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Palladium-catalyzed seven-membered N,O-heterocycle ring formation [1]

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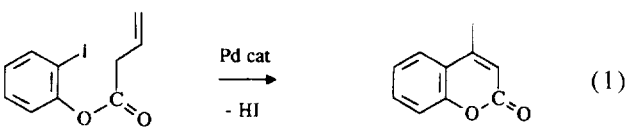
Abstract

3-Methyl-5-methylene-1,3-benzoxazepin-2-one (**3**) has been prepared starting from *o*-iodophenyl *N*-allyl-*N*-methylcarbamate in the presence of tetrakis(triphenylphosphine) palladium(0) as catalyst. The X-ray structure of the intermediate palladium complex (**2**), resulting from oxidative addition of the aromatic iodide to palladium, is reported. It consists of a square planar arrangement of aryl, iodide and two mutually *cis* triphenylphosphine ligands. The double bond being not coordinated to palladium, its insertion to generate the seven-membered ring almost quantitatively requires the use of thallium acetate in dimethylacetamide, otherwise intermolecular reactions predominate, leading to carbon–carbon bond formation between the aryl and double bond carbon of two and three substrate molecules, respectively, with formation, in the latter case, of a 24-membered ring. © 1998 Elsevier Science S.A.

Keywords: Palladium complexes; Carbamate complexes; Crystal structures; N,O-heterocycles

1. Introduction

During the past years the use of transition metal complexes to effect ring closure of substituted aromatics to condensed aromatic or heterocyclic compounds has attracted the attention of several research groups [1]. Several syntheses of five- and six-membered heterocycles based on the use of palladium complexes as catalysts [1–4] have been reported. In particular some years ago we described the utilization of *ortho*-iodophenol in a palladium-catalyzed reaction with norbornadiene and carbon monoxide leading to coumarin [2]. More recently we also achieved the synthesis of 4-methylcoumarin [3c] according to Eq. (1):



(1)

The methods followed to effect the latter reaction [3e] were based on the use of: (i) anisole as solvent and potassium acetate as base; (ii) anisole and silver acetate; (iii) dimethylformamide (DMF) and magnesium oxide. Methods (ii) and (iii) gave practically quantitative yields while method (i) did not suppress competitive reactions originating from double bond isomerization and allylpalladium bond formation.

We then addressed our efforts towards seven-membered nitrogen heterocycles [5] also in view of the pharmaceutical interest of many members of this class such as benzazepines [6]. To this aim we started from a new material, the *N*-allyl-*N*-methyl carbamate of *ortho*-iodophenol (**1**) which could lend itself to the application of the methods utilized by us for the synthesis of 4-methylcoumarin.

2. Results and discussion

2.1. Synthesis

When applied to substrate **1** all the three methods mentioned above failed to give satisfactory yields. Indeed the reaction, carried out at 80°C for 24 h in the presence of $Pd(PPh_3)_4$ (5% in respect to the substrate), proceeded according to Eqs. (2)–(5).

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[1] Dedicated to Professor Jack Halpern in recognition of his outstanding contribution to organometallic chemistry.

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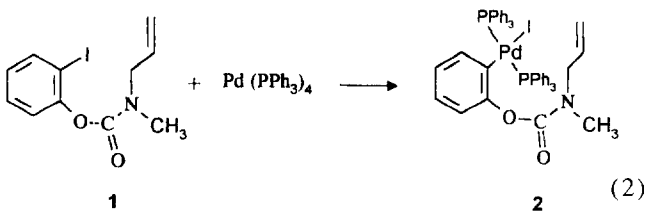

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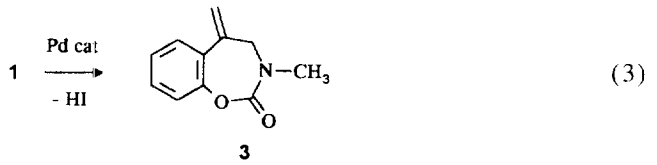

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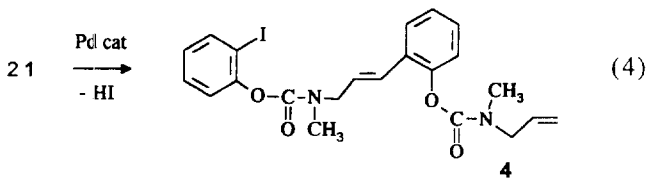

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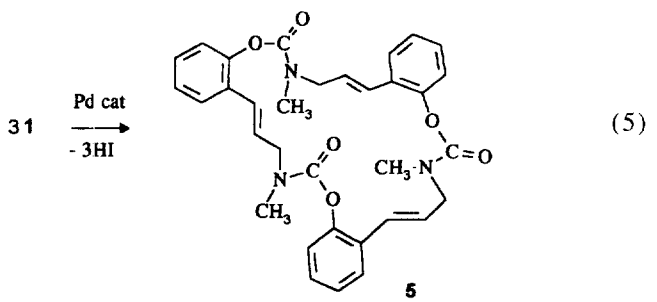


(5)

With method (i) the yield of **3** was lower than 5% and conversion was low too; with method (ii) the yield was 10% in the presence of one mole of silver acetate per mole of substrate and 20% with two mole at complete conversion; correspondingly products **4** (13 and 15%) and **5** (35 and 27%) were obtained (isolated yields); with method (iii) the yield of **3** was 5% at 45% conversion. Interestingly, the last method led to the formation of complex **2** in substantial amounts. Besides isolating this complex and submitting the sample to X-ray analysis we also prepared it starting from the substrate and $Pd_2(dba)_3 \cdot CHCl_3$ in THF (see Section 3).

Complex **2** as well as the organic compounds here described are characterized by hindered rotation about the carbamic group, which is revealed in the NMR spectra by broadening and an increased number of signals. Compounds **4** and **5** possess *trans* double bonds as confirmed by the NMR coupling constant of the vinylic protons. Compound **5** turns out to be fluxional even at −60°C.

2.2. Structural description of complex 2

The structure is represented in Fig. 1.

Atomic coordinates are given in Table 1 while Table 2 lists selected bond lengths and interbond angles within the complex. The Pd atom shows a distorted planar square conformation (max. deviation from the plane 0.67(1) Å at C61). The significant deviation from planarity is due to the steric hindrance of the bulky ligands at the palladium atom.

Bond distances and angles of the two triphenylphosphine groups are in the normal range and their reciprocal orientation

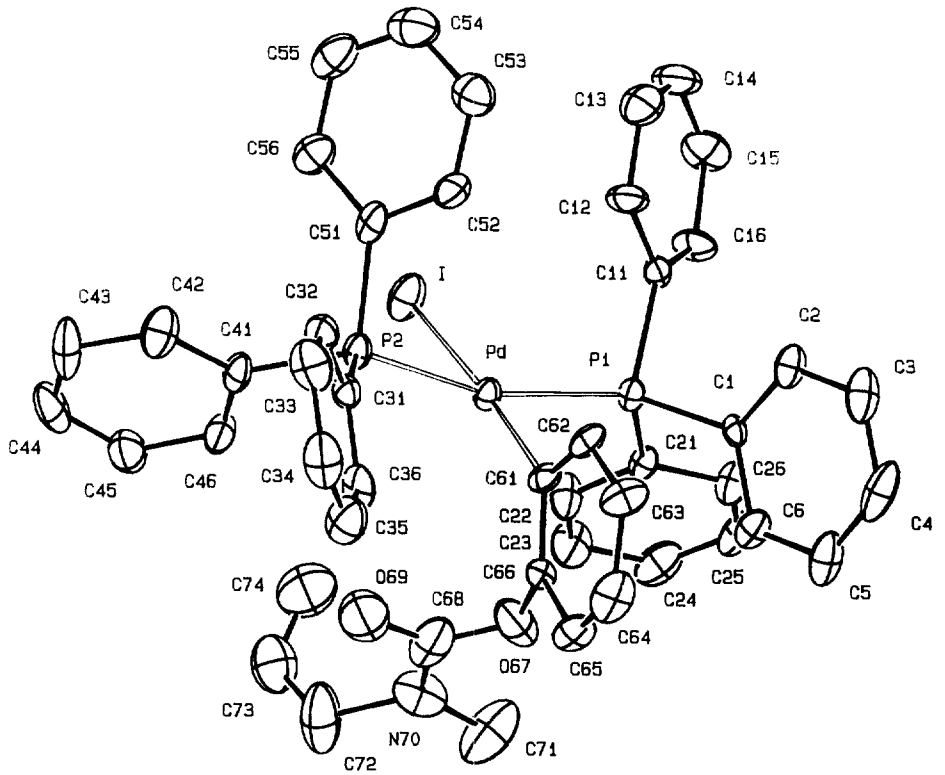


Fig. 1. Projection of complex **2** with arbitrary numbering, showing 30% probability displacement of ellipsoids. Hydrogen atoms were omitted for clarity.

Table 1
Fractional atomic coordinates ($\times 10^4$) and U_{eq} ($\times 10^4$ Å^2) for complex **2**

	x/a	y/b	z/c	U_{eq}
I1	3839(1)	4629(1)	8021(1)	571(3)
Pd2	4855(1)	5021(1)	7347(1)	312(2)
P1	4940(1)	3123(1)	7159(1)	300(7)
P2	4458(1)	6899(2)	7229(1)	346(9)
C1	5414(4)	2740(5)	6535(4)	282(32)
C2	5000(6)	2582(7)	5840(5)	464(47)
C3	5369(7)	2398(7)	5362(5)	603(52)
C4	6177(8)	2369(8)	5588(7)	747(64)
C5	6624(7)	2528(7)	6281(6)	595(53)
C6	6247(5)	2722(7)	6758(5)	465(44)
C11	3943(4)	2592(6)	6765(4)	297(30)
C12	3386(5)	3307(8)	6308(5)	505(41)
C13	2617(7)	2961(10)	6021(6)	670(54)
C14	2365(6)	1985(11)	6218(6)	695(56)
C15	2910(6)	1303(9)	6661(6)	661(51)
C16	3687(6)	1606(8)	6945(6)	491(45)
C21	5402(4)	2223(6)	7903(4)	320(32)
C22	5542(5)	2571(9)	8573(5)	516(46)
C23	5855(6)	1901(10)	9153(5)	646(50)
C24	6068(6)	837(9)	9064(7)	661(51)
C25	5951(5)	457(9)	8414(6)	600(51)
C26	5622(5)	1138(7)	7820(5)	495(43)
C31	4895(5)	7935(6)	6818(4)	384(34)
C32	4465(5)	8706(7)	6322(5)	465(37)
C33	4809(7)	9499(8)	6037(5)	645(49)
C34	5606(7)	9537(9)	6271(6)	689(60)
C35	6052(8)	8829(9)	6742(7)	697(60)
C36	5706(6)	8025(7)	7017(6)	509(45)
C41	4454(5)	7659(6)	8000(5)	412(41)
C42	4085(6)	8670(7)	7942(6)	630(50)
C43	4083(8)	9281(9)	8519(7)	758(61)
C44	4477(7)	8888(11)	9160(7)	729(60)
C45	4874(6)	7903(10)	9240(6)	630(46)
C46	4857(6)	7289(9)	8659(5)	561(50)
C51	3451(5)	6827(6)	6630(5)	423(38)
C52	3328(6)	6438(7)	5959(5)	516(45)
C53	2581(7)	6264(8)	5481(6)	631(53)
C54	1936(8)	6484(9)	5668(8)	802(61)
C55	2038(7)	6868(8)	6311(8)	711(64)
C56	2797(6)	7029(8)	6797(6)	553(50)
C61	5700(4)	5319(5)	6911(4)	341(30)
C62	5524(5)	5506(6)	6212(5)	393(33)
C63	6098(6)	5741(8)	5919(6)	577(45)
C64	6884(6)	5801(8)	6387(5)	624(51)
C65	7060(6)	5578(7)	7059(6)	515(43)
C66	6475(4)	5337(5)	7316(3)	258(27)
O67	6754(4)	4896(6)	8047(3)	766(33)
C68	6804(6)	5534(9)	8544(8)	930(69)
O69	6567(4)	6520(7)	8462(4)	980(43)
N70	7136(5)	5038(8)	9187(4)	681(36)
C71	7467(10)	3994(14)	9335(8)	1072(93)
C72	7204(11)	5781(12)	9780(9)	1086(120)
C73	6629(10)	5563(11)	10172(8)	903(79)
C74	6031(9)	5007(12)	9926(9)	1050(86)

Table 2
Selected bond distances (Å) and angles (°) for complex **2**

I1–Pd2	2.687(1)	C66–O67	1.492(9)
Pd2–P1	2.321(2)	O67–C68	1.246(17)
Pd2–P2	2.351(2)	C68–O69	1.249(14)
Pd2–C61	2.044(9)	C68–N70	1.372(16)
P1–C1	1.819(9)	N70–C71	1.375(19)
P1–C11	1.817(7)	N70–C72	1.471(20)
P1–C21	1.811(7)	C72–C73	1.537(30)
P2–C31	1.822(9)	C73–C74	1.221(22)
P2–C41	1.817(10)		
P2–C51	1.810(8)		

is influenced by the presence both of iodine and of the carbamate groups in such a way that the aromatic rings overlap if viewed along the P1···P2 direction. There is no indication of any π–π interaction between pairs of benzene rings and their orientation seem to be determined totally by the need of minimizing steric interactions.

The normal to the plane of the aromatic ring of the carbamate moiety is rotated in such a manner to be practically parallel to the P1···P2 direction. In the aliphatic chain a π delocalization was found in the bonds involving the C68 atom. The apparent shortening of the C73=C74 bond distance with respect to the normal value is likely to depend on the stronger thermal motion of the atoms involved.

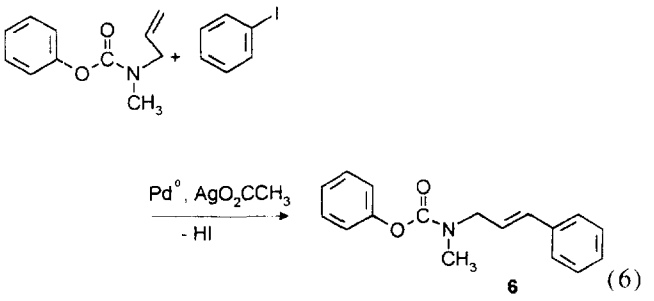
The packing of the molecules in the complex is mainly determined by van der Waals interactions and the shortest intermolecular contact involves the O69 carbonyl atom: O69···H5^i = 2.50(9) Å, O69···H5–C5 = 143(6)°, i = 3/2 − x, y − 1/2, 3/2 − z.

The most interesting feature turns out to be the spatial arrangement of the carbamic chain which is not coordinated to palladium and shows a rather rigid conformation around the carbamic group. This accounts for its reluctancy to coordinate even in the subsequent reaction steps. In fact it has to be recalled that the substrate used in Eq. (1) for the synthesis of 4-methylcoumarin also gave a complex which in the NMR did not show coordination of the double bond [3c]: the latter, however, must coordinate in a subsequent step (after removal of the iodide ligand by silver acetate or magnesium oxide) to give the product in quantitative yield. Non-coordination of the double bond was also observed by Brown et al. [7] in a similar case.

2.3. Promotion of reactivity

In the present case both silver acetate and magnesium oxide turn out not to be able to push the reaction towards the desired product. Although there is an intrinsic difficulty in forming a seven-membered ring in place of the six-membered coumarinic one, there must be other reasons for the failure of methods (ii) and (iii). In the case of silver acetate we suspected that coordination with the *N*-allyl group of the substrate should render the ring closure more difficult in favor of an intermolecular reaction. In fact even the use of more than two mole of silver acetate per mole of substrate did not improve the yield of **3** significantly, thus the intermolecular reactions leading to **4** and **5** must be strongly favored by coordination of the *N*-allylcarbamate to silver. As a matter of fact both olefins and nitrogen compounds are known to give complexes with

silver salts [8]. To get further information on this point we caused iodobenzene to react with the allylcarbamate of phenol in the presence of palladium and either silver acetate or potassium acetate in anisole: in the former case we observed a satisfactory Heck-type reaction [9] (Eq. (6)) while in the latter one very poor results were obtained.



(6)

We thus reasoned that if we replaced silver acetate with a salt of a metal not displaying special affinity for unsaturated nitrogen compounds we could obtain the desired reaction in an acceptable yield. A salt of this type had largely been used in place of silver acetate to promote Heck-type reactions with similar results: this is thallium acetate [10]. Complex **2** in 1:1.4 ratio with the thallium salt in dimethylacetamide (DMA) at 80°C decomposed to **3** almost quantitatively. On the other hand, the use of silver acetate in place of thallium acetate under the same conditions gave mainly product **5** (25%) along with **3** (20%) and unconverted complex. In consideration of these results a catalytic reaction was performed using complex **2** as catalyst in 1 to 10 molar ratio to the substrate: almost complete conversion and quantitative yields of **3** were obtained.

Thallium and silver acetates behave similarly in the case of reaction (6), where competition with the intramolecular reaction does not exist: the same product **6** was obtained in ~50% yield after 5 h at 80°C in DMA.

Although no detailed mechanistic study has been carried out so far, on the basis of the results reported above the reaction can be seen as proceeding through dissociation [11], promoted by thallium acetate according to Scheme 1.

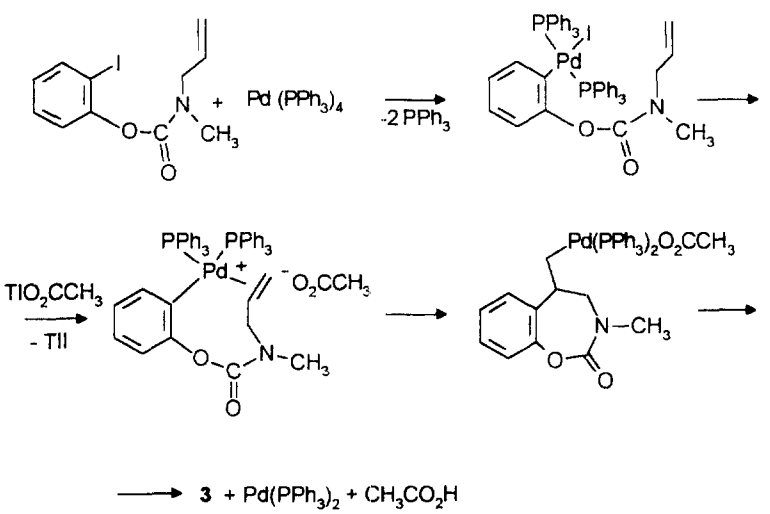
After dissociation the double bond becomes able to coordinate. Ring closure by double bond insertion is favored by the cationic complex [12]. Reduction by β-hydrogen elimination leads to **3** and palladium(0).

Scheme 1 can also explain the difficulty encountered with magnesium oxide in DMF or DMA (method iii) to push the reaction beyond the stage of complex **2**. For sake of comparison we repeated the experiment using the 3:1 substrate to palladium ratio used with thallium. Complex **2** was formed in 75% yield in respect to palladium, while compound **3** was present to the extent of 3% along with unconverted substrate. Magnesium oxide thus appears to be not sufficient to cause the required dissociation, which is best effected by thallium acetate.

3. Experimental

3.1. Materials and measurements

Starting materials were commercial products (Inalco and C. Erba) and were used without further purification except for thallium acetate which was dissolved in acetic acid and precipitated with hexane. $Pd(PPh_3)_4$ [13] and $Pd_2(dba)_3 \cdot CHCl_3$ (dba = *E,E*-dibenzylideneacetone) [14] were prepared according to the literature. Anisole, CH_2Cl_2, DMF and DMA were dried over 4 Å molecular sieves; THF was purified by distillation from sodium/benzophenone and used immediately. All reactions were carried out under nitrogen using Schlenk techniques. Pure products were isolated by flash chromatography on silica gel column (ICN Silica 32-63, 60 A) using hexane–ethyl acetate mixtures as eluent. GC analyses were performed with a C. Erba HRGC 5300 instrument fitted with a 30m SE-30 capillary column. Melting points were determined with an Electrothermal apparatus and are uncorrected. ^1H NMR spectra were acquired using Bruker



Scheme 1. Ring closure by double bond insertion into the arylpalladium bond of complex **2**.

AMX-400 and AC-300 spectrometers in $CDCl_3$ as solvent and with TMS as internal standard at 20°C; ^{13}C NMR spectra were run on Bruker AC-300 at 75.4 MHz. Owing to hindered rotation about the carbamic group the class of compounds described here exhibits signals which do not correspond to a single conformation. For this reason frequencies are indicated as double signals or intervals where appropriate. IR spectra were obtained with a Nicolet 5PC FT-IR spectrophotometer. Mass spectra (m/z, relative intensity (%)) were performed with a Finnigan Mat SSQ 710 instrument working at 70 eV ionization energy.

3.1.1. Preparation of o-iodophenyl N-allyl-N-methylcarbamate (1)

The compound was obtained by modification of the procedures reported in the literature [15]. Into a 50 ml Schlenk-type flask equipped with a magnetic stirring bar triphosgene (353 mg, 1.19 mmol) was introduced under nitrogen and dissolved in CH_2Cl_2 (2 ml). Diisopropylethylamine (DIEA, 448 mg, 3.47 mmol) and *N*-allyl-*N*-methylamine (249 mg, 3.51 mmol) in CH_2Cl_2 (2.5 ml) were slowly added under stirring over ~30 min using a dropping funnel. Stirring was continued for a further 15 min, then a CH_2Cl_2 solution (2.5 ml) of *o*-iodophenol (769 mg, 3.49 mmol) and DIEA (450 mg, 3.49 mmol) was added. The resulting solution was stirred at 40°C for 72 h under nitrogen. After conventional work-up, pure *o*-iodophenyl *N*-allyl-*N*-methylcarbamate (**1**) (517 mg, 46%) was obtained as a colorless viscous oil by silica gel flash chromatography using hexane–ethyl acetate 95:5 as eluent. *o*-Iodophenol (323 mg, 42%) was also recovered.

^1H NMR (300 MHz): $\delta = 7.80, 7.79$ (1H, 2d, $J = 7.9$ Hz, H3), 7.34 (1H, m, H5), 7.18 (1H, m, H6), 6.94 (1H, m, H4), 5.90 (1H, m, =CH), 5.27 (2H, m, $=CH_2$), 4.12, 4.00 (2H, 2d, CH_2), 3.14, 3.00 (3H, 2s, N–CH_3). IR (neat): $\nu = 1726$, 1653, 990, 915 cm^{-1}. MS (EI): M^+ 317 (10) m/z 220 (15), 190 (90), 98 (100).

3.1.2. Preparation of phenyl N-allyl-N-methylcarbamate

The compound was obtained analogously to **1** by adding DIEA (382 mg, 3.03 mmol) and phenol (293 mg, 3.11 mmol) in CH_2Cl_2 (2 ml) to a CH_2Cl_2 (2 ml) solution of triphosgene (295 mg, 0.99 mmol). After 15 min stirring *N*-allyl-*N*-methylamine (221 mg, 3.12 mmol) and DIEA (391 mg, 3.1 mmol) dissolved in CH_2Cl_2 (2 ml) were added and the resulting mixture was allowed to react for 24 h at room temperature. After work-up and purification phenyl-*N*-allyl-*N*-methylcarbamate was obtained as a colorless oil (344 mg, 58%). Phenol (120 mg, 1.27 mmol, 41%) was also recovered.

^1H NMR (300 MHz): $\delta = 7.36$ (2H, m, H3, H5), 7.19 (1H, tt, $J = 7.3$, 1.1 Hz, H4), 7.15 (2H, m, H2, H6), 5.84 (1H, m, =CH), 5.27, 5.22 (2H, m, $=CH_2$), 4.04, 3.98 (2H, 2d, CH_2), 3.05, 2.99 (3H, 2s, CH_3). IR (neat): $\nu = 1723$, 1646, 990, 915 cm^{-1}. MS (EI): M^+ 191 (8) m/z 98 (49), 77 (41), 65 (62), 51 (21), 41 (100).

3.2. Synthesis of trans-$PdIC_6H_4OCON(CH_3)$-$CH_2CH=CH_2(PPh_3)_2$ (2)

$Pd(PPh_3)_4$ (81 mg, 0.07 mmol) and MgO (4 mg, 0.1 mmol) were introduced into a Schlenk-type flask under nitrogen and a DMF solution (5 ml) of **1** (57 mg, 0.18 mmol) was then added. The mixture was heated in an oil bath at 80°C for 24 h. After conventional work-up the crude was purified by flash chromatography using hexane–ethyl acetate 7:3 as eluent. Complex **2** (50 mg, 75%) was obtained as a white solid which gave prismatic crystals suitable for X-ray analysis by recrystallization in acetone. Compound **3** was also isolated (4 mg, 11% on **1**). Alternatively complex **2** was prepared according to the method reported by Novak and coworkers [16]: $Pd_2(dba)_3 \cdot CHCl_3$ (83 mg, 0.08 mmol) was dissolved in THF (5 ml) under nitrogen and cooled at −30°C. Triphenylphosphine (92 mg, 0.35 mmol) and compound **1** (55 mg, 0.17 mmol) dissolved in THF (2 ml and 3 ml, respectively) and cooled at −30°C were then added. The reaction mixture was allowed to reach room temperature and stirred until the dark color changed to yellow (~30 min). The solvent was removed under reduced pressure and the resulting solid was washed several times with diethyl ether to obtain a white solid which was dried under vacuum (65 mg, 43%).

The complex decomposes under N_2 at 142–143°C. ^1H NMR (400 MHz): $\delta = 7.60$–7.49 (12H, m, *ortho* protons PPh_3), 7.30 (6H, brt, *para* protons PPh_3), 7.26–1.80 (12H, m, *meta* protons PPh_3), 6.50–6.25 (3H, m), 5.94 (1H, m), 5.80 (1H, m, =CH), 5.18 (2H, m, $=CH_2$), 4.10, 3.69 (2H, 2d, CH_2), 3.04, 2.68 (3H, 2s, NCH_3). IR (KBr): $\nu = 1714$, 1655, 990, 915 cm^{-1}.

3.3. Synthesis of compounds 3, 4 and 5

To complex **2** (12 mg, 0.012 mmol) and TlOAc (58 mg, 0.22 mmol) a DMA solution (3.0 ml) of compound **1** (51 mg, 0.16 mmol) was added under nitrogen. The resulting mixture was stirred in an oil bath at 80°C for 12 h. After conventional work-up the crude was purified by flash column chromatography using a 7:3 mixture of hexane–ethyl acetate as eluent. 3-Methyl-5-methylene-1,3-benzoxazepin-2-one (**3**) was isolated in 87% yield (27 mg). No by-product was found except for traces of compound **5**.

When a catalytic reaction ($Pd(PPh_3)_4$:substrate 1/20) was carried out under the same conditions but in the presence of AgOAc as base and in anisole as solvent compounds **3**, **4** and **5** were obtained in 20, 15 and 27% isolated yield, respectively, after separation as above.

3-Methyl-5-methylene-1,3-benzoxazepin-2-one (**3**): m.p. (CH_2Cl_2–hexane 8:2) 130°C (dec.). ^1H NMR: $\delta = 7.65$ (1H, dd, $J = 8.0$, 1.7 Hz, H6), 7.30 (H, ddd, H8), 7.23 (1H, dd, $J = 8.1$, 1.7 Hz, H9), 7.15 (1H, ddd, H7), 5.66 (1H, s, =CH *syn* to the aromatic ring), 5.10 (1H, t, $J = 1.0$ Hz, =CH *anti* to the aromatic ring), 4.14 (2H, m, CH_2), 3.05 (3H, s, NCH_3). ^{13}C NMR: δ 150.8, 130.1, 126.2, 125.0, 122.7, 111.6,

55.0, 35.2. IR (KBr): $\nu = 1734, 1644\ cm^{-1}$. MS (CI, CH_4): M^+ 192 (100) m/z 133 (11), 131 (16), 98 (9), 57 (7).

o-Iodophenyl *N*-methyl-*N*-3-(2-*N*-methyl-*N*-prop-2-enylcarbamoyloxy)phenylprop-2-enyl carbamate (**4**): viscous oil. ^1H NMR (400 MHz, protons of the vinyl-substituted aryl group are marked by an apex): $\delta = 7.80$ (1H, d, $J = 7.8$ Hz, H6), 7.54 (1H, m, H3'), 7.34 (1H, m, H5), 7.27 (1H, m, H5'), 7.23–7.18 (2H, m, H3, H4'), 7.10 (1H, m, H6'), 6.95 (1H, t, H4), 6.69 (1H, d, $J = 15.8$ Hz, =CHAr), 6.32, 6.23 (1H, 2dt (one sharp with $J = 15.8$, 6.0 Hz and the other one broad) CH=*CH*CH_2N), 5.84 (1H, m, *CH*=CH_2), 5.22 (2H, m, =CH_2), 4.28, 4.20 (2H, 2 br signals, *CH*$_2$CH=CH), 4.07, 3.96 (2H, 2 br signals, *CH*$_2$CH=CH_2), 3.13, 3.04 (3H, brs, *CH*$_3$NCH$_2$CH=CH_2), 3.08, 2.97 (3H, *CH*$_3$NCH$_2$CH=CH). IR (neat): $\nu = 1718$, 1663, 990, 975, 915 cm^{-1}. MS (CI, CH_4): $(M+1)^+$ 507 (5) m/z 378 (100), 322 (95), 230 (95), 190 (25).

N-Methyl-*N*-3-(*o*-oxyphenyl)prop-2-enylcarbamoyl cyclic trimer (**5**): m.p. (hexane–CH_2Cl_2) 161–162°C. ^1H NMR (300 MHz): $\delta = 7.57, 7.49, 7.42$ (3H, 3dd), 7.33–7.20 (6H, m), 7.17, 7.08, 7.01 (3H, 3m), 6.68, 6.47 (3H, 2 complex signals with $J \sim 16$ Hz), 6.30–6.12 (2H, m), 4.81 (1H, 2 partly overlapping dt, $J \sim 17.0$, 2.0 Hz), 4.23, 3.84, 3.79, 3.55, 3.48 (6H, dd), 3.18, 3.06, 3.03 (9H, brs). IR (KBr): $\nu = 1718$, 1653, 967 (broad) cm^{-1}. MS (CI, CH_4): $(M+1)^+$ 568 (30) m/z 507 (5), 378 (100), 321 (45), 230 (25), 190 (15).

3.4. Synthesis of phenyl N-methyl-N-3-phenylprop-2-enylcarbamate (6)

An anisole solution (5 ml) of iodobenzene (92 mg, 0.45 mmol) and phenyl *N*-allyl-*N*-methylcarbamate (86 mg, 0.45 mmol) was added under nitrogen to $Pd(PPh_3)_4$ (52.1 mg, 0.045 mmol) and AgOAc (87 mg, 0.52 mmol). The mixture was heated in an oil bath at 80°C for 5 h. After work-up and separation by flash chromatography using a 8:2 mixture of hexane–ethyl acetate phenyl *N*-allyl-*N*-3-phenylprop-2-enylcarbamate (55 mg, 46%) was isolated together with unreacted carbamate (11 mg, 13%). ^1H NMR (300 MHz): $\delta = 7.50$–7.10 (10H, m, aromatic protons), 6.59 (1H, d, $J = 15.9$ Hz, =CHPh), 6.26 (1H, m, =*CH*CH_2), 4.21, 4.15 (2H, 2brd, CH_2), 3.11, 3.06 (3H, 2s, CH_3). IR (neat): $\nu = 1718$, 1646, 990, 915 cm^{-1}. MS (EI): $M+267$ (3) m/z 117 (100), 115 (21), 91 (12).

3.4.1. Crystal structure of 2

The intensity data were collected on a Philips PW1100 single crystal diffractometer equipped with a PC and a new system of programs [17] using Mo Kα radiation ($\lambda = 0.71069$ Å). A prismatic crystal of $0.11 \times 0.19 \times 0.21$ mm was employed. Crystal data: $C_{47}H_{42}INO_2P_2Pd$, $M_r = 948.11$, monoclinic, $P2_1/n$, $a = 18.084(2)$, $b = 11.993(3)$, $c = 20.337(3)$ Å, $\beta = 110.18(4)°$, $Z = 4$, $D_c = 1.52$ g cm^{-3}, $V = 4139.96$ Å^3, $\mu = 12.93$ cm^{-1}, $F(000) = 1904$. Cell dimensions were determined from goniometer accurate setting of 24 reflections. A total of 8998 reflections, $\pm h$, $+k$, $+l$, was measured in the θ range 3–27° and 3115 were considered observed having $I \geq 2\sigma(I)$. A standard reflection, measured every 100, did not show indications of decomposition or misalignment. The experimental data were corrected for Lorentz and polarization effects. The structure was solved by direct methods through SIR92 program [18] and refined by full-matrix least-squares using SHELX92 program [19] with anisotropic thermal parameters of heavy atoms. All hydrogens were found in a ΔF map and refined isotropically. A total of 656 parameters was refined and the final R agreement factor was 0.045. The wR_2 value for all the reflections was 0.138 with $w = 1/[\sigma^2 F_o^2 + (0.0744P)^2 + P]$ with $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The atomic scattering factors are those of SHELX92.

4. Supplementary material

Atomic fractional coordinates ($\times 10^3$) for hydrogen atoms and U_{iso} ($\times 10^4$ Å^2), thermal parameters ($\times 10$ Å) for heavy atoms and bond distances (Å) for hydrogen atoms of complex **2** are available from the authors on request.

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