions, thus requiring the use of pre-functionalized substrates. Very recently, several efforts have been aimed at avoiding substrate pre-functionalization, like halogenation, in order to render the process more convenient both economically and environmentally.^[1] For example, the group of Fujiwara reported that several aromatic heterocycles react very fast with terminal and internal alkynes, at room temperature in acetic acid, employing Pd(OAc)₂ as catalyst.^[2] In this case, products of formal hydroarylation of the triple bond are obtained. The generally accepted mechanism implies the initial coordination of the alkyne to the metal, followed by attack of the heterocycle to the resulting activated triple bond; finally, acetic acid provides the proton necessary to protonolyse the formed Pd-vinyl bond, affording the coupling product.^[3] In the recent literature, several other catalysts for this reaction, based on various metal centres, like nickel(II),^[4] palladium(II),^[5] platinum(II),^[6] ruthenium(0),^[7] rhodium(0),^[8] gold(I),^[9] gold(III)^[10] and group 13 metals^[11] have been proposed.

Our group is interested in the C–H bond functionalization of aromatic substrates and very recently has reported that palladium(II) and platinum(II) complexes with chelating dicarbene ligands^[12] are very efficient catalysts for alkyne hydroarylations with simple arenes.^[13] The high stability of these complexes under acidic conditions, together with the possibility of creating highly electrophilic dicationic species by using appropriate additives, renders them superior in performance with respect to other reported catalysts.

Herein, we extend our work to the evaluation of the reactivity of chelating dicarbene metal complexes towards aromatic heterocycles and report that palladium(II) and platinum(II) complexes with chelating dicarbene ligands (Fig. 1) catalyse the addition of heteroaromatic rings to ethyl phenylpropiolate with a broad substrate scope. We also show that the outcome of the reaction can be controlled through the proper choice of anionic ligands at the metal centre, obtaining in some cases products different from the ones commonly reported in the literature.

Experimental

General Remarks

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or dinitrogen. Complexes $I_{r}^{(13b]} II_{r}^{(13c]} III_{r}^{(13c]} III_{r}^{(14c]}$ and $Pt_{4}(OAc)_{8}^{(15c]}$ were synthesized according to literature procedures. The reagents were purchased from Aldrich

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Reactivity of chelating dicarbene metal complex catalysts, V; for Part IV, see Biffis et al.^[13c].

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Figure 1. NHC carbene complexes employed in this work.

as high-purity products and generally used as received. All solvents were used as received as technical grade solvents. NMR spectra were recorded on a Bruker Avance 300 MHz (300.1 MHz for ¹H and 75.5 for ¹³C) at room temperature; chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals. GC-MS analyses were carried out with a Varian Saturn 2100T gas chromatograph/mass spectrometer (injector temperature 220 °C, column Supelco SPB 50); temperature was programmed from 100 (1 min) to 240 with a gradient of 15 °C/min. Elemental analysis were carried out by the microanalytical laboratory of our department with a Fisons EA 1108 CHNS-O apparatus.

Synthesis of Complex IV

Silver trifluoroacetate (166 mg, 0.75 mmol) was added to a suspension of complex III (200 mg, 0.37 mmol) in acetonitrile (20 ml). The mixture was heated at 60 °C for 4 h, and then filtered through Celite to remove the silver bromide; the solvent was removed under vacuum and the off-white residue was treated with diethylether (3 \times 5 ml), filtered and recrystallized from acetonitrile-diethylether. The resulting solid was finally dried under vacuum; yield 55%; anal. calcd for C₁₃H₁₂F₆N₄O₄Pt (M = 597.36), C 26.13, H 2.02, N 9.38; found, C 25.87, H 2.10, N 9.08. Crystals of complex IV suitable for X-ray diffraction were grown by slow diffusion of diethylether into a solution of the complex in acetonitrile. The ¹H NMR spectrum of the redissolved crystals shows the presence of a major species together with two other sets of signals of similar nature and lower intensity, presumably stemming from equilibria in solution in which the complex becomes involved. ¹H NMR (DMSO-d₆, 25 $^{\circ}$ C): $\delta = 7.58$ (s, 1H, CH), 7.32 (s, 1H, CH), 6.07 (s, 1H, CH₂), 3.66 (s, 3H, CH₃).

X-ray Structure Determination of IV

Data of **IV** (Table 1) were collected at 293 K on a Bruker AXS SMART 1000 single-crystal diffractometer (Mo-K_{α} graphite monocromated radiation, $\lambda = 0.71073$ Å) equipped with an area detector.^[16] Details for the X-ray data collection are reported in Table 1. The structure was solved by Patterson methods with SHELXS-97 and refined against F^2 with SHELXL-97,^[17] with anisotropic thermal parameters for all non-hydrogen atoms. The fluorine atoms of one of the two trifluoroacetate anions were found disordered in two positions. The hydrogen atoms were placed in the geometrical positions and refined riding on the corresponding carbon atoms.

General Procedure for the Catalytic Tests

The solid heterocycle and the complex (together with the silver cocatalyst, where used) were placed in a Schlenk tube. After three vacuum/argon cycles, acetic acid (1 ml) was added through the rubber septum and the reaction mixture was stirred at room temperature for 5 min before addition of the liquid reagents (heterocycle and/or alkyne). Portions of solutions were drawn off

Table 1. Summary of X-ray crystallographic data for complex IV					
Formula	C ₁₃ H ₁₂ F ₆ N ₄ O ₄ Pt				
Formula weight	597.36				
Crystal system	Monoclinic				
Space group	P21/c				
a (Å)	8.460(3)				
<i>b</i> (Å)	14.225(4)				
<i>c</i> (Å)	15.044(5)				
eta (deg)	95.662(5)				
<i>V</i> (Å ³)	1801.6(9)				
Z, D_{calcd} (g cm ⁻³)	4, 2.202				
F(000)	1128				
μ (cm $^{-1}$)	78.76				
Refl. collected	23 692				
Refl. unique	5036 [$R_{\rm int} = 0.0316$]				
Obs. refl. $[l > 2\sigma(l)]$	3782				
Parameters	280				
Final <i>R</i> indices $[l > 2\sigma(l)]$	$R_1 = 0.0234, wR_2 = 0.0529$				
Final R indices [all data]	$R_1 = 0.0378, wR_2 = 0.0569$				
$R_1 = \Sigma F_0 - F_c / \Sigma(F_0); wR_2 = [\Sigma[w]]$	$V(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]]^{1/2}.$				

from the reaction mixture and analysed by NMR or GC-MS to determine the yield. The products were identified by comparison with characterization data found in the literature;^[2a] in the case of previously unreported reaction products, they were isolated and characterized (see the Supporting Information). The reaction mixture at the end of the reaction was poured into a saturated aqueous solution of NaCl and extracted with diethylether. The organic layers were dried over MgSO₄ and concentrated under reduced pressure. The obtained residue was separated by column chromatography on silica gel with AcOEt-hexane 1:6 or Et₂O-hexane 1:1 as eluent. The characterization of the isolated products was performed by NMR techniques, whereby the assignement of *Z* or *E* geometry to the olefinic products was done on the basis of NOE experiments.

Results and Discussion

We first investigated the catalytic efficiency of our standard complexes I and II (Fig. 1) in a model hydroarylation reaction (Fig. 2) under the reaction conditions adopted by Fujiwara (1 mmol alkyne, 2 mmol heterocycle, 1 ml HOAc, room temperature)^[2] but decreasing the catalyst load from 5 to 1 mol%.

In the reaction between pyrrole **1a** and ethyl phenylpropiolate **2**, complex **I** was found to be inactive at room temperature. On the other hand, using complex **II** bearing trifluoroacetates instead of bromides as anionic ligands, the conversion of **1a** after 24 h turned out to be very high (90%). Therefore, as in the case of simple arenes,^[13c] the reactivity of **1a** with a dicarbene palladium(II) catalyst bearing halide ligands turned out to be poor at room temperature, but it can be considerably enhanced by exchanging the halides with less coordinating anionic ligands. The reaction selectivity was however low, providing the desired product **Z-3a** in only 46% yield. The selectivity of the reaction towards this product was found to be decreased by hydration of the alkyne and, most notably, by the formation of 3-dipyrrolylpropanoate **4a** in 18% yield (Fig. 2).



Figure 2. Investigated model reaction between pyrroles and ethyl phenylpropiolate 2.

The same reaction was also performed with catalyst **II** and *N*-methylpyrrole **1b**, since several recent reports have pointed out that *N*-substituted heterocycles react more selectively in C–H functionalization reactions than their N–H analogues.^[11] Indeed, in this case, although the alkyne conversion under the same reaction conditions dropped to 43%, the desired product **Z-3b** was formed in 36% yield with only 1% **4b** as byproduct.

These preliminary results demonstrated that chelating dicarbene palladium(II) complexes with weakly coordinating anionic ligands were catalytically competent in the hydroarylation reaction with model heterocycles, but also that catalyst optimization was needed in order to improve catalytic activity and tune the reaction selectivity, especially between mono- and diaddition of the heterocycle to the alkyne moiety.

We therefore performed a screening of different catalytic systems in the reaction between 1b and 2. In particular, we employed simple metal salts [Pd(OAc)₂ and Pt₄(OAc)₈] as reference catalysts, dicarbene palladium(II) complexes with the same dicarbene ligand but different counteranions (prepared in situ by exchange of the bromide ligands in complex I with 2 equiv. of AqX), as well as dicarbene platinum(II) complexes. The latter complexes bearing halides as anionic ligands (e.g. complex III) were previously found to exhibit good catalytic activity in hydroarylation reactions with simple arenes.^[13a] In the frame of the present catalyst screening, we have also prepared the previously unreported platinum(II) complex IV bearing less coordinating trifluoroacetate ligands, and have determined its crystal structure. The complex was obtained from complex III by exchange of the anionic ligands with silver trifluoroacetate. Crystals of complex IV suitable for X-ray diffraction were grown by slow diffusion of diethylether into a solution of the complex in acetonitrile. An ORTEP view of IV is shown in Fig. 3; the most important bond distances and angles are reported in the caption.

The crystal structure of the complex is very similar to that reported for the analogous palladium compound (1,1'dimethyl-3-3'-methylene-diimidazol-2,2'-divlidene)palladium(II) bis (trifluoroacetate).^[18] The coordination around the metal centre is square planar, with angles at platinum slightly deviating from 90°, in particular the C6–Pt1–C1 angle is $85.38(15)^{\circ}$. The C-Pt bond distances are 1.942(3) and 1.946(3) Å, in agreement with other Pt-carbene distances found in the Cambridge Crystal Data Base for very similar compounds.^[14,19] The six-membered chelating ring is in a boat conformation in accordance with reported palladium and platinum complexes bearing analogous chelating carbene ligands.^[14,18,19] The trifluoroacetate anions coordinate the metal through the O atom. The hydrogen atom of the methylene bridge is involved in a hydrogen interaction with the carbonyl oxygen atom of the trifluoroacetate anion, forming dimers in the solid state, as observed also in the Pd compound, [C5-H5a···O4, C5-H5b···O2 distances of 2.589(2)



Figure 3. ORTEP view of complex **IV**. Ellipsoids are drawn at 30% probability level. Selected bond distances (Å) and angles (deg): C1–N2 1.354(4), C1–N1 1.354(4), C1–Pt1 1.946(3), C5–N1 1.445(5), C5–N3 1.452(4), C6–N4 1.345(4), C6–N3 1.366(4), C6–Pt1 1.942(3), O1–Pt1 2.087(2), O3–Pt1 2.086(2); N1–C5–N3 109.2(3), C6–Pt1–C1 85.38(15), C1–Pt1–O3 97.13(13), C6–Pt1–O1 94.37(13), O3–Pt1–O1 83.14(11).

and 2.520(2) Å, respectively, and C5–H5a···O4, C5–H5b···O2 angles of 99.56(13) and 152.14(12)°, respectively].

The results of the catalyst screening are reported in Table 2. First, a comparative test was done using, as in Fujiwara's case, 5 mol% palladium(II) acetate with a heterocycle-alkyne ratio of 2:1 (entry 1), obtaining quantitative conversion with 70% selectivity towards the desired product Z-3b. In contrast with the results originally reported by Fujiwara, [2a] we also detected other products in the reaction mixture, identified as ethyl (2E)-3-(2-pyrryl)-phenylpropenoate **E-3b** and ethyl (2E)-3-(3-pyrryl)phenylpropenoate **3b**['], in 11 and 19% yields, respectively (Fig. 4). Whereas the former byproduct may derive from the slow, acidinduced isomerization of the originally formed Z-isomer (see below), the mechanism of formation of the latter product, formally deriving from electrophilic attack at the 3-position of the heterocycle, is at present less clear, also considering its stereochemistry (i.e. its being a product of formal exclusive syn-hydroarylation). The reaction proceeded very smoothly with excellent yields also in the presence of a smaller load of palladium(II) acetate (1 mol%, entry 2), even using substrates in a stoichiometric ratio (entry 3). Platinum(II) acetate displayed a slightly lower efficiency than palladium(II) acetate under the same reaction conditions (entry 4), but similar selectivity. We also tested a palladium(0) compound (entry 5), which also exhibited some catalytic activity. Since the catalytic cycle proposed in the literature involves exclusively palladium(II) species,^[3] the observed activity was probably due to a partial oxidation of the metal to palladium(II) under the employed reaction conditions.

Table 2.	Conversion (%) and product distributions for the reaction between 1-methylpyrrole 1b and ethyl phenylpropiolate 2 catalysed by different
catalytic s	ystems

			Yield (%) ^a					
Entry	Catalyst	Conversion(%) ^a 2	Z-3b	<i>E</i> -3b	3b′	4b	4b′	Selectivity(%) ^a in Z-3b
1	Pd(OAc) ₂ ^b	>99	69	11	19	_	_	70
2	Pd(OAc) ₂	98	72	7	19	-	-	73
3	Pd(OAc) ₂ ^c	92	65	10	17	-	-	71
4	Pt ₄ (OAc) ₈ ^d	94	69	10	15	-	-	73
5	Pd(P ^t Bu ₃) ₂	47	38	3	6	-	-	81
6	AgBF ₄	0	-	-	-	-	-	-
7	I-AgBF ₄	>99	50	20	2	21	7	50
8	I-AgOTf	>99	50	20	2	21	7	50
9	I–AgOAc	22	14	4	4	-	-	64
10	II	43	34	2	5	1	1	79
11	III-AgBF ₄	58	24	13	1	15	5	41
12	IV	40	27	5	6	1	1	68

Reaction conditions: 0.01 mmol catalyst, 0.02 mmol silver salt, 1 mmol alkyne, 2 mmol heterocycle, 1 ml HOAc, 25 °C, 24 h. ^a Conversions (%) and yields (%) determined by GC-MS and/or ¹H-NMR. ^b 0.05 mmol catalyst, 1 mmol alkyne, 2 mmol heterocycle. ^c 0.01 mmol catalyst, 1 mmol alkyne, 1 mmol heterocycle; ^d 0.0025 mmol catalyst, 0.01 mmol Pt.



Figure 4. Observed products in the reaction between 1-methylpyrrole 1b and ethyl phenylpropiolate 2.

Carbene-based complexes display a catalytic performance heavily dependent on the nature of the metal centre as well as of the anionic ligands. Preformed complex **I** or complex **I** in the presence of an excess AgOAc reacted more sluggishly with respect to the systems formed by complex **I** – AgBF₄ or **I** – AgOTf, which allow quantitative conversions to be reached (compare entries 7 and 8 with entries 9 and 10), albeit at a lower selectivity compared with simple Pd(OAc)₂ (see below). Silver additives possessing poor or non-coordinating anions efficiently extract halide ligands from the metal providing cationic complexes which catalyse the reaction more efficiently. A control experiment allowed us to verify that, under the employed conditions, AgBF₄ itself has only the role of removing the halides from the metal and does not take part in the catalytic hydroarylation of ethyl phenylpropiolate (entry 6).

Dicarbene platinum(II) complex III (Fig. 1) in combination with 2 equiv. AgBF₄ (entry 11) as well as preformed complex IV (entry 12) were also tested as catalysts in the reaction, but they showed lower activities with respect to the corresponding complexes of palladium(II) (entries 7 and 10).

Concerning the selectivity of the reaction with dicarbene complex catalysts, important differences were recorded in comparison with the reactions with simple metal salts. Formation of product $\mathbf{3b}'$ was largely suppressed, whereas the diaddition product 4b (together with smaller amounts of its regioisomer 4b') was additionally obtained (Fig. 4). In particular, the more weakly coordinating is the anionic ligand ($CF_3SO_3^-$, BF_4^-), the higher is the yield in these adducts, so that their formation seems to be coherently favoured by less-hindered complexes (entries 7, 8 and 11). We confirmed by a control experiment performed without any metal catalyst that the formation of these adducts is indeed promoted by the metal complex and not by the acidic environment in which the reaction takes place, which only enables slow isomerization of the initially formed olefin to the more stable E-isomer. Clearly, weakly coordinating species allow the generation of dicationic complexes, thus increasing the metal electrophilicity and consequently activating the initially formed heteroarylalkene towards reaction with a second heterocycle molecule.^[3] On the other hand, the formation of diadducts is less favoured with these palladium(II) and platinum(II) complexes compared with catalysts based on other metal centres, which are known to yield the diadducts exclusively.^[9-11] In conclusion, in the reaction between 1-methylpyrrole **1b** and ethyl phenylpropiolate 2, simple palladium(II) acetate together with complex $I-\mbox{AgBF}_4$ or AgOTf afforded the best activities among the investigated catalysts. The latter two catalytic systems exhibit an enhanced tendency to yield 3-dipyrrolylpropanoates, which can be potentially be an advantage in the synthesis of non-



Figure 5. Heterocycles employed as substrates.

determined by GC-MS and/or ¹H-NMR.

Table 3.	Conversions (%) and	yields(%)	for the	e reaction	of ethyl	
phenylpropiolate 2 with different aromatic heterocycles catalysed by							
complex I	-AgBF ₄						

Heterocycle	Conversion (%) ^a 2	Yield (%) ^a (<i>Z</i> : <i>E</i>)				
1a	>99	3a	35	4a	27	
1b	>99	3b	70 (5:2)	4b	21	
1c	36	3c	16 (1:4)	4c	20	
1d	96	3d	66 (1:23)	4d	30	
1e	87	3e	77 (60:17)	4e	9	
1f	93	3f	79 (57:22)	4f	13	
1g	35	3g	17 (1:0)	4g	18	
1h	0	3h	0	4h	0	
1i	0	3i	0	4i	0	
Reaction conditions: 0.01 mmol catalyst, 1 mmol alkyne, 2 mmol heterocycle, 1 ml HOAc, 25 °C. ^a Conversions (%) and yields (%)						

symmetrical diheteroarylpropanoates. We are currently working along this strategy.

The system formed by complex $I-AgBF_4$ was subsequently tested in the reaction of **2** with other heterocycles in order to evaluate the conversions and selectivities towards mono- and diaddition products upon changing the substrates. We screened the aromatic heterocycles shown in Fig. 5, keeping constant ethyl phenylpropiolate **2** as the alkyne. The site of prevalent C-H functionalization for each heterocycle is shown in the figure. The results are described in Table 3, which reports conversions and yields after 24 h; the reaction time was not further optimized for any of the heterocycles employed.

The obtained results confirmed the general trend in this type of reactions: pyrrole and furane substrates undergo reaction at 2-position of the heteroaromatic ring, as is invariably the case in aromatic substitution reactions. However, if the 2-position is occupied by substituents, the reaction can occur at the 3-position. For indole substrates, instead, functionalization takes place at 3-position, but it can occur at 2-position if the 3-position of the heteroaromatic ring is substituted. The conversions and the selectivities of the reaction were found to be strongly dependent on the nature of the employed heterocycle. In particular, the monoaddition product **3** was the major product in nearly all cases. Generally, the *Z* isomer was mainly obtained, with the exception

of substrates 1c and 1d, where a reversal in stereoselectivity was observed and the E isomer was preferentially formed; an analogous stereoselectivity reversal with the same substrates was reported by Fujiwara.^[2a] Diadduct product formation was minimal with substrate 1e, whereas with the other substrates the yield in this product was quite high, eventually making out the main reaction product in the case of substrate 1c (although at an unexpectedly low conversion). Unsubstituted pyrrole 1a displayed very high reactivity but the selectivity was rather low because of concurrent reactions involving the alkyne, such as hydration and especially oligomerization. We are currently investigating the reason for this phenomenon in more detail. S-containing heterocycles 1h and 1i, instead, turned out to be unreactive, whereas the O-heterocycle 2-methylfuran 1g reacted very slowly, affording the arylalkene Z-3g (yield 17%) and the diaddition product 4g (yield 18%). The observed low reactivity of these aromatic substrates bearing donor heteroatoms, such as O an S, can be at least in part attributed to their tendency to bind metal centres in medium-low oxidation states,^[20,21] thus saturating the coordination sphere of the metal catalyst.

In general, our catalytic system exhibited good activities compared with Fujiwara's one, which usually required higher amounts of catalyst (5 mol%). Yields can be increased by prolonging the reaction time, although this entails a certain degree of acid-induced isomerization of **Z-3** to the *E* product. Moreover, in the case of the heterocycles affording diaddition products, prolonging the reaction time increases the amount of the diaddition product **4** at the expense of **3**. This may be interesting for the production of 3-diheteroarylpropanoates, so that we are currently investigating the possibility of developing a new reaction protocol for the production of these molecules, particularly in the case of non-symmetrical heterocycle substitution.

Conclusions

In conclusion, dicarbene-based palladium(II) systems catalysed the direct coupling of ethyl phenylpropiolate with a broad selection of aromatic heterocycles. They appear superior to related platinum(II) complexes, whose reactivity also turned out to be lower than that of simple platinum(II) acetate. Moreover, the design of dicationic and low-hindering complexes adopting suitable additives led to a significant change in the outcome of the reaction. The increased formation of diheteroarylpropanoates at long reaction times was observed, together with an increase in the efficiency of the catalyst. This particular feature of our catalytic system together with its broad substrate scope opens the possibility to develop a new reaction protocol towards production of these kinds of molecules bearing different heteroaryl substituents.

Supporting information

Supporting information may be found in the online version of this article.

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