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Unconjugated diimine palladium complexes as Heck coupling catalysts

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Abstract

Four unconjugated diimine palladium complexes have been synthesized, and spectroscopically and structurally characterized. All four palladium complexes were used as catalysts in the Heck coupling reaction between iodobenzene and methyl acrylate or butyl acrylate with very good conversion to either methyl (2*E*)-3-phenylacrylate or butyl (2*E*)-3-phenylacrylate.

Keywords: Unconjugated diimine ligands; Palladium complexes; Crystal structures; Heck coupling catalysts

1. Introduction

The Heck coupling reaction is one of the most important C–C bond forming processes in organic synthesis [1]. It features applications that range from the preparation of hydrocarbons and industrial production of pharmaceuticals, to advanced synthesis of natural products [2]. The most extensively used catalysts to date are phosphine palladium complexes [3]. However, the cost and sensitivity of phosphines to air and moisture have led to the search for less expensive and more stable ligands as synthons for new palladium Heck coupling catalysts. Some of these so-called phosphine-free catalysts are palladium complexes bearing *N*-heterocyclic carbene ligands [4] or nitrogen-donor ligands [5]. Effective phosphine-free catalysts for the Heck coupling reaction contain either less expensive ligands or moieties that are more stable under ambient conditions, or both. However, in a number of cases reactions catalyzed by phosphine-free ligand palladium complexes require high temperatures and long reaction times and the complexes function as precursors for colloidal particles [6]. Complexes containing nitrogen-based ligands remain the least explored phosphine-free Heck coupling catalysts/catalyst precursors, and only scarce information is available for imine ligands in spite of the extensive use of α-diimine complexes of late transition metals complexes as olefin oligomerization and polymerization catalysts [7]. Nolan and co-workers [8] have used the β-diimine ligand 1,4-diaza-1,3-butadiene in the Suzuki coupling reaction.

Recently, Qian et al. have utilized unconjugated diimine cobalt complexes as catalysts for ethylene oligomerization [9]. Other examples of the use of unconjugated diimines are zinc complexes as asymmetric catalysts for enantioselective synthesis of 1-phenyl-1-propanol [10] and the photoluminescence of copper complexes [11]. Here, we report the catalytic behavior of four unconjugated diimine palladium complexes that are capable of catalyzing Heck coupling. To the best of our knowledge, this is the first report on the use of unconjugated diimine complexes in Heck coupling catalysis.

2. Experimental

2.1. General

All experiments were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. All solvents were purchased from Sigma–Aldrich and refluxed over appropriate drying agents and distilled: diethyl ether was dried

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over sodium, dimethylformamide (DMF) over calcium hydride, acetonitrile and dichloromethane over phosphorus pentoxide and acetone over anhydrous calcium chloride and kept over 4 Å molecular sieves. *N*,*N*-dimethylacetamide (DMA) was purchased from Sigma–Aldrich and was used without further purification. The ligand, **L1**, (*N*,*N*′-bis(diphenylmethylene)1,2-ethanediamine) was synthesized according to the modified method which has been published by Chowdhury et al. [11], and [PdClMe(COD)] [12] and [$PdCl_2(NCMe)_2$] [13] were prepared by literature procedures.

IR spectra were recorded as nujol mulls on a PerkinElmer Paragon 1000 PC FT-IR spectrometer. NMR spectra were recorded on a Varian Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50 MHz). Chemical shifts are reported in ppm and referenced to residual proton and carbon signals (7.25 and 77.0 ppm for $CDCl_3$ and 2.50 and 39.0 ppm for DMSO-d_6). Elemental analysis was performed in the Department of Chemistry at the University of the Cape Town. Heck coupling reaction products were analyzed on a Shimadzu GCMS-QP 2010 version 2 gas chromatograph; fitted with a flame ionization detector (FID) and a 30 m × 0.25 mm, 100% dimethoxypolysiloxane ZB1 column. Products were quantified *via* internal standard techniques.

2.2. Ligand synthesis

2.2.1. (*N*,*N*′-bis(diphenylmethylene)1,3-propanediamine (**L2**)

A solution of benzophenone (10.87 g, 60.00 mmol) and freshly distilled 1,3-propanediamine (2.5 mL, 30.0 mmol) in anhydrous methanol (50 mL) were refluxed for 10 days. Three pieces of Drierite were added to the solution every two days. The yellow solution was filtered and the volume of the filtrate reduced to half its volume *in vacuo*. The white solid that precipitated was filtered and the crude product recrystallized from boiling heptane to give fine white crystals. Yield: 3.10 g (26%), m.p.: 82–85 °C, MS (*m/z*): 402 (M^+, 100%). ^{1}H NMR ($CDCl_3$): δ 7.32 (m, 20H, C_6H_5), 3.46 (t, 4H, CH_2), 2.05 (quintet, 2H, CH_2).

2.3. Synthesis of complexes

2.3.1. [$PdCl_2\{(C_6H_5)_2C{=}N(CH_2)_2N{=}C(C_6H_5)_2\}$] (**1**)

To a solution of [$PdCl_2(NCMe)_2$] (0.08 g, 0.30 mmol) in acetone (5.0 mL) was added a solution of **L1** (0.11g, 0.30 mmol) in acetone (5.0 mL). The resultant orange solution changed to yellow with immediate precipitation of a yellow solid. The mixture was stirred for 15 min at room temperature, the precipitate was then allowed to settle and the supernatant liquid decanted. The residue was washed twice with acetone (2 × 10 mL) and the product was dried *in vacuo*. Yield: 76% (0.13 g). Anal. Calcd. for $C_{28}H_{24}Cl_2N_2Pd$: C, 54.44; H, 4.28; N, 4.95. Found: C, 54.84; H, 3.70; N, 4.82. ^{1}H NMR (DMSO-d_6): δ 7.53 (m, 20H, C_6H_5), 4.15 (s, 4H, CH_2).

2.3.2. [$PdCl_2\{(C_6H_5)_2C{=}N(CH_2)_3N{=}C(C_6H_5)_2\}$] (**2**)

Complex **2** was prepared from [$PdCl_2(NCMe)_2$] (0.08 g, 0.30 mmol) and **L2** (0.11 g, 0.30 mmol), following the synthetic procedure described for **1**. Yield: 0.14 g (82%). Anal Calcd. for $C_{29}H_{26}Cl_2N_2Pd$: C, 60.07; H, 4.52; N, 4.83. Found: C, 59.53; H, 4.56; N, 4.81. ^{1}H NMR (DMSO-d_6): δ 7.65 (m, 20H, C_6H_5), 3.88 (t, 4H, CH_2), 2.51 (m, 2H, CH_2).

2.3.3. [$PdClMe\{(C_6H_5)_2C{=}N(CH_2)_2N{=}C(C_6H_5)_2\}$] (**3**)

To a mixture of [PdClMe(COD)] (0.20 g, 0.77 mmol) and **L1** (0.30 g, 0.77 mmol) was added diethyl ether (20 mL). The color changed to light yellow and a precipitate formed after stirring at room temperature for 6 h. The product was isolated as a light yellow solid and recrystallized from CH_2Cl_2/hexane at −4 °C. Yield: 0.29 g (69%). Anal Calcd. for $C_{29}H_{27}ClN_2Pd{\cdot}2CH_2Cl_2$: C, 52.04; H, 4.37; N, 3.92. Found: C, 52.82; H, 4.18; N, 3.82. ^{1}H NMR ($CDCl_3$): δ 8.30 (d, 2H, J = 7.40 Hz, C_6H_5), 7.66 (d, 2H, J = 7.20 Hz, C_6H_5), 7.54 (m, 16H, C_6H_5), 0.40 (s, 3H, Pd–Me).

2.3.4. [$PdClMe(C_6H_5)_2C{=}N(CH_2)_3N{=}C(C_6H_5)_2$] (**4**)

Complex **4** was prepared from [PdClMe(COD)] (0.20 g, 0.76 mmol) and **L2** (0.30 g, 0.76 mmol) as described for **3**. Crystals suitable for X-ray analysis were obtained after 2 days. Yield: 0.23 g (47%). Anal Calcd. for $C_{30}H_{29}ClN_2Pd{\cdot}CH_2Cl_2$: C, 57.78; H, 4.85; N, 4.35. Found: C, 57.83; H, 4.31; N, 4.43. ^{1}H NMR ($CDCl_3$): δ 8.37 (d, 2H, J = 7.00 Hz, C_6H_5), 7.78 (d, 2H, J = 7.20 Hz, C_6H_5), 7.34 (m, 16H, C_6H_5), 0.32 (s, 3H, Pd–Me).

2.4. Crystallographic experimental section

Details regarding the data collections are summarized in Table 1 and are fully described in the Supplementary Material. The data were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [14]. For both **3a** and **4**, the systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement [14]. For both compounds, a successful solution by direct methods provided most non-hydrogen atoms from the electron density map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms (except C29 in the case of **3a**) were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

In the structure of complex **3a**, the Pd complex resides on a crystallographic inversion centre. There is Cl/Me compositional disorder about the Pd centre. The Cl/Me ratio is 0.736(3):0.264(3); thus, three different compositions of the complex are possible: [$PdCl_2$(**L1**)$_2$] [$PdMe_2$(**L1**)$_2$] and [PdClMe(**L1**)$_2$], and the complexes of different composition have apparently co-crystallized. For complex **4**, there is one molecule of solvate dichloromethane per Pd complex in the lattice. The final difference Fourier map contained two high peaks (ca. 2.8 and 1.5 e/Å^3) in the vicinity of the solvent molecule in

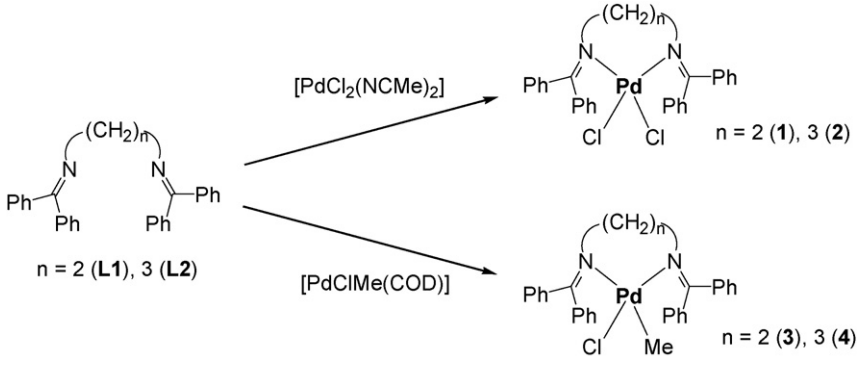
Table 1
Crystal data and structure refinement for **3a** and **4**

	3a	**4**
Empirical formula	$C_{28}H_{24}N_2Cl_{1.472}Me_{0.528}Pd$	$C_{31}H_{31}Cl_3N_2Pd$
Formula weight	943.46	644.33
Temperature (K)	105(2)	100(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a	9.1303(9) Å	12.5058(4) Å
b	18.2917(17) Å	12.5694(4) Å
c	14.0500(13) Å	17.7373(6) Å
β	103.913	93.0020(10)
Volume	2277.31(16) Å^3	2784.31(16) Å^3
Z	2	4
Density (calculated)	1.376 Mg/m^3	1.537 Mg/m^3
Absorption coefficient	0.537 mm^{-1}	0.978 mm^{-1}
$F(0\,0\,0)$	976	1312
Crystal size	0.26 mm × 0.24 mm × 0.20 mm	0.42 mm × 0.34 mm × 0.33 mm
θ range for data collection	1.86–29.16°	2.04–26.39°
Index ranges	$-12 \le h \le 12$ $25 \le h \le 24$ $-19 \le h \le 19$	$-15 \le h \le 15$ $-15 \le k \le 15$ $-22 \le l \le 22$
Reflections collected	39614	22582
Independent reflections	6099 [R(int) = 0.0409]	5676 [R(int) = 0.0216]
Completeness to $\theta = 26.39°$	99.3%	99.6%
Absorption correction	Empirical with SADABS	Multi-scan with SADABS
Max. and min. transmission	0.9002 and 0.8730	0.7384 and 0.6841
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6099/0/292	5676/0/335
Goodness-of-fit on F^2	1.022	1.022
Final R indices [I > 2sigma(I)]	$R1 = 0.0295$, w$R2 = 0.0699$	$R1 = 0.0373$, w$R2 = 0.1012$
R indices (all data)	$R1 = 0.0387$, w$R2 = 0.1025$	$R1 = 0.0387$, w$R2 = 0.1025$
Largest diff. peak and hole	0.530 and −0.281 e Å^{-3}	2.796 and −1.614 e Å^{-3}

chemically unreasonable positions; these peaks were considered noise.

2.5. General procedure for Heck reactions

Iodobenzene (15 mmol), triethylamine (15 mmol) and 15 mmol of an appropriate olefinic substrate (methyl acrylate or butyl acrylate) were mixed in a two-necked round-bottomed flask fitted with a reflux condenser. The mixture was dissolved in 30 mL of acetonitrile and palladium complex (0.15 mmol) added before the mixture was heated at 80 °C in an oil bath. Samples of 0.25 mL were withdrawn periodically by syringe, diluted with dichloromethane and analyzed by GC–MS.



Scheme 1. Synthetic routes to palladium complexes **1**–**4**.

3. Results and discussion

The palladium complexes **1**–**4** were prepared as depicted in Scheme 1. Complexes **1** and **2** were formed by reacting ligands **L1** and **L2** with $[PdCl_2(NCMe)_2]$ in an inert atmosphere. The products were isolated as yellow solids in moderate to good yields. Both complexes were found to be only sparingly soluble in $CHCl_3$ or CH_2Cl_2. ^{1}H NMR spectra of both complexes exhibited characteristic peaks and peak intensities of the respective ligands, with slight chemical shifts from those of the free ligands. The NMR data thus suggested that the two complexes could be formulated as shown in Scheme 1. The results of elemental analyses agreed with the proposed formulae.

Complex **3** was synthesized by adding a diethyl ether solution of **L1** to a suspension of [PdClMe(COD)] in diethyl ether. Similarly, addition of **L2** to [PdClMe(COD)] yielded **4**. In the case of the synthesis of **3**, the reaction took 6 h to complete while the reaction with **L2** to form **4** required only 30 min to go to completion. However, in one experiment for the synthesis of **3** where 1.3 equivalents of **L1** was used instead of the usual 1 equivalent, our attempts to purify the crude **3** from a CH_2Cl_2 solution yielded single crystals of an entirely new material (**3a**). Complex **3a** resides on a crystallographic inversion center and only one half of it is symmetry independent. Thus, in the asymmetric unit (Fig. 1(a)), the Pd atom is bound to an **L1** ligand while the other site is 73.6(3)% occupied by a chloride and 26.4(3)% by a methyl substituent due to compositional disorder. The entire complex contains two **L1** ligands and two disordered ligands in *trans* positions relative to each other (Fig. 1(b)).

All expected peaks were clearly resolved in the room temperature ^{1}H NMR spectra of complexes **3** and **4**, with the exception of the protons in the propane backbone of **4** which appeared as a broad peak at 4.20 ppm. The ^{13}C resonances of the propane backbone of **4** were, however, resolved in the room temperature ^{13}C NMR spectrum where these carbons appeared at 59.4, 56.4 and 33.9 ppm. The NMR data suggested that the propane backbone undergoes inversion at the carbons at a rate that makes the motion of the protons on the backbone more rapid than the NMR timescale can detect, but the motion of carbons during this inversion is not as rapid. Variable temperature ^{1}H NMR spectra of **4** showed that the fluxional behavior could be frozen out at −50 °C when the distinct environments of all six protons are evident (Fig. 2); these give rise to two triplets at 4.64 and 4.58 ppm, three doublets at 4.18, 3.72 and 1.90 ppm, and a quartet at 1.27 ppm. The two most upfield signals are assigned to the protons on the central carbon atom of the propane backbone. The two triplets belong to protons on the two carbons next to the imine nitrogens, and the remaining two doublets are resonances from the geminal protons associated with the protons that give rise to the triplets (cf. Fig. 2). The solid-state structure of **4**·CH_2Cl_2 (Fig. 3) did indeed confirm the presence of the propane backbone.

3.1. Molecular structures of *3a* and *4*

Crystals of **3a** and **4**·CH_2Cl_2, suitable for X-ray structure determination, were obtained by slow diffusion of hexane into solutions of each complex in dichloromethane. The molecular structures are depicted in Figs. 1 and 3, crystallographic data are listed in Table 1 and selected bond lengths and bond angles are listed in Table 2. Complex **3a** crystallized without solvent, while **4** crystallized with one mole of dichloromethane in the unit cell.

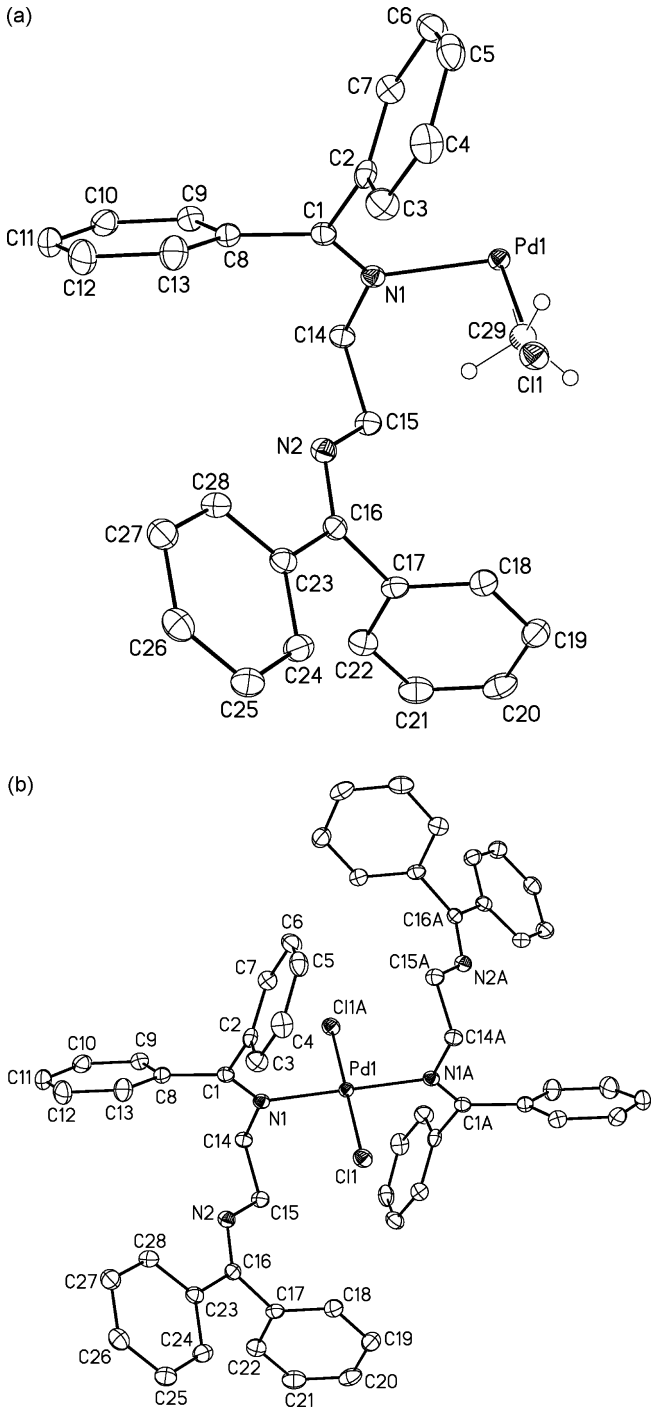


Fig. 1. (a) A molecular drawing of the asymmetric unit of **3a**. All H atoms except those on C29 are omitted. Atom C29 was refined isotropically. (b) A molecular drawing of one of the three possible Pd complexes (**3a**, see text) present in the lattice, drawn with 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

The structure of complex **3a** has two **L1** ligands instead of one, and a Cl and a compositional disorder of Cl and Me in the

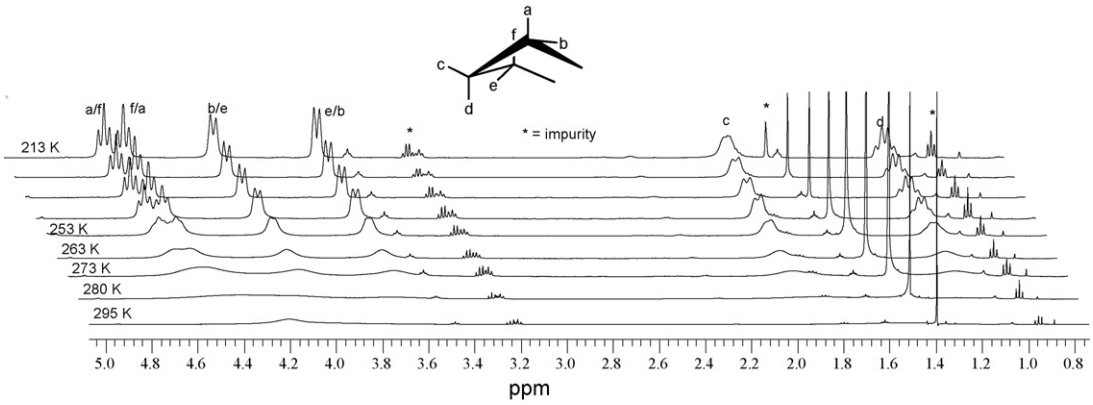


Fig. 2. Variable temperature ^{1}H NMR spectra of complex **4**.

remaining position of a square planar arrangement, in which the imine ligands are *trans* to each other. Unexpectedly **L1** in **3a** is coordinated to Pd not as a bidentate ligand but in a monodentate fashion *via* only one imine nitrogen, while the other imine group in the ligand remains uncoordinated. The geometry around the Pd is a distorted square planar. The Pd–Cl and Pd–C bonds in **3a** are 2.3595(12) and 2.005(12) Å respectively, and are within the expected range for each of these bond types [15,16].

The structure of complex **4** shows a bidentate co-ordination of **L2** to Pd to give a distorted square planar geometry around the palladium with the chelating angle C(1)–Pd–N(1) being close to 90° (89.36(11)°). The Pd(1)–N(2) bond distance of 2.209(2) Å is significantly longer than the Pd(1)–N(1) bond distance of 2.045(2) Å due to the difference in the ligand *trans* influence.

3.2. Catalytic Heck reaction

The catalytic activity of complexes **1**–**4** were tested towards the Heck coupling of iodobenzene with methyl acrylate or butyl acrylate (Scheme 2). Reactions were carried out under nitrogen at 80 °C in CH_3CN (15 mL) and triethylamine as a base; using equivalent molar ratios of iodobenzene, methyl acrylate and triethylamine. The catalyst precursors were added at a Pd:substrate molar ratio of 1:100. After addition of the catalyst precursor, samples were drawn at periodic intervals and the consumption of iodobenzene monitored by GC over 8 h. The results of these experiments are summarized in Table 3.

For each catalyst precursor evaluated, the major product formed by the Heck coupling reaction was the *trans* stereoisomer, methyl (2*E*)-3-phenylacrylate or butyl (2*E*)-3-phenylacrylate. The *cis* stereoisomer, alkyl (2*Z*)-3-phenylacrylate, comprised less than 1% of the isomeric products formed. Table 3 shows all four complexes have similar trends of activity in the arylation reaction of methyl

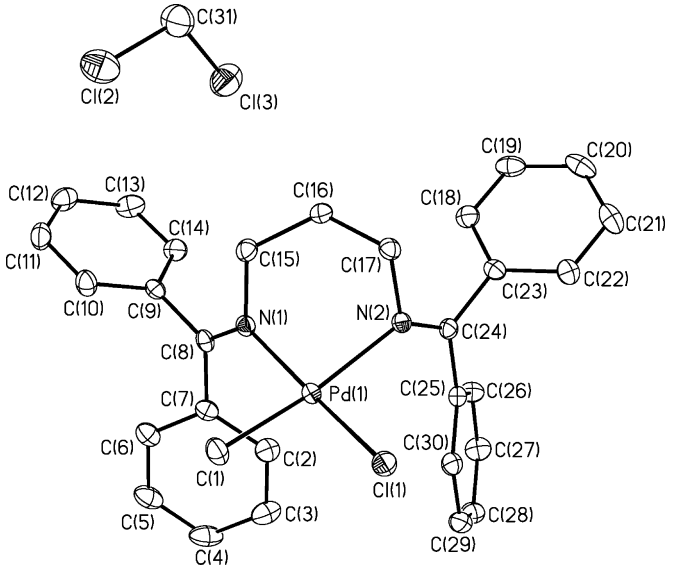
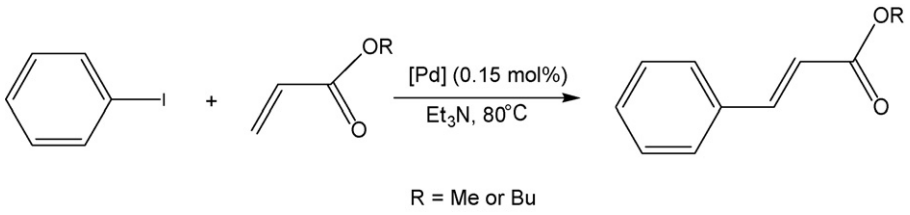


Fig. 3. Molecular drawing of **4** with 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Table 2
Bond distances [Å] and angles [°] for complexes **3a** and **4**

3a			
Bond lengths (Å)			
Pd(1)–C(29)	2.005(12)	N(1)–C(1)	1.283(2)
Pd(1)–N(1)	2.0189(13)	N(1)–C(14)	1.472(2)
Pd(1)–Cl(1)	2.3595(12)	N(2)–C(16)	1.278(4)
Bond angles [°]			
C(29)–Pd(1)–N(1)	92.0(4)	N(1)–Pd(1)–Cl(1)	94.40(4)
C(29)A–Pd(1)–N(1)	88.0(4)	C(29)–Pd(1)–N(1)A	88.0(4)
4			
Bond lengths (Å)			
Pd(1)–C(1)	2.027(3)	Cl(3)–C(31)	1.775(4)
Pd(1)–N(1)	2.045(2)	N(1)–C(8)	1.291(4)
Pd(1)–N(2)	2.209(2)	N(1)–C(15)	1.485(4)
Pd(1)–Cl(1)	2.3286(7)	N(2)–C(17)	1.475(4)
Cl(2)–C(31)	1.765(4)	N(2)–C(24)	1.288(4)
Bond angles [°]			
C(1)–Pd(1)–N(1)	89.36(11)	C(8)–N(1)–Pd(1)	130.8(2)
C(1)–Pd(1)–N(2)	173.74(11)	C(15)–N(1)–Pd(1)	108.28(17)
N(1)–Pd(1)–N(2)	85.13(9)	C(24)–N(2)–C(17)	119.3(2)
N(1)–Pd(1)–Cl(1)	168.79(7)	C(24)–N(2)–Pd(1)	136.2(2)
N(2)–Pd(1)–Cl(1)	97.20(6)	C(17)–N(2)–Pd(1)	104.00(17)
C(8)–N(1)–C(15)	120.7(2)	C(3)–C(2)–C(7)	119.9(3)



Scheme 2. The Heck coupling reactions studied in this investigation.

acrylate. All four catalysts achieved about 70% conversion of iodobenzene after 1 h and 90% conversion after 8 h (Table 3, entry 1–8). However, the activity trend of these catalysts in the arylation reaction of butyl acrylate was slightly lower. In these reactions about 55% conversion was achieved after 1 h; increasing up to 75–80% conversion after 8 h (Table 3, entries 9–16). This observation highlights that the initial rates are faster with methyl acrylate compared to butyl acrylate.

The similarity in catalytic activities of our catalysts for a particular alkene is not surprising, since the structures of these catalyst precursors are similar. It is also well established that in using preformed palladium complexes as Heck coupling catalysts the palladium complex is first reduced from Pd(II) to Pd(0); thereafter the ligand in the complex plays the role of stabilizing the Pd(0) species, which then acts as the active catalyst in the reaction [17]. Even in so-called ligand-free catalysts described by de Vries [6], the initial palladium colloids formed are stabilized by acetate ions before the aryl halide used in the coupling reaction oxidatively adds to the colloids.

It is noteworthy that the activity of our catalyst precursors are slightly higher compared to the α-diimine palladium complexes utilized in the Heck coupling reaction of 1-bromo-4-methylbenzene with methyl acrylate by Grasa et al. [8b] using a 1,4-dicyclohexyl-diazabutadiene (DAB-Cy) catalyst precursor at a higher temperature of 100 °C. The 58% conversion achieved after 6 h with the DAB-Cy catalyst precursor is lower compared to the 80% conversion achieved with our diimine ligand complexes at 80 °C. As shown graphically in Figs. 4 and 5, the catalysts are active for approximately 1 h, after which they lose much of their activity. However, very little palladium black formation – a process usually associated with catalyst deactivation in Heck catalysis, was observed to accompany the loss of activity.

Table 3
Heck coupling data using complexes **1–4** and reaction times of 1 and 8 h[a]

Catalyst	Alkene	Conversion (%)[b] 1 h	Conversion (%)[b] 8 h
1	Methyl acrylate	74	88
2	Methyl acrylate	71	87
3	Methyl acrylate	69	88
4	Methyl acrylate	72	86
Average	Methyl acrylate	71	87
1	Butyl acrylate	71	81
2	Butyl acrylate	55	79
3	Butyl acrylate	57	82
4	Butyl acrylate	53	76
Average	Butyl acrylate	59	80

[a] Amounts: PhI, 15 mmol; methyl acrylate or butyl acrylate, 15 mmol; Et_3N, 15 mmol; catalyst, 0.15 mmol; solvent = CH_3CN, 30 mL; temperature, 80 °C.
[b] Determined by GC.

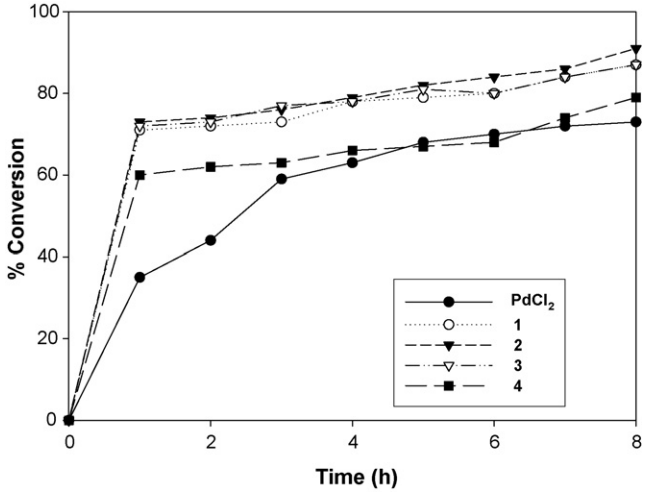


Fig. 4. Conversion as a function of time for the arylation of methyl acrylate with iodobenzene at 80 °C.

To investigate the effect of temperature and solvent on the catalytic activities of all four catalysts precursors, the Heck reactions were performed at 120 °C (Table 4). As expected, the higher reaction temperature led to an increase in conversion rate after 1 h of reaction time (Table 4, entries 1–16). Heck coupling reactions are generally performed between 120–140 °C, precisely due to the improvement in the initiation rates and

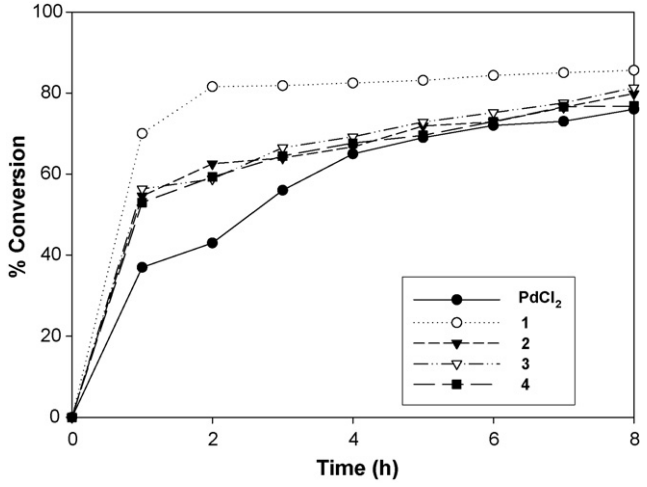


Fig. 5. Conversion as a function of time for the arylation of butyl acrylate with iodobenzene at 80 °C.

Table 4
Heck coupling data using complexes **1**–**4** at 120 °C for 1 h[a]

Catalyst	Alkene	Conversion (%)[b] DMA	Conversion (%)[b] DMF
1	Methyl acrylate	93	91
2	Methyl acrylate	89	93
3	Methyl acrylate	94	92
4	Methyl acrylate	91	88
Average	Methyl acrylate	92	91
1	Butyl acrylate	90	95
2	Butyl acrylate	87	92
3	Butyl acrylate	93	94
4	Butyl acrylate	90	91
Average	Butyl acrylate	90	93

[a] Amounts: PhI, 15 mmol; methyl acrylate or butyl acrylate, 15 mmol; Et_3N, 15 mmol; catalyst, 0.15 mmol.
[b] Determined by GC.

reduction of the catalyst precursors to Pd(0). No dependence of catalytic activity on the solvent used (DMA or DMF) was observed.

4. Conclusions

The unconjugated diimine complexes have been shown to be active catalysts for the Heck coupling of iodobenzene and methyl acrylate or butyl acrylate at temperatures much lower than the traditional temperatures used for conventional palladium-catalyzed Heck reactions. Conversions were found to be quite good within the first hour of the reaction, which makes these unconjugated palladium complexes attractive catalysts in comparison to the more expensive phosphine-based catalysts. The higher catalytic activities of complexes **1**–**4** compared to $PdCl_2$ suggest that the diimine ligands used effectively stabilize the Pd(0) colloids that act as the active catalytic sites in the Heck reaction.

Supplementary material

CCDC 666494 and 666495 contains the supplementary crystallographic data for **3a** and **4**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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