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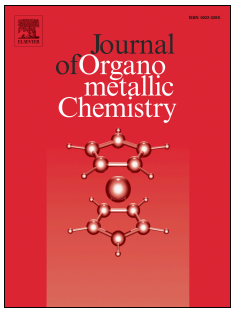

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Meliha Çetin Korukçu, Necdet Coşkun

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Synthesis and catalytic activities of 1-alkoxycarbonyl- and 1-carbamoylmethyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II) complexes

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Abstract: 4-Phenyl-1-aryl-1*H*-imidazoles were reacted with α-haloesters and amides to give the corresponding imidazolium salts. The latter were used as starting materials for the synthesis of Pd(NHC) complexes. The catalytic activities of the newly prepared compounds were screened in a model coupling reaction. 1-Alkoxycarbonyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II) were shown to be better catalyst than the 1-carbamoylmethyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II) complexes. The catalysts were shown to be insensitive to the air oxygen and water.

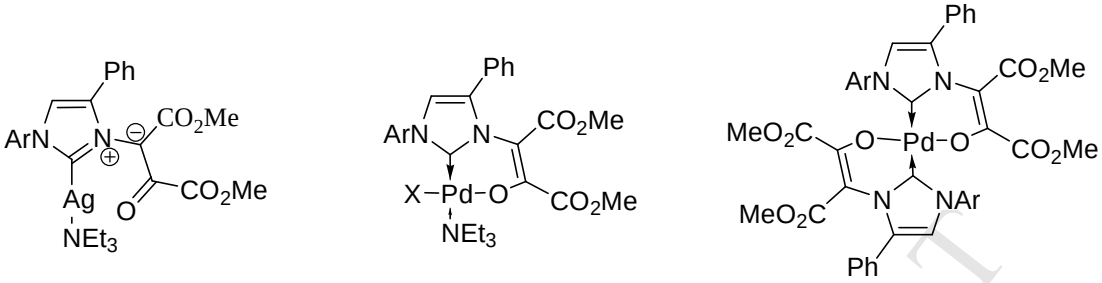
Keywords: NHCs; NHC Enolates; Ag(I)-NHC complexes. Pd(II)-NHC complexes; Heck reaction.

I. INTRODUCTION

The carbon-carbon bond forming reaction between alkenes and aryl halides in the presence of a palladium catalyst has found an extensive usage following the pioneering reports of Mizoroki[1] and Heck[2] from the early 1970s.

Numerous excellent surveys on a wide variety of different aspects of the Heck reaction have been published.[3] A variety of ligands[3a] have been developed for the reaction, and it has been a key step in the total synthesis of many natural products and commercially important products.[3b,3d] The selectivity and mechanistic aspects of the carbon-carbon bond forming reactions have been thoroughly reviewed,[3c-e,4] and are still important subject of research.[5] Our laboratory has recently described the utility of isoxazolo[3,2-*a*]isoquinolines as precursors for the synthesis of stable azomethine ylides;[6a] while the adducts of acyclic nitrones were shown to undergo a cascade reaction leading to the formation of iminocarbenes.[6b] We have also reported the rearrangement of isoxazolines from the reaction of imidazoline 3-oxides with dimethyl acetylenedicarboxylate to give the corresponding 3*H*-imidazol-1-ium ylides. The reaction of the latter with $AgNO_3$ in the presence of Et_3N at room temperature provides C-2 metallated N-heterocyclic carbine enolates (Ag-NHCE) precursors such as **1** (Scheme 1).[7] The silver compounds reported so far in the formation of Ag(I)-NHC complexes are AgOAc,[8] Ag_2O[9] and Ag_2CO_3.[10] Silver N-heterocyclic carbene complexes have been important in the development of other metal–carbene systems due to facile transmetallation reactions from the silver carbenes to a wide range of other transition metals.[11-12] Palladium complexes of NHC ligands, in particular, have proved to be

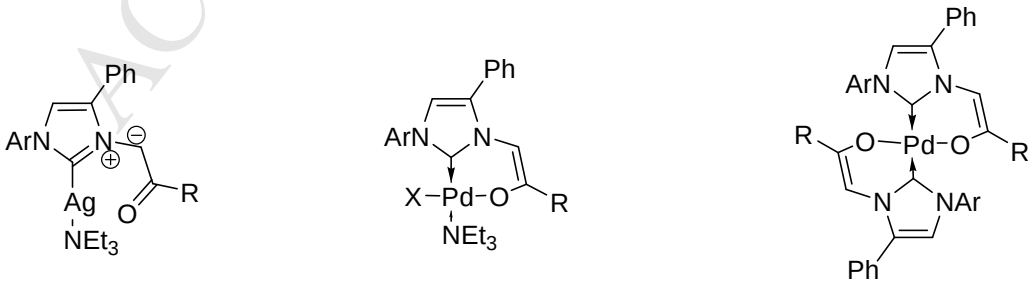
excellent catalysts not only for the Heck reactions but also for the Suzuki, Stille and Sonagashira cross-couplings.[3e]



NHCE precursors **1** **2** **3**

Figure 1. The structures of NHC Enolate precursors and Pd(II)-NHCE complexes

Recently we have demonstrated the utility of compounds **1** as *N*-heterocyclic carbene-enolate (NHCE) ligand precursors.[13] The reaction of **1** with equimolar Pd(II) salts in CH_2Cl_2 provides complexes **2** in equilibrium with **3**. The screen in coupling reactions (e.g. Heck and Suzuki) revealed their efficiencies as catalysts at 80°C for the favorable combinations of aryl halide (electron deficient) and styrene (electron rich) and 100 or 120 °C for the unfavorable cases (electron rich aryl halide and electron deficient styrene). The catalysts were extremely effective in Suzuki reaction at room temperature and in aqueous media. Hammett type correlations confirmed the effect of substituents on the aryl halide and styrene to be opposite. The electron donating groups on the aryl halide decelerate while the same on the styrene ring accelerate the coupling reaction rate. Similar effects were found for the Suzuki coupling reaction: Electron-deficient aryl halides and electron-rich arylboronic acids are more reactive than the corresponding electron rich aryl halide and electron-deficient boronic acids. Reasonable mechanisms for these couplings in the presence of Pd-NHCE complexes were discussed. The synthetic potential of the newly prepared catalysts were demonstrated in the synthesis of stylbenes, biaryls as well as arylated heterocycles.



NHCE precursors **1'** **2'** **3'**

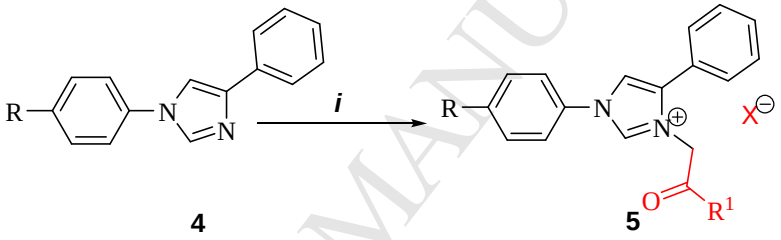
Figure 2. Structures of the expected NHC Enolate precursors and Pd(II)-NHCE complexes from 1-alkoxycarbonyl- and carbamoylmethyl-5-phenyl-3-p-tolyl-3H-imidazol-1-ium salts.

Encouraged by the above mentioned results we have planned to prepare a series of imidazole based salts **1'** and convert them to **2'** and **3'** and test their activity in a coupling reaction (e.g. Heck reaction). Here we report on the unusual behaviour of imidazolium salts **5** in regard to their reactions with Ag_2O and $AgNO_3$.

II. RESULTS AND DISCUSSION

II.1 Alkylations of imidazoles 4 with α-halocarbonyl compounds

The treatment of imidazoles **4** available by the previously reported methods[7] with an excess of α-halogenated ester in toluene at 90 °C provided compounds **5** in high yield and purity.[14] The reaction of **4** with α-chloroamides at the same conditions was a very slow process, however the use of KI as a catalyst provided the formation of **5** in high yields (Scheme 1 and Table 1). The elemental analyses and spectral data confirmed the proposed structures.



Scheme 1. Alkylations of imidazoles **4** with α-halocarbonyl compounds.
Reaction conditions: ***i***) R^1COCH_2X, toluene, 90 °C, 18-24 h.

Table 1. Synthesis of **5** from the alkylations of **4** with α-halocarbonyl compounds

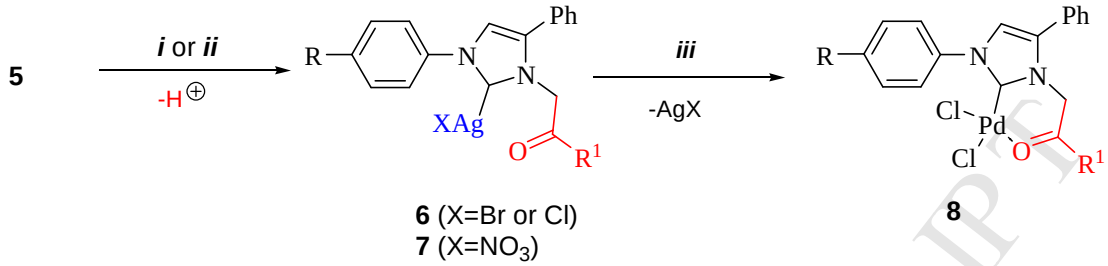
5	R	X	R^1	Yield[b] (%)	Mp (°C)
a	*p*-Me	Br	OEt	76	152–154
b	*p*-MeO	Br	OEt	87	195–196
c	*p*-Me	Br	*O*-(-)-menthyl	84	171–172
d	*p*-Me	Cl	NH_2	75	263–264
e	*p*-Me	Cl	NHAr[a]	73	252–253

[a]Ar = 2,6-dimethylphenyl; [b]Isolated yield

II.2 Synthesis of Ag(I)- and Pd(II)-NHC complexes.

The treatment of compounds **5** in CH_2Cl_2 at room temperature with Ag_2O in the presence of molecular sieve[15] provides complexes **6a-e** in quantitative yields and high purity. The use of the protocol we have recently reported[7, 13] (Scheme 2, Table 2) ensures the formation of compounds **7a-e**. The most characteristic evidence for the formation of complexes **6** is the disappearance of the peak at *ca* 10 ppm in the ^{1}H NMR spectra of **5** due to metallation of C-2 carbon. The down-field shifts of C4-H peaks (*ca*

0.5 ppm) in the imidazolium ring as well as the methylene protons (*ca* 0.2 ppm) points to an enhanced electron density at the corresponding carbon atoms to which they are bounded. The Ag bounded carbon resonates at ca 182.0 ppm in DMSO-d_6.



Scheme 2. Synthesis of Ag(I)- and Pd(II)-NHC complexes. *Reaction conditions*: ***i***) Ag_2O, molecular sieve, CH_2Cl_2, rt 0.5 h ***ii***) Et_3N, $AgNO_3$, CH_2Cl_2, rt, 1 h ***iii***) $Pd(CH_3CN)_2Cl_2$, CH_2Cl_2, rt 1 h.

Table 2. Synthesis of NHC-metal complexes **6-8**.

							Isolated Yield (%)	
6-8	**R**	**X for 6**	**X for 7**	**R^1**	**6**	**7**	**8 Meth. A[b]**	**8 Meth. B[c]**
a	*p*-Me	Br	NO_3	OEt	98	81	93	89
b	*p*-MeO	Br	NO_3	OEt	96	85	95	86
c	*p*-Me	Br	NO_3	*O*-(-)-menthyl	62	77	92	92
d	*p*-Me	Cl	NO_3	NH_2	40	75	76	91
e	*p*-Me	Cl	NO_3	NHAr[a]	67	83	93	72

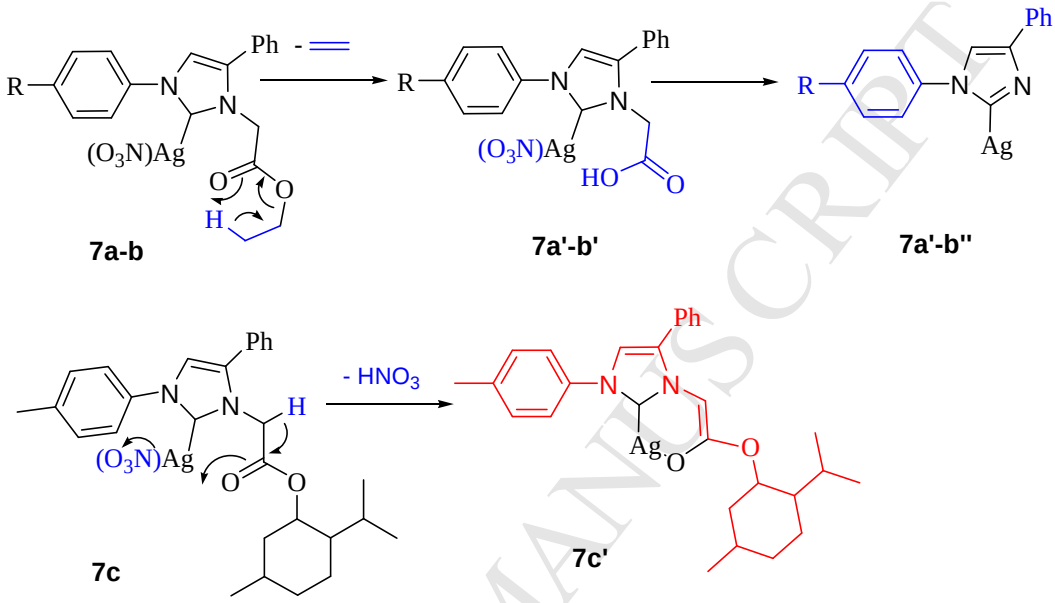
[a]Ar = 2,6-dimethylphenyl. [b]Starting from **6**; [c]Starting from **7**.

The treatment of compounds **6** or **7a-e** with $Pd(CH_3CN)_2Cl_2$ in dichloromethane[16] at room temperature for short time provides compounds **8** in high yields (Scheme 2 and Table 2). The reactions were monitored by ^{1}H NMR. At the end of the reaction the characteristic peak of **6** and **7** at *ca* 5 ppm assigned to the methylene protons disappears and the same peak for the product appears as an AB system. The latter fact implies that the ester carbonyl is coordinated to the metal centre in such a way that the symmetry of the molecule should be distorted. The carbene carbon in the ^{13}C NMR spectra of **8** appears at 145.4 ppm. The HMBC spectra revealed also the presence of cross peaks with C-4H of the imidazole ring.

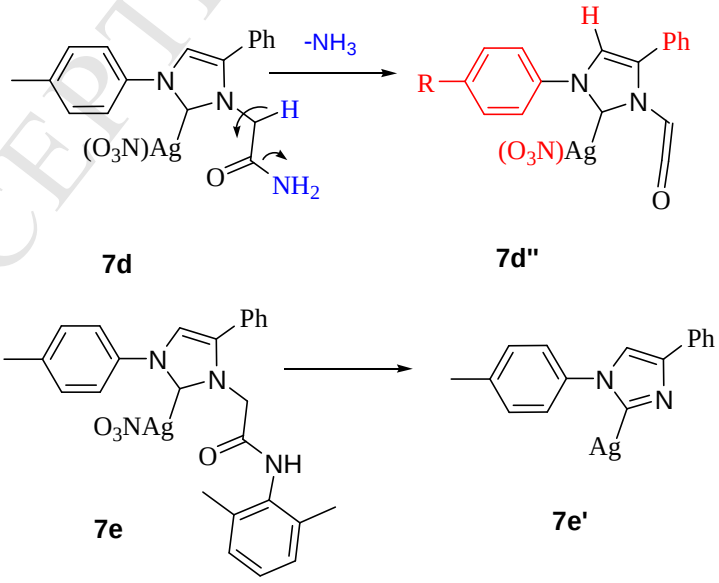
II.3 Thermal reactions of complexes 7 and 8.

The thermal behaviours of complexes **7a-e** were investigated under nitrogen atmosphere in the 25-950 ^{o}C range. Ester type complex **7a-b** lose ethylene at around 120 ^{o}C (Scheme 3). In the case of cyclohexyl ester **7c** the low molecular compound lost is not the corresponding cyclohexene derivative but HBr,

probably due to steric reasons the (-)-menthyl group can not provide a hydrogen coplanar with the carbonyl group to undergo the expected fragmentation. The amide type complex **7d** was shown to undergo β-elimination at quite mild conditions, to give probably the corresponding ketene substituted complex and NH_3 (Scheme 4). The all above discussed thermal reactions in fact can find synthetic applications in the design of new metallacyclic compounds.

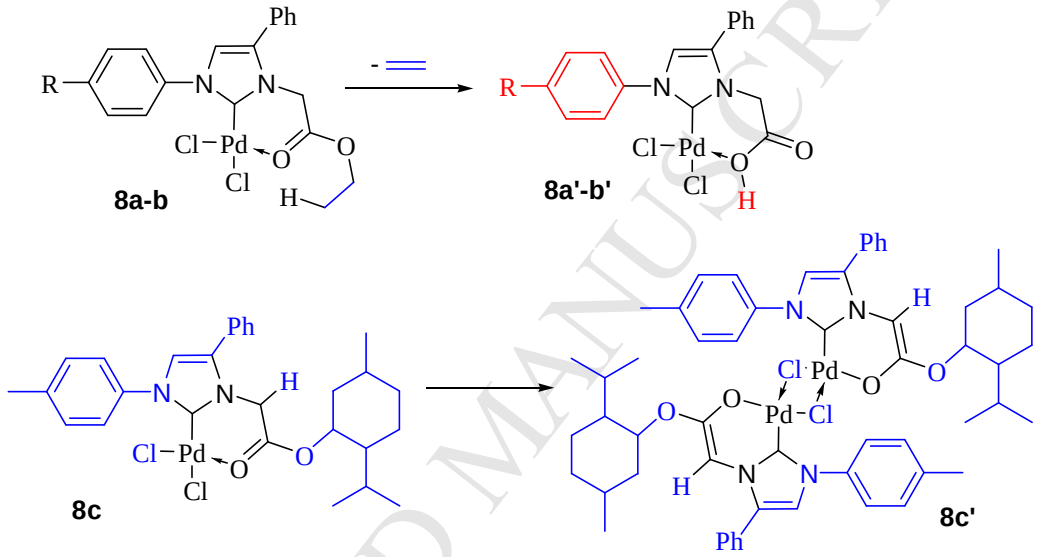


Scheme 3. Thermal decomposition pathways for 1-alkoxycarbonyl-5-phenyl-3-p-tolyl-3H-imidazol-1-yliden-Ag(I) complexes **7a-c**.

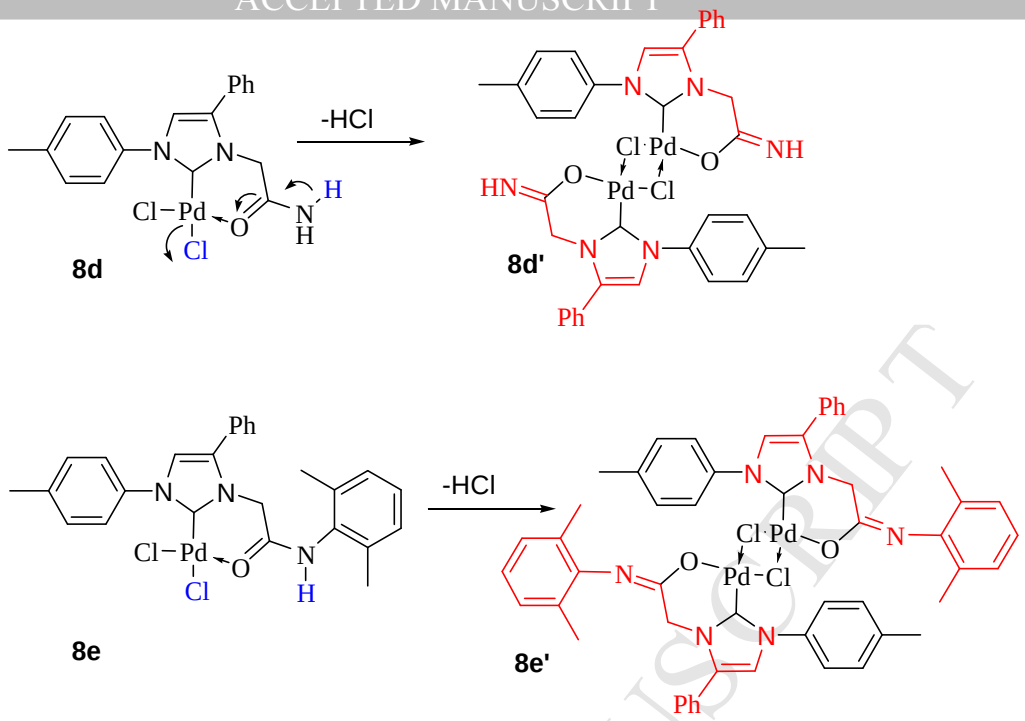


Scheme 4. Decomposition pattern of 1-carbamoylmethyl-5-phenyl-3-p-tolyl-3H-imidazol-1- yliden-Ag(I) complexes **7d-e**.

Pd-NHC complex **8a-b** behaves as their silver analogues **7a-b**. The loss of ethylene occurs even at a little lower temperature, 113 ^{o}C (Scheme 5). TGA analysis revealed that the compound forming **8a'-b'** after the loss of ethylene is stable to 225 ^{o}C. This should be taken in consideration for the catalytic species in the reactions performed over 113 ^{o}C. The heating of **8c** produces **8c'**, a decomposition pattern similar to those of silver complex **7c**. Amide type Pd-complexes **8d-e** behaves differently from the corresponding silver complexes (Scheme 6). The heating of the latter under nitrogen lead to the elimination of HCl probably due to intramolecular substitution at the metal centre to produce the corresponding cyclic structures **8d'-e'** as depicted in Scheme 6.



Scheme 5. Thermal decomposition pathways for 1-alkoxycarbonyl-5-phenyl-3-p-tolyl-3H-imidazol-1-yliden-Pd(II) complexes **8a-c**.



Scheme 6. Decomposition pattern of 1-carbamoylmethyl-5-phenyl-3-p-tolyl-3H-imidazol-1- yliden-Pd(II) complexes **8d-e**.

II.4 Optimization of the Heck reaction conditions for the styrene arylation in the presence of NHC-Pd complex 6.

To determine the best catalyst in the series **8a-e** the arylation of styrene (Scheme 7) was performed in DMF in the presence of NaAcO as a base, Table 3 entries 1-5. The total conversions were followed by ^{1}H NMR and the kinetic curves depicted in Figure 3.

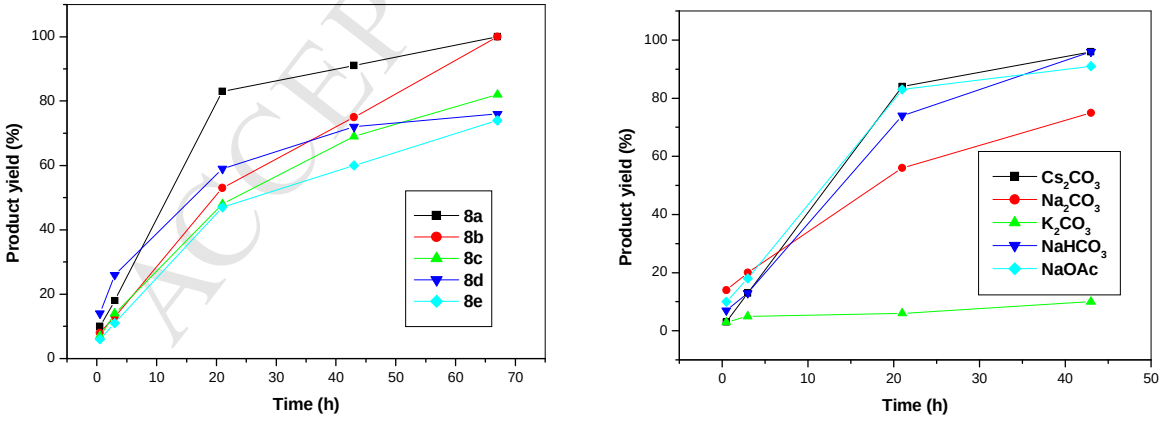


Figure 3. Catalitic efficiencies of **8a-e** (left graph) and effect of the base on the catalytic activity with **8a** in DMF at 120 ^{o}C.

Albeit a comparison of the initial conversion rates shows that **8a** is superior to all other at the end of the reactions **8b** successfully competes with it. As a whole, ester type complexes are better catalyst than the amide type **8d-e**. Therefore, we have selected **8a** as a lead and searched for the best base in DMF, Table 3, entries 6-9. The reactions were performed with 1 mol% catalyst and as is shown in Figure 3, the right graph, Cs_2CO_3, NaOAc and Na_2CO_3 provide nearly the same conversion rates. Due to the higher selectivity in the case of NaOAc we have selected it for the experiments to reveal the solvent effect, Table 3, entries 1,10-12, Figure 4, left graph.

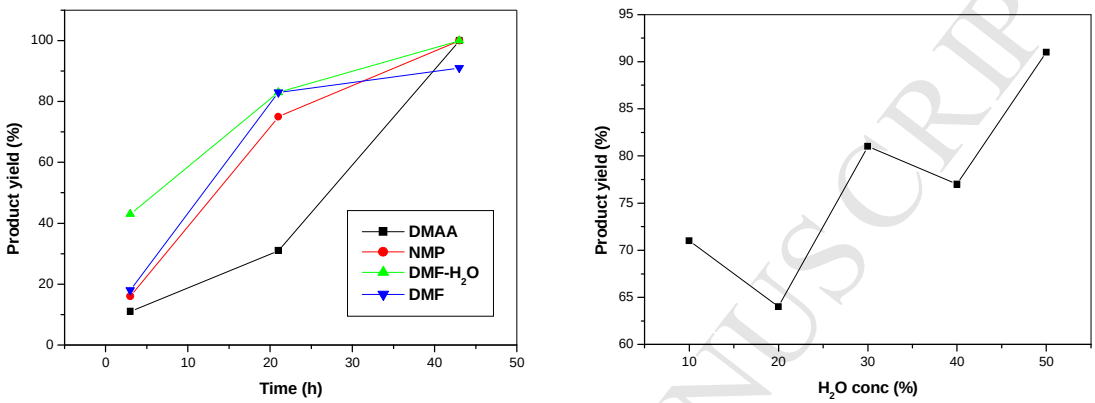
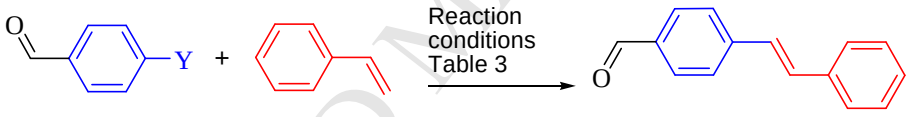


Figure 4. Solvent (left) and water concentration in DMF effect.



9 **10** **11**

Scheme 7. Arylation of styrene with 4-bromobenzaldehyde in the presence of compounds **8**.

Surprisingly DMF-H_2O mixture (1:1) was as equally good as all other solvents. To prove the effect of water concentration on the conversion rate of the model Heck reaction we have used different concentrations (Table 3, entries 13-17). The results are plotted in Figure 4, the right graph. There was not a linear increase or decrease, instead a polynomial changes at the 99th hours of the reaction were determined. After optimization of the solvent and the base the model reaction was performed in the presence of **8a** with 0.1, 0.01, 0.001 and 0.0001 mol% concentrations (Table 3, entries 18-21). The experiments revealed that TON's of 10^4 can be achieved with high regio- and diastereoselectivity.

Table 3. Substituent, solvent and base effect in the Heck-Mizoroki reaction catalyzed by compounds **8**.

Entry	Cat	Y	Cat. mol %	Base	Base eqv	Solvent	Time (h)	Total [a]convrsn	TON_{max}
1	**8a**	Br	1	NaOAc	4	DMF	67	100	100
2	**8b**	Br	1	NaOAc	4	DMF	67	100	100

3	**8c**	Br	1	NaOAc	4	DMF	67	87	87
4	**8d**	Br	1	NaOAc	4	DMF	67	81	81
5	**8e**	Br	1	NaOAc	4	DMF	67	75	75
6	**8a**	Br	1	Cs_2CO_3	2	DMF	43	96[b]	96
7	**8a**	Br	1	Na_2CO_3	2	DMF	43	77	77
8	**8a**	Br	1	K_2CO_3	2	DMF	43	13[c]	13
9	**8a**	Br	1	$NaHCO_3$	4	DMF	43	96	96
10	**8a**	Br	1	NaOAc	4	DMAA	43	100	100
11	**8a**	Br	1	NaOAc	4	NMP	43	100	100
12	**8a**	Br	1	NaOAc	4	DMF-H_2O (5:5)	43	100	100
13	**8a**	Br	0.1	NaOAc	4	DMF-H_2O (9:1)	99	72	720
14	**8a**	Br	0.1	NaOAc	4	DMF-H_2O (8:2)	99	68	680
15	**8a**	Br	0.1	NaOAc	4	DMF-H_2O (7:3)	99	86	860
16	**8a**	Br	0.1	NaOAc	4	DMF-H_2O (6:4)	99	80	800
17	**8a**	Br	0.1	NaOAc	4	DMF-H_2O (5:5)	99	91	910
18	**8a**	Br	0.1	NaOAc	4	DMF	99	63	630
19	**8a**	Br	0.01	NaOAc	4	DMF	99	33	3300
20	**8a**	Br	0.001	NaOAc	4	DMF	99	0	
21	**8a**	Br	0.0001	NaOAc	4	DMF	99	0	
22	**8a**	Cl	1	NaOAc	4	DMF	21	0	

[a]No Pd black formations was observed. [b]The Z-isomer is forming in 20% yield. [c]Benzaldehyde is forming in 3%.

Catalyst **8a** was also screened for its activity in the reaction of 4-chlorobenzaldehyde with styrene, however no conversion was observed, Entry 22.

III. CONCLUSIONS

Thus, imidazolium salts **5** react with Ag_2O and $AgNO_3$ in the presence of Et_3N to give Ag-NHC and Pd-NHC complexes instead of the expected NHC Enolate precursors. The transmetallation reaction of the latter give again the Pd(II)NHC complexes contrary to our expectations (Figure 2). The thermal analysis of the latter complexes revealed interesting synthetically useful transformations depending on the structure of the aliphatic substituent on the N-1 of the NHC ligand. Structure and catalytic activity screen for compounds **8** have shown that 1-alkoxycarbonyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II) are better catalyst than the 1-carbamoylmethyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II)

complexes. Having in mind the thermal transformations shown by TGA we can conclude that at the temperature we have conducted the model reaction the precatalyst is the corresponding **8'**. The preparation, characterisation and screening their catalytic potential in some other coupling reactions is underway.

IV. EXPERIMENTAL

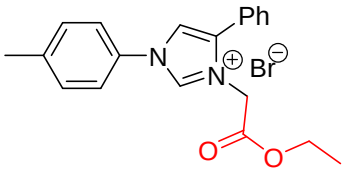
IV.1 General

Melting points were recorded on an Electrothermal Digital melting point apparatus. Infrared spectra were recorded on a Thermo-Nicolet 6700 FTIR. 1D and 2D NMR experiments were performed on a Varian Mercury Plus 400 MHz spectrometer. The elemental analyses were performed on a EuroEA 3000 CHNS analyser. Thermogravimetric curves were obtained using a SII Exstar TG/DTA 6200 analyzer in the range 25-1000 ^{o}C in platinum crucibles under nitrogen at a heating rate of 10 ^{o}C min^{-1} using alumina as reference.

IV.2 Synthesis of 1-alkoxycarbonyl-5-phenyl-3-p-tolyl-3*H*-imidazol-1-ium salts (5a-c). General Procedure: To a solution of imidazole **4** (1 mmol) in toluene (3 mL) alkyl bromoacetate (3 mmol) was added and the reaction mixture stirred for 18 h at 90 ^{o}C. The precipitated product was filtered, washed with toluene (3X5 mL) and dried under vacuum.

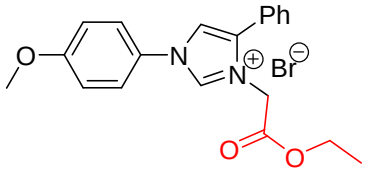
IV.3 Synthesis of 1-carbamoylmethyl-5-phenyl-3-p-tolyl-3*H*-imidazol-1-ium salts (5d-e). General Procedure: To a solution of imidazole **4** (1 mmol) in toluene (3 mL) α-haloamide (3 mmol and KI (0.3 mmol, 0.050 g) were added and the reaction mixture stirred for 24 hrs at 90 ^{o}C. In the case of **4d** the solvent was evaporated and the crude mixture washed with toluene (3X5 mL) and CH_2Cl_2 (6X5 mL). In the case of **4e** the solvent was evaporated and the solid mixture was washed with hot toluene (5X5 mL).The residual solids were dried under vacuum.

1-Ethoxycarbonylmethyl-5-phenyl-3-(*p*-tolyl)-3H-imidazol-1-ium bromide 5a. Yield 0.305 g, 76%. Colourless crystals, mp 152–154 ^{o}C. IR (KBr) $\nu_{C=O}$ 1744 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.06 (3H, t, J = 6.8 Hz), 2.40 (3H, s), 4.07 (2H, q, J = 6.8 Hz), 5.33 (2H, s), 7.49 (2H, d, J = 8.0 Hz), 7.58 (5H, s), 7.74 (2H, d, J = 8.0 Hz), 8.58 (1H, d, J = 1.2 Hz), 9.99 (1H, d, J = 1.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.2; 21.1; 48.9; 62.6; 119.7; 121.9; 125.2; 129.6; 129.8; 131.0; 131.2; 132.6; 135.7; 137.3; 140.5; 166.6. Anal. Calcd for $C_{20}H_{21}BrN_2O_2$ (401.30) C, 59.86; H, 5.27; N, 6.98; Found C, 60.00; H, 4.95; N, 7.30.



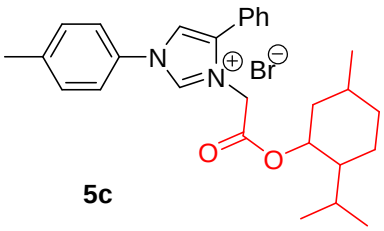
5a

1-Ethoxycarbonylmethyl-5-phenyl-3-(*p*-methoxyphenyl)-3H-imidazol-1-ium bromide 5b. Yield 0.363 g, 87%. Colourless crystals, mp 195–196 °C. IR (KBr) $\nu_{C=O}$ 1744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.07 (3H, t, J = 6.8 Hz), 3.84 (3H, s), 4.08 (2H, q, J = 6.8 Hz), 5.31 (2H, s), 7.22 (2H, d, J = 9.2 Hz), 7.58 (5H, s), 7.74 (2H, d, J = 9.2 Hz), 8.53 (1H, d, J = 1.2 Hz), 9.86 (1H, d, J = 1.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.2; 48.9; 56.3; 62.6; 115.8; 119.9; 123.8; 125.3; 128.0; 129.6; 129.8; 131.0; 135.6; 137.2; 160.7; 166.6. Anal. Calcd for $C_{20}H_{21}BrN_2O_3$ (417.30) C, 57.56; H, 5.07; N, 6.71; Found C, 58.00; H, 4.73; N, 7.00.



5b

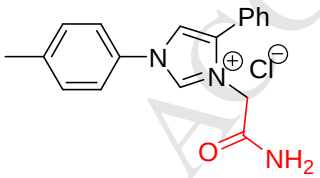
1-(-)-Menthyloxycarbonylmethyl-5-phenyl-3-(*p*-tolyl)-3H-imidazol-1-ium bromide 5c. Yield 0.430 g, 84%. Colourless crystals, mp 171–172 °C. IR (KBr) $\nu_{C=O}$ 1757 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 0.52-0.85 (12H, m), 1.23-1.63 (6H, m), 2.40 (3H, s), 4.53 (1H, dt, J = 11.2; 1.1 Hz), 5.35 (1H, d, J = 18.4 Hz), 5.41 (1H, d, J = 18.4 Hz), 7.49 (2H, d, J = 8.0 Hz), 7.56-7.58 (5H, s), 7.73 (2H, d, J = 8.0 Hz), 8.57 (1H, d, J = 1.2 Hz), 9.89 (1H, d, J = 1.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.5; 20.9; 21.1; 22.2; 23.2; 26.0; 31.1; 33.8; 46.6; 49.0; 76.4; 119.9; 122.0; 125.3; 129.5; 129.7; 131.0; 131.2; 132.6; 135.7; 137.3; 140.5; 166.1. Anal. Calcd for $C_{28}H_{35}BrN_2O_2$ (511.49) C, 65.75; H, 6.90; N, 5.48; Found C, 65.60; H, 6.66; N, 5.68.



5c

1-Carbamoylmethyl-5-phenyl-3-(*p*-tolyl)-3H-imidazol-1-ium chloride 5d. Yield 0.246 g, 75%. Colourless crystals, mp 263–264 °C. IR (KBr) $\nu_{C=O}$ 1691; ν_{NH2} 3244 and 3399 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.40 (3H, s), 5.00 (2H, s), 7.26 (1H, brs), 7.39 (1H, brs), 7.48 (2H, d, J = 8.4 Hz), 7.57 (5H, s), 7.75 (2H, d, J = 8.4 Hz), 8.55 (1H,s), 10.17 (1H, s). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.0; 49.8; 119.2; 121.7; 125.4; 129.6; 129.7; 130.9; 131.1; 132.6; 135.8; 137.4; 140.3; 166.7.

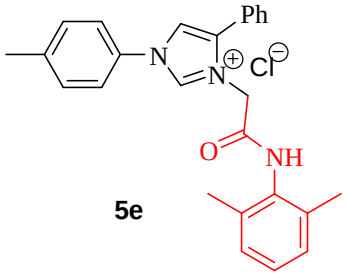
Anal. Calcd for $C_{18}H_{18}ClN_3O$ (327.81) C, 65.95; H, 5.53; N, 12.82; Found C, 65.50; H, 5.45; N, 12.53.



5d

1-(*N*-2,6-Dimethylphenyl)carbamoylmethyl-5-phenyl-3-(*p*-tolyl)-3H-imidazol-1-ium chloride 5e.

Yield 0.315 g, 73%. Colourless crystals, mp 252–253 ^{o}C. IR (KBr) $\nu_{C=O}$ 1665 cm^{-1}; ν_{NH} 3397 and 3359 cm^{-1} ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.94 (6H, s), 2.40 (3H, s), 5.33 (2H, s), 7.01-7.03 (3H, m),7.50 (2H, d, J = 8.4 Hz), 7.59-7.63 (5H, m), 7.75 (2H, d, J = 8.4 Hz), 8.55 (1H, d, J = 1.6 Hz), 9.85 (1H, s), 10.04 (1H, d, J = 1.6 Hz). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 18.3; 21.0; 49.9; 119.4; 121.7; 125.5; 127.3; 128.2; 129.7; 129.8; 130.9;131.2; 132.6; 134.3; 135.4; 135.8; 137.5; 140.3; 163.4.

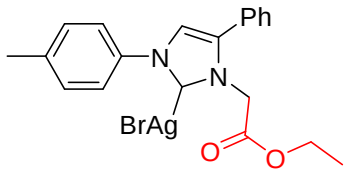


5e

Anal. Calcd for $C_{26}H_{26}ClN_3O$ (431.96) C, 72.29; H, 6.07; N, 9.73; Found C, 71.90; H, 5.85; N, 9.49.

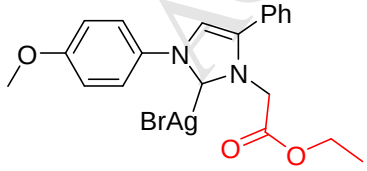
IV.3 Synthesis of Ag(I) metalated 3*H*-imidazol-1-ium salts 7a-e. General procedure. To a solution of **5a-e** (0.3 mmol) in CH_2Cl_2 (3 mL) in the presence of molecular sieve (4A, 0.300 g) Ag_2O (0.15 mmol, 0.035 g) was added portion-wise within 5 min and the reaction mixture stirred for 20 min at dark. The reaction mixture was filtered and the filtrate evaporated at 25 ^{o}C under vacuum. The pure compound (by ^{1}H NMR) solidifies after standing in a vacuum oven for overnight.

5a Ag(I) complex 6a. Yield 0.149 g, 98%. Colourless crystals, mp 78–80 ^{o}C. IR (KBr) $\nu_{C=O}$ 1745 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (3H, t, J = 7.2 Hz), 2.41 (3H, s), 4.17 (2H, q, J = 7.2 Hz), 5.02 (2H, s), 7.23 (1H, s), 7.26-7.28 (2H, d, m), 7.37-7.39 (2H, m), 7.46-7.52 (5H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1; 21.1; 51.0; 62.2; 119.6; 123.7; 126.9; 129.1; 129.5; 129.9; 130.4; 136.1; 137.3; 139.1; 167.8; 182.0. Anal. Calcd for $C_{20}H_{20}AgBrN_2O_2$ (508.16) C, 47.27; H, 3.97; N, 5.51; Found C, 46.68; H, 3.68; N, 5.26.



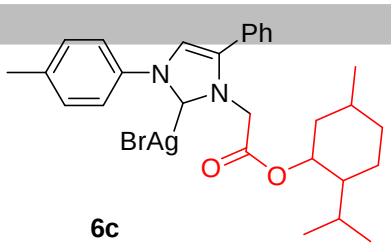
6a

5b Ag(I) complex 6b. Yield 0.150 g, 96%. Colourless crystals, mp 93–95 ^{o}C. IR (KBr) $\nu_{C=O}$ 1740 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (3H, t, J = 7.6 Hz), 3.87 (3H, s), 4.19 (2H, q, J = 7.6 Hz), 4.94 (2H, s), 7.00 (2H, d, J = 8.4 Hz), 7.21 (1H, s), 7.37-7.39 (2H, m), 7.48-7.54 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1; 50.9; 55.6; 62.3; 114.9; 125.2; 129.1; 129.5; 129.9; 132.8; 136.0; 159.9; 167.7; 182.4. Anal. Calcd for $C_{20}H_{20}AgBrN_2O_3$ (524.16) C, 45.83; H, 3.85; N, 5.34; Found C, 46.05; H, 3.46; N, 5.34.



6b

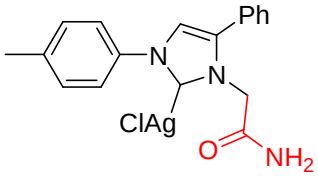
5c Ag(I) complex 6c. Yield 0.115 g, 62%. Colourless crystals, mp 88–90 ^{o}C. IR (KBr) $\nu_{C=O}$ 1741 cm^{-1},^{1}H NMR (400 MHz, $CDCl_3$): δ 0.66 (3H, d, J = 6.4), 0.83 (3H, d, J = 7.2), 0.89 (3H, d, J = 6.4), 0.93-1.86 (8H, m), 2.42 (3H, s), 4.68 (1H, dt, J = 10.8; 4.0 Hz), 4.94 (1H, d,



6c

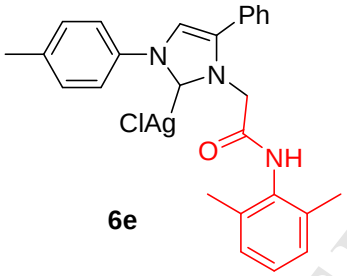
J = 17.6), 5.00 (1H, d, J = 17.6), 7.23 (1H, s), 7.28-7.31 (3H, m), 7.38-7.40 (2H, m), 7.46-7.52 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1; 20.8; 21.1; 21.9; 23.1; 26.0; 31.4; 33.9; 40.6; 46.8; 51.3; 76.5; 119.8; 121.3; 123.7; 124.9; 126.9; 128.6; 129.1; 129.9; 130.5; 136.1; 137.3; 139.2; 167.2; 183.5. Anal. Calcd for $C_{28}H_{34}AgBrN_2O_2$ (618.35) C, 54.39; H, 5.54; N, 4.53; Found C, 54.34; H, 5.69; N, 4.94.

5d Ag(I) complex 6d. Yield 0.050 g, 40%. Colourless crystals, mp 124-125 ^{o}C. IR (KBr) ν_{NH2} 3328 and 3177 cm^{-1}; $\nu_{C=O}$ 1686 ,^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (3H, s), 5.19 (2H, s), 5.72 (1H, br s), 7.10 (2H, d, J = 8.4 Hz), 7.19 (1H, s), 7.35 (2H, d, J = 8.4 Hz), 7.45-7.49 (5H, m), 8.98 (1H, brs). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1; 29.7 51.4; 118.8; 123.6; 126.9; 129.0; 129.6; 129.9; 130.1; 137.4; 137.5; 138.7; 169.8. Anal. Calcd for $C_{18}H_{17}AgClN_3O$ (434.67) C, 49.74; H, 3.94; N, 9.67; Found C, 50.01; H, 3.56; N, 9.78.



6d

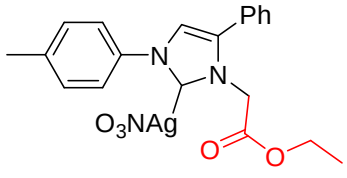
5e Ag(I) complex 6e. Yield 0.108 g, 67%. Colourless crystals, mp 158–159 ^{o}C. IR (KBr) ν_{NH} 3394 cm^{-1}; $\nu_{C=O}$ 1691, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (6H, s), 2.42 (3H, s), 5.29 and 5.84 (2H, 2Xs), 6.96-7.02 (3H, m), 7.10 (2H, d, J = 8.4 Hz), 7.20 (1H, s), 7.1 (2H, d, J = 8.4 Hz), 7.42-7.46 (3H, m), 7.58-7.60 (2H, m), 10.71 (1H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0; 21.1; 51.7; 118.5; 123.6; 126.8; 126.9; 127.9; 128.9; 129.8; 129.9; 130.1; 134.1; 135.3; 137.5; 138.8; 166.4. Anal. Calcd for $C_{26}H_{25}AgClN_3O$ (538.82) C, 57.96; H, 4.68; N, 7.80; Found C, 58.00; H, 5.08; N, 7.90.



6e

IV.4 Synthesis of Ag(I) metalated 3*H*-imidazol-1-ium salts 7a-e. General procedure. To a solution of **3a-e** (0.15 mmol) in CH_2Cl_2 (25 mL) $AgNO_3$ (0.263 mmol, 0.044 g) and Et_3N (10.8 mmol, 1.095 g, 1.5 mL, 0.73 kg/L) were added successively and the reaction mixture stirred for 2 h at dark. The reaction mixture was washed with water (25 mL) and the organic phase separated and dried over Na_2SO_4. The solvent was evaporated and the residual solid was dried under vacuum at dark.

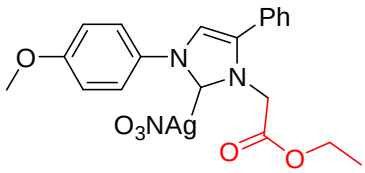
5a Ag(I) complex 7a. Yield 0.062 g, 84%. Colourless crystals, mp 78–80 ^{o}C (decomp). IR (KBr) $\nu_{C=O}$ 1747 cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.02 (3H, t, J = 7.6 Hz), 2.36 (3H, s), 4.01 (2H, q, J = 7.6 Hz), 5.18 (2H, s), 7.29 (2H, d, J = 8.0 Hz), 7.48-7.51 (5H, m), 7.61 (2H, d, J = 8.0 Hz), 8.04 (1H, s). ^{13}C NMR (100 MHz, DMSO-d_6):



7a

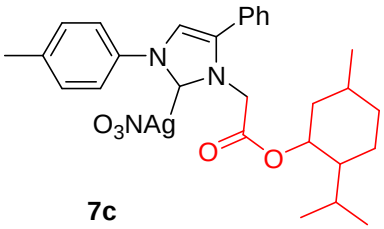
δ 14.2; 21.0; 51.4; 61.9; 121.2; 123.9; 127.5; 129.5 (2C); 130.0; 130.5; 136.1; 135.5; 138.9; 168.2 (C-Ag is not observed). Anal. Calcd for $C_{20}H_{20}AgN_3O_5$ (490.26) C, 49.00; H, 4.11; N, 8.57; Found C, 49.15; H, 4.17; N, 8.70.

5b Ag(I) complex 7b. Yield 0.067 g, 88%. Colourless crystals, mp 93–95 ^{o}C (decomp). IR (KBr) $\nu_{C=O}$ 1747 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.03 (3H, t, J = 7.6 Hz), 3.81 (3H, s), 4.01 (2H, q, J = 7.6 Hz), 5.17 (2H, s), 7.04 (2H, d, J = 8.4 Hz), 7.48-7.51 (5H, s), 7.65 (2H, d, J = 8.4 Hz), 7.99 (1H, S). ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.2; 46.2; 51.4; 56.0; 61.9; 115.2; 121.4; 123.8; 125.5; 127.5; 129.5; 133.0; 135.9; 159.8; 168.3 (C-Ag is not observed). Anal. Calcd for $C_{20}H_{20}AgN_3O_6$ (506.26) C, 47.45; H, 3.98; N, 8.30; Found C, 47.55; H, 4.15; N, 8.25.



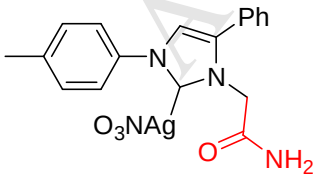
7b

5c Ag(I) complex 7c. Yield 0.072 g, 80%. Colourless crystals, mp 88–90 ^{o}C (decomp). IR (KBr) $\nu_{C=O}$ 1743 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.49-0.94 (12H, m), 1.18-1.64 (6H, m), 2.38 (3H, s), 4.49 (1H, dt, J = 10.8; 4.0 Hz), 5.21 (2H, s), 7.33 (2H, d, J = 7.6 Hz), 7.50 (5H, s), 7.61 (2H, d, J = 7.6 Hz), 8.03 (1H, s). ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.5; 20.9; 21.1; 22.2; 23.2; 26.0; 31.1; 33.9; 46.2; 46.8; 51.5; 75.6; 121.3; 122.0; 123.9; 127.4; 129.4; 129.5; 130.6; 137.6; 138.9; 167.7 (C-Ag is not observed). Anal. Calcd for $C_{28}H_{34}AgN_3O_5$ (600.45) C, 56.01; H, 5.71; N, 7.00; Found C, 56.11; H, 5.85; N, 7.10.



7c

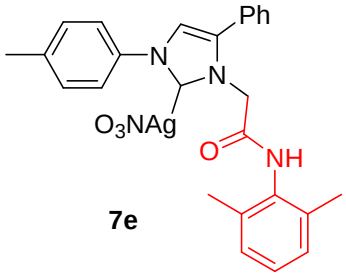
5d Ag(I) complex 7d. Yield 0.054 g, 78%. Colourless crystals, mp 124-125 ^{o}C (decomp). IR (KBr) ν_{NH2} 3370 and 3334 cm^{-1}; $\nu_{C=O}$ 1688 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.36 (3H, s), 4.82 (2H, s), 7.31 (2H, d, J = 8.0 Hz), 7.36 (1H, brs), 7.47-7.54 (5H, m), 7.57 (5H, s), 7.60 (2H, d, J = 8.0 Hz), 7.63 (1H, brs), 7.99 (1H,s). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.0; 52.0; 120.8; 123.7; 127.7; 129.4; 129.5; 129.9; 130.6; 136.3; 137.6; 138.8; 168.7 (C-Ag is not observed). Anal. Calcd for $C_{18}H_{17}AgN_4O_4$ (461.22) C, 46.87; H, 3.72; N, 12.15; Found C, 46.95; H, 3.50; N, 11.95.



7d

5e Ag(I) complex 7e. Yield 0.073 g, 86%. Colourless crystals, mp 158–159 ^{o}C (decomp). IR

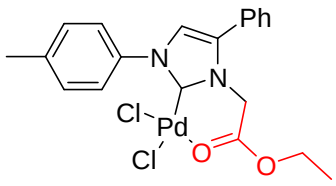
(KBr) ν_{NH} 3443; $\nu_{C=O}$ 1696 cm^{-1}. 1H NMR (400 MHz, DMSO-d_6): δ 1.86 (6H, s), 2.30 (3H, s), 5.20 (2H, s), 6.97-7.01 (3H, m), 7.29 (2H, d, J = 7.2 Hz), 7.53-7.55 (5H, m), 7.62 (2H, d, J = 7.2 Hz), 8.03 (1H, s), 9.53 (1H, brs). ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.3; 21.0; 46.2; 121.8; 123.7; 127.1; 127.7; 128.1; 129.5; 129.7; 130.6; 131.2; 134.6; 135.4; 136.3; 137.6; 138.9; 165.3 (C-Ag is not observed). Anal. Calcd for $C_{26}H_{25}AgN_4O_4$ (565.37) C, 55.23; H, 4.46; N, 9.91; Found C, 55.35; H, 4.60; N, 10.10.



7e

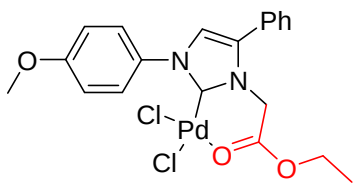
IV.5 Synthesis of 3*H*-imidazol-1-ium 2-yliden Pd (II) complexes 8a-e. Method A. General Procedure. To a solution of Ag(I) complexes **6a-e** (0.25 mmol) in CH_2Cl_2 (5 mL) $Pd(CH_3CN)_2Cl_2$ (0.25 mmol, 0.065 g,) was added and the reaction mixture stirred for 20 min at dark. The precipitated AgX was removed by filtration through a celite bed. The solvent of the filtrate was evaporated under reduced pressure at room temperature. The formed orange coloured solids were dried under vacuum.

5a Pd(II) complex 8a. Yield, 0.116 g, 93%. Orange powder. Mp 183–186 ^{o}C (decomp). IR (KBr) $\nu_{C=O}$ 1744 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (3H, t, J = 7.6 Hz), 2.44 (3H, s), 4.14 (2H, q, J = 7.6 Hz), 5.27 (1H, d, J = 18.0 Hz), 5.60 (1H, d, J = 18.0 Hz), 7.43-7.53 (7H, m), 7.95 (2H, d, J = 8.4 Hz), 8.04 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 14.1; 21.3; 50.2; 62.4; 121.5; 125.5; 126.6; 129.0; 129.1; 129.7; 130.0; 130.3; 130.6; 135.9; 137.1; 169.3. ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.3; 21.1; 50.3; 62.1; 122.0; 125.5; 127.1; 129.4; 129.6; 130.1; 130.4; 136.3; 136.6; 139.5; 167.8. Anal. Calcd for $C_{20}H_{20}Cl_2N_2O_2Pd$ (497.71) C, 48.26; H, 4.05; N, 5.63; Found C, 48.38; H, 4.19; N, 5.71.



8a

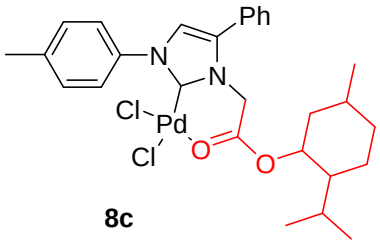
5b Pd(II) complex 8b. Yield, 0.122 g, 95%. Orange powder. Mp 115-118 ^{o}C (decomp). IR (KBr) $\nu_{C=O}$ 1748 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.14 (3H, t, J = 7.2 Hz), 3.86 (3H, s), 4.14 (2H, q, J = 7.2 Hz), 5.26 (1H, d, J = 17.6 Hz), 5.59 (1H, d, J = 17.6 Hz), 7.27 (2H, d, J = 9.2 Hz), 7.47-7.50 (5H, m), 7.96 (2H, d, J = 9.2 Hz), 7.99 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1; 50.1; 55.7; 62.5; 114.8; 121.7; 126.6; 127.2; 129.0; 129.6; 130.0; 131.4; 137.1; 145 (C-Pd); 160.1; 166.9. ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.3; 50.3; 56.2; 62.1; 115.0; 126.7; 127.1; 127.2; 129.3; 129.6; 130.1; 131.6; 136.4;



8b

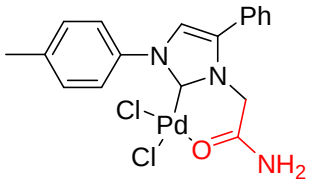
160.1; 167.8. Anal. Calcd for $C_{20}H_{20}Cl_2N_2O_3Pd$ (513.71) C, 46.76; H, 3.92; N, 5.45; Found C, 46.13; H, 4.12; N, 5.55.

5c Pd(II) complex 8c. Yield 0.112 g, 92%. Orange powder. Mp 113-115 ^oC (decomp). IR (KBr) $\nu_{C=O}$ 1744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 0.52-1.64 (18H, m), 2.44 (3H, s), 4.53 and 4.66 (1H, 2X dt, J = 10.8; 4.0 Hz), 5.29-5.39 (1H, m, overlapping A parts of an AB system), 5.59-5.75 (1H, m, overlapping B parts of an AB system), 7.44-7.53 (7H, m), 7.94 (2H, d, J = 7.6 Hz), 8.03 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 16.2; 20.9; 21.4; 21.9; 23.2; 25.9; 31.4; 34.1; 40.4; 46.9; 50.3; 76.3; 121.6; 125.7; 126.8; 128.9; 129.5; 129.9; 130.2; 130.7; 136.1; 137.0; 139.2; 141.2; 166.4. Anal. Calcd for $C_{28}H_{34}Cl_2N_2O_2Pd$ (607.91) C, 55.32; H, 5.64; N, 4.61; Found C, 55.00; H, 5.53; N, 4.71.



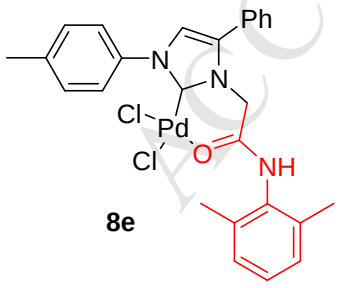
8c

5d Pd(II) complex 8d. Yield 0.089 g, 76%. Orange powder. Mp 248-250 ^oC (decomp). IR (KBr) ν_{NH2} 3323.9 and 3419.8; $\nu_{C=O}$ 1687 cm^{-1}, ^1H NMR (400 MHz, DMSO-d_6): δ 2.43 (3H, s), 4.61 (1H, d, J = 17.6 Hz), 5.54 (1H, d, J = 17.6 Hz), 7.43-7.56 (7H, m), 7.99 (2H, d, J = 8.8 Hz), 8.00 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2; 50.2; 117.8; 122.3; 125.5; 129.5; 130.1; 130.3; 131.0; 132.1; 134.5; 137.2; 140.8; 164.9. Anal. Calcd for $C_{18}H_{17}Cl_2N_3OPd$ (468.67) C, 46.13; H, 3.66; N, 8.97; Found C, 46.25; H, 3.55; N, 9.00.



8d

5e Pd(II) complex 8e. Yield 0.134 g, 93%. Mp 294-296 ^oC (decomp). IR (KBr) ν_{NH} 3254; $\nu_{C=O}$ 1684 cm^{-1}, ^1H NMR (400 MHz, DMSO-d_6): δ 2.16 (6H, s), 2.43 (3H, s), 4.99 (1H, d, J = 16.8 Hz), 5.91 (1H, d, J = 16.8 Hz), 7.08 (3H, s), 7.49-7.55 (7H, m), 8.00 (2H, d, J = 8.4 Hz), 8.03 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 18.8; 21.3; 42.8; 122.3; 125.6; 127.5; 127.9; 128.1; 128.4; 128.9; 129.3; 130.1; 130.2; 130.4; 133.2; 135.4; 135.5; 135.8; 137.7; 139.5; 164.4. Anal. Calcd for $C_{26}H_{25}Cl_2N_3OPd$ (572.82) C, 54.52; H, 4.40; N, 7.34; Found C, 54.60; H, 4.47; N, 7.60.



8e

IV.6 Synthesis of 3*H*-imidazol-1-ium 2-yliden Pd (II) complexes 8a-e. Method B. General Procedure. To a solution of Ag(I) complexes **7a-e** (0.25 mmol) in CH_2Cl_2 (5 mL), $Pd(CH_3CN)_2Cl_2$ (0.15 mmol, 0.039 g, 99%) was added and the reaction mixture stirred for 1 h at dark. The precipitated

AgX was filtered through celite and the filtrate evaporated under reduced pressure at room temperature.

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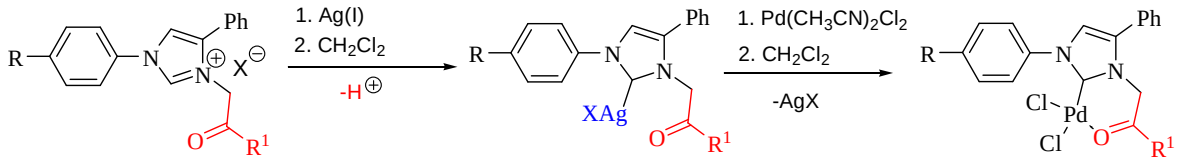
Synthesis and catalytic activities of 1-alkoxycarbonyl- and 1-carbamoylmethyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II) complexes

Meliha Çetin Korukçu and Necdet Coşkun*



5 **6** (X=Br or Cl) **8**
7 (X=NO_3)

4-Phenyl-1-aryl-1*H*-imidazoles were converted to Pd(NHC) complexes.

1-Alkoxycarbonyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II) were shown to be better catalyst than the 1-carbamoylmethyl-5-phenyl-3-aryl-3*H*-imidazol-1-yliden-Pd(II) complexes.

The catalysts were shown to be insensitive to the air oxygen and water.