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Orthopalladacycles derived from α-diphenylhydrazonoketene dithioacetals and their reactivity with terminal alkynes

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Abstract

In this paper, we present the synthesis and characterization of new orthopalladated complexes derived from α-diphenylhydrazonoketene dithioacetals. From their reaction with terminal alkynes, the intermediates of the expected C_{sp}–C_{sp2}coupling reaction were isolated in stable form and their structures were confirmed by X-ray diffraction studies.

Keywords: Alkynes; Palladium complex; X-ray diffraction

1. Introduction

The formation and characterization of cyclopalladated compounds have been of great interest for the last decade [1] due to the great variety of applications in organic and organometallic areas [2], i.e., in coupling and insertion reactions [3,4] (the cyclopalladated complexes show an enhanced reactivity towards alkynes to give mono, bis or tris insertion reactions, according to the complex structure [3a–c]), for enantiomeric excess determination [5], formation of new mesogenic compounds [4], as asymmetric catalysts and more recently in polymerization reactions [6]. Furthermore, they have also been used in supramolecular chemistry [7] and several of them have biological activity [8].

An interesting synthetic route to cyclopalladated compounds occurs when tridentate ligands, such as semicarbazones [9], hydrazones [10], thiosemicarbazones [11,12] or Schiff bases [13,14] are used. These ligands react with palladium (II) to form cyclopalladated complexes having a characteristic structural moiety that is a five-five membered heterocyclic fused ring system.

Recently, we reported the syntheses of several cyclopalladated complexes derived from diphenylhydrazones and their transmetallation reaction [10a], Scheme 1. These cyclopalladated complexes have shown excellent catalytic activity for ethylene polymerization [15].

In this paper, we present the synthesis, characterization and reactivity with terminal alkynes of new orthopalladated complexes derived from α-diphenylhydrazonoketene dithioacetals.

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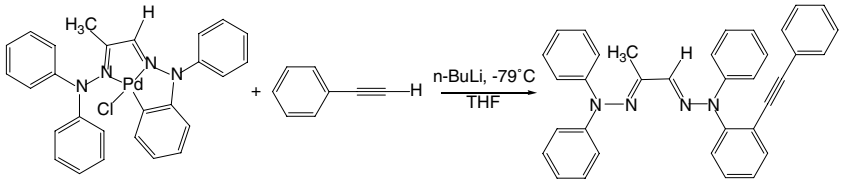


Scheme 1.

2. Discussion and results

The α-diphenylhydrazonoketene dithioacetals ligands **1.1** and **1.2** were prepared from *N*,*N*-diphenylhydrazine and the corresponding α-oxo ketene dithioacetal by a condensation reaction in moderate yield. These ligands react with $Na_2[PdCl_4]$ [16], to achieve orthopalladated complexes **2.1** and **2.2**, Scheme 2.

The infrared spectra of **2.1** and **2.2** show an absorption band in 1588 cm^{-1}, which is assigned to the vibration of the C=N bond. We were surprised to find that this band is no different than the one observed for the free ligands.

In the MS-FAB$^+$ spectra, we found the corresponding molecular ion for **2.1** and **2.2** in 470 *m*/*z* and 469 *m*/*z*, respectively.

The data obtained for ^1H and ^{13}C NMR for **2.1** and **2.2** are presented in Table 1. In ^1H NMR spectra, we observe the typical substitution patterns of a 1,2-disubstituted aromatic ring, additionally, the chemical shift of H11 at δ 7.76 is in accord with reported values for analogue our orthopalladate complexes. Similarly, the ^{13}C NMR data for these complexes also reveal the formation of the orthopalladated cycle since the signals for C7 and C11 appear at higher frequencies and the signals for C8 and C9 are presented at lower frequencies, [10,17,18].

An appropriate monocrystal of complex **2.1** was used to obtain the X-ray difractogram. An ORTEP diagram, Fig. 1, shows the molecular geometry, the thermal ellipsoids (35%) and the numbering scheme. Selected bond distances and angles are listed in Table 3. In agreement with the obtained structure for **2.1**, the ligand **1.1** acts a tridentate moiety (C, N, S), in the palladium complex, where *ortho* carbon atom of one phenyl group, one nitrogen atom and one sulfur atom are bonded to the palladium atom to give an interesting six–five–six membered tricycle. The palladium atom structure exhibits a distorted square planar geometry. These data are in accord with those reported for related compounds [11,14,19,20].

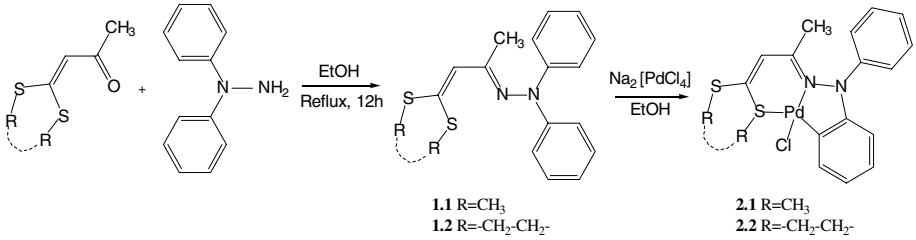
2.1. Reactivity with terminal alkynes

In accord with our previous studies [10], we expected that the orthopalladated complexes **2.1** and **2.2** would react with terminal alkynes via a transmetallation reaction to give the C_{sp}–C^2_{sp} coupling. Instead this reaction affords the unexpected new complexes **4.1** and **4.2** (Scheme 3), in which only the substitution of chlorine by the alkyne occurs. Reductive elimination does not take place.

The infrared spectra of compounds **3.1**, **4.1** and **4.2** show a typical band around 2000–2100 cm^{-1} which is assigned to the carbon–carbon triple bond stretching vibration. The ^1H and ^{13}C NMR spectra are listed in Table 4.

The structure of the complex **3.1** was confirmed by a single crystal X-ray diffraction analysis. An ORTEP diagram of **3.1** is shown in Fig. 2. The crystal data and bond distance and angles are presented in Tables 2 and 5. The metal center exhibits a square-planar coordination. The coordinated methylsulfanyl group and the aromatic ring of the phenylacetylene group are disordered (64:36) over two orientations, only the major contributors are shown in Fig. 2.

In order to demonstrate that the complexes **3.1**, **4.1** and **4.2** could be the intermediates in cross-coupling reactions to give **5.1**, **6.1** and **6.2,** respectively, via a reductive elimination (Scheme 3), we carried out different experiments in several conditions (refluxing in benzene, toluene, xylene, addition of PPh_3) recovering in all the cases the starting material. This unexpected stability in the complexes could be due to the higher *trans*

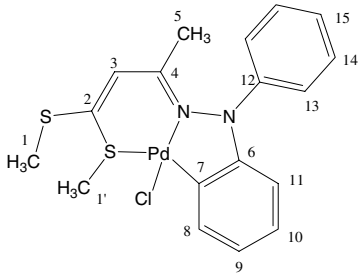


Scheme 2.

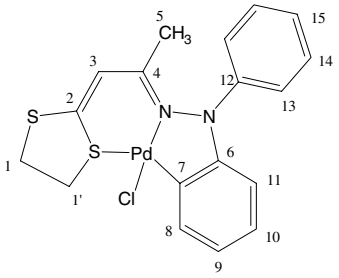
Table 1
^{1}H and ^{13}C NMR data for complexes **2.1** and **2.2**

	H1	H1′	H3	H5	H8	H9	H10	H11	H13	H14	H15
2.1	2.46 (3H,s)	3.02 (3H,s)	5.96 (1H,s)	2.16 (3H,s)	6.85 (2H,m)		6.95 (1H,td, J = 7.44, 1.35)	7.76 (1H,dd, J = 7.41, 1.11)	7.23 (2H,t, J = 7.41)	7.50 (2H, d, J = 4.40)	7.35 (1H,t, J = 7.68)
2.2	3.61 (2H,t, J = 6.06)	3.98 (2H,t, J = 6.06)	6.18 (1H,s)	2.15 (3H,s)	6.87–7.05 (3H, m)			7.53 (1H,d, J = 7.98)	7.16–7.21 (3H,m)	7.35 (2H,t, J = 7.68)	7.16–7.21 (3H,m)

	C1	C1′	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15
2.1	17.6	21.7	154.2	123.4	161.0	27.2	144.6	150.1	113.3	125.9	125.9	134.8	142.9	127.0	125.0	129.7
2.2	37.2	41.5	–	123.2	162.8	24.2	145.1	153.0	113.7	126.0	126.0	134.5	–	126.5	124.3	129.7



2.1



2.2

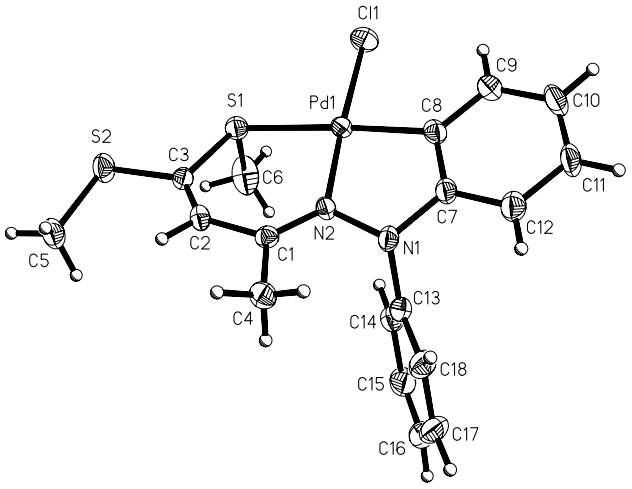
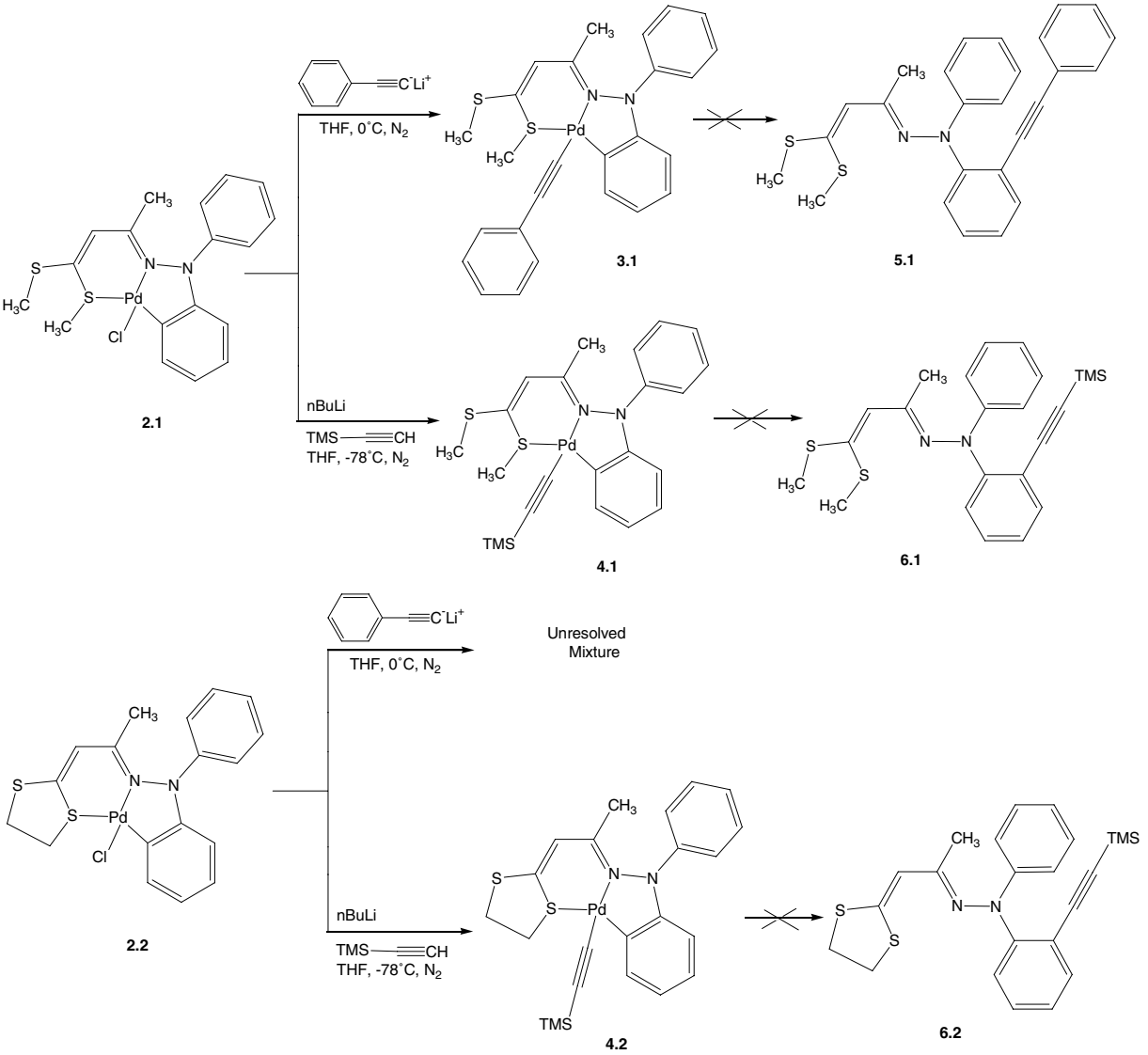


Fig. 1.

influence of nitrogen and sulfur atoms over carbon atoms.

2.2. Conclusion

New mononuclear orthopalladated complexes were synthesized by using tridentate ligands containing carbon, nitrogen and sulfur. In some cases, their characterizations were carried out by means of single-crystal X-ray diffraction analyses. The reactivity of these orthopalladated complexes with terminal alkynes results in unusual complexes with six membered rings different to that reported in the literature, due to an interchange between the halogen ligand and the alkyne. In these displacement reactions, we propose that the *trans* influence of the nitrogen and sulfur atoms over the carbon atoms



Scheme 3.

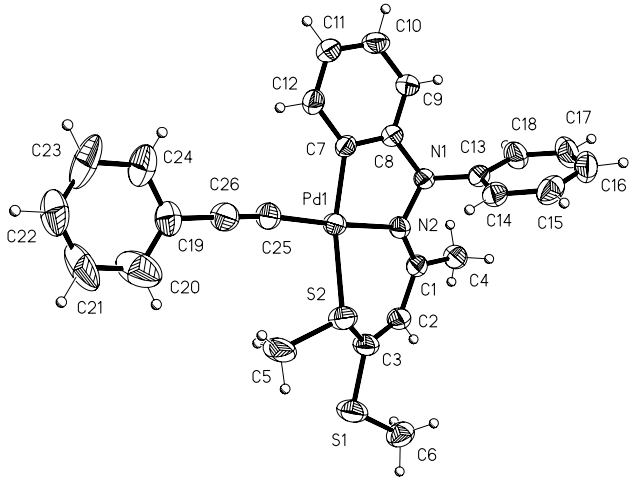


Fig. 2.

gives very stable Pd–C σ bonds and Csp-Csp_2 coupling does not occur.

3. Experimental

Reagents were obtained from commercial sources and were used as received. Tetrahydrofuran was dried by reflux over sodium using benzophenone as indicator and was freshly distilled under an argon atmosphere.

The ^1H (300 MHz) y ^{13}C (75 MHz) NMR spectra were obtained from a JEOL ECLIPSE+300 spectrometer, $CDCl_3$ was used as solvent and TMS as internal reference (for **4.1** y **4.2** complexes TMS was not used).

The IR spectra were recorded from a FT-IR NICOLET MAGNA 750 spectrophotometer in solutions. The mass spectra were obtained by using a JEOL-AX505 spectrometer with IE and FAB^+ techniques.

3.1. Ligands syntheses

The α-oxoketene dithioaketals were synthesized by using the Larsson methodology previously described. [21] The α-diphenylhydrazonoketene dithioaketals **1.1** and **1.2** were prepared according to literature methods [22].

N′-(1-Methyl-3,3′-bis-ethylsulfanylallylidene)-N,N-diphenylhydrazone (**1.1**). $C_{18}H_{20}N_2S_2$, MW 328 g/mol; yellow solid; m.p. 79 °C; 60% yield. IR ($CHCl_3$) cm^{-1}: 1588 (C=N); 1488 (C = Car). MS (EI), *m/z* (% ra): 328 [M^+ (35)]; 221 [$M^+ - C_3H_7S_2$ (20)]; 168 [$M^+ - C_6H_{10}S_2N$ (100)]; 77 [$M^+ - C_{12}H_{15}N_2S_2$ (20)]. ^1H NMR (300 MHz, $CDCl_3$) ppm: 1.83 (1H, s, H-5); 2.41 (6H, s, H-1, H-1′); 6.02 (1H, s, H-3); 7.01 (2H,

Table 2
Crystal and structure refinement data for **2.1** and **3.1**

	2.1	**3.1**
Empirical formula	$C_{18}H_{19}ClN_2PdS_2$	$C_{26}H_{24}N_2PdS_2$*0.5 (H_2O)
Formula weight	469.32	542.99
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimension		
a (Å)	8.878(1)	8.908(1)
b (Å)	11.433(1)	12.909(1)
c (Å)	19.433(2)	12.977(2)
α (°)	80.02(1)	113.266(1)
β(°)	79.58(1)	93.341(1)
γ (°)	84.73(1)	97.852(1)
V (Å^3)	1906.8(3)	1347.7(2) Å^3
Z	4	2
D_{calc} (mg/m^3)	1.635	1.338
Absorption coefficient (mm^{-1})	1.334	0.860
F(000)	944	552
Crystal size/color/shape	0.40 × 0.26 × 0.18 mm^3/orange/parallelepiped	0.396 × 0.168 × 0.132 mm/red/prism
Theta range for data collection (°)	1.96–25.00	1.72–25.00
Index ranges	$0 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $-22 \leqslant l \leqslant 23$	$-10 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 15$
Reflections collected	7195	16085
Independent reflections [R_{int}]	6718 [0.0362]	4756 [0.0362]
Completeness to theta = 25.00°	99.8%	100.0 %
Absorption correction	Analytical: face-indexed	Analytical: face-indexed
Maximum and minimum transmission	0.8009 and 0.7085	0.9079 and 0.7806
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6718/0/439	4756/0/286
Goodness-of-fit on F_2	1.030	1.010
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0438$, $wR_2 = 0.0814$	$R_1 = 0.0679$, $wR_2 = 0.2147$
R indices (all data)	$R_1 = 0.0812$, $wR_2 = 0.0944$	$R_1 = 0.0810$, $wR_2 = 0.2262$

Table 3
Bond lengths (Å) and angles (°) for Chloro-[*N*′-(1-methyl-3,3-bis-methylsulfanyl-allylidene)-*N*,*N*-diphenylhydrazine-C,*N*′,S]-palladium(II), (**2.1**)

Bond lengths			
Pd(1)–C(8)	1.989(6)	Pd(2)–C(26)	1.986(6)
Pd(1)–N(2)	2.004(4)	Pd(2)–N(4)	2.005(4)
Pd(1)–CI(1)	2.3113(17)	Pd(2)–CI(2)	2.3096(18)
Pd(1)–S(1)	2.3620(17)	Pd(2)–S(3)	2.3416(17)
S(1)–C(3)	1.769(6)	S(3)–C(21)	1.764(6)
S(1)–C(6)	1.812(7)	S(3)–C(24)	1.819(7)
S(2)–C(3)	1.740(6)	S(4)–C(21)	1.750(6)
S(2)–C(5)	1.781(6)	S(4)–C(23)	1.786(7)
N(1)–C(7)	1.432(7)	N(3)–N(4)	1.425(6)
N(1)–N(2)	1.438(6)	N(3)–C(25)	1.432(7)
N(1)–C(13)	1.474(7)	N(3)–C(31)	1.458(7)
N(2)–C(1)	1.311 (7)	N(4)–C(19)	1.315(7)
Bond angles			
C(8)–Pd(1)–N(2)	81.7(2)	CI(1)–Pd(1)–S(1)	87.56(6)
C(8)–Pd(1)–CI(1)	94.99(19)	C(3)–S(1)–C(6)	101.3(3)
N(2)–Pd(1)–CI(1)	176.71(14)	C(3)–S(1)–Pd(1)	107.0(2)
C(8)–Pd(1)–S(1)	176.96(18)	C(6)–S(1)–Pd(1)	107.0(3)
N(2)–Pd(1)–S(1)	95.73(14)	C(3)–S(2)–C(5)	105.1(3)
C(7)–N(1)–N(2)	109.9(4)	Cl(2)–Pd(2)–S(3)	86.37(7)
C(7)–N(1)–C(13)	115.1(5)	C(21)–S(3)–Pd(2)	108.1(2)
N(2)–N(1)–C(13)	112.8(5)	C(24)–S(3)–Pd(2)	104.6(3)
C(1)–N(2)–N(1)	114.8(5)	C(21)–S(4)–C(23)	103.4(3)
C(1)–N(2)–Pd(1)	130.1(4)	N(4)–N(3)–C(25)	110.5(4)
N(1)–N(2)–Pd(1)	114.8(3)	N(4)–N(3)–C(31)	113.0(4)
N(2)–C(1)–C(2)	124.3(5)	C(25)–N(3)–C(31)	114.1(4)
N(2)–C(1)–C(4)	122.0(5)	C(19)–N(4)–N(3)	114.7(5)
C(19)–N(4)–Pd(2)	129.8(4)	N(3)–N(4)–Pd(2)	115.2(3)

td, $J = 7.44$, 1.38 Hz, H-9, H-9′); 7.14 (4H, dd, $J = 7.41$, 1.11 Hz, H-7, H-7′); 7.27 (4H, td, $J = 7.44$, 1.38 Hz, H-8, H-8′). ^{13}C NMR (75 MHz, $CDCl_3$) ppm: 16.76 (C-1), 17.40 (C-1′); 21.22 (C-5); 121.39 (C-3); 121.65 (C-7, C-7′); 122.89 (C-9, C-9′); 129.04(C-8, C-8′); 144.17 (C-6); 148.37 (C-2); 162.46 (C-4).

N′*-(2-[1,3]-dithiolan-2-ylidene-1-methylylidene)-N,N-diphenylhydrazone* (**1.2**). $C_{18}H_{13}N_2S_2$, MW 326 g/mol; yellow solid; m.p. 152 °C; 30% yield. IR ($CHCl_3$) cm^{-1}: 1588 (C═N); 1488 (C = Car). MS (EI), *m/z* (% ra). 326 [M^+ (60)]; 168 [$M^+ - C_6H_8NS_2$ (100)]; 77 [$M^+ - C_{12}H_{13}N_2S_2$ (15)]. ^{1}H NMR (300 MHz, $CDCl_3$) ppm: 1.74 (1H, s, H-5); 3.33 (4H, m, H-1, H-1′); 6.16 (1H, s, H-3); 7.00 (2H, td, $J = 7.00$, 1.08 Hz, H-9, H-9′); 7.15 (4H, dd, $J = 7.00$, 1.08 Hz, H-7, H-7′); 7.24 (4H, td, $J = 7.00$, 1.08 Hz, H-8, H-8′). ^{13}C NMR (75 MHz, $CDCl_3$) ppm: 21.12 (C-5); 35.86 (C-1); 39.16 (C-1′); 113.07 (C-3); 121.51 (C-7, C-7′); 122.66 (C-9, C-9′); 128.97 (C-8, C-8′); 148.57 (C-2); 165.09 (C-4).

3.2. Orthopalladacycles synthesis

In a typical procedure one equivalent of the α-diphenylhydrazonoketene dithioaketal was dissolved in 10 mL of ethanol. Then, one equivalent of $Na_2[PdCl_4]$ was added and the mixture was stirred for 6 (**2.1**) or 12 h (**2.2**). After this time a colored solid precipiated. It was filtered and then further purified by column chromatography over alumina using a hexane-CH_2Cl_2 solvent mixture.

Chloro-[N′-(1-Methyl-3,3-bis-methylsulfanyl-allylidene)-N,N-diphenylhydrazone-C,N′S]-palladium(II) **2.1**. $C_{18}H_{19}ClN_2PdS_2$; MW 469 g/mol; red solid; m.p. 174–176 °C_{dec}; 80% yield. IR ($CHCl_3$) cm^{-1}: 1585 (C═N); 1488 (C = Car). MS (FAB^+), *m/z* (% ra): 470 [$M^+ + 1$ (20)]; 168 [$M^+ - C_6H_{10}ClNPdS_2$ (25)]; 154 [$M^+ - C_6H_{10}ClN_2PdS_2$ (100)]. ^{1}H NMR (300 MHz, $CDCl_3$) ppm: 2.16 (3H, s, H-5); 2.46 (3H, s, H-1′); 3.02 (3H, s, H-1′); 5.96 (1H, s, H-3), 6.85 (2H, m, H-8, H-9); 6.95 (1H, td, $J = 7.44$, 1.35 Hz, H-10); 7.23 (2H, t, $J = 7.41$ Hz, H-13); 7.35 (1H, t, $J = 7.68$ Hz, H-15); 7.50 (2H, d, H-14); 7.76 (1H, dd, $J = 7.41$, 1.11 Hz, H-11). ^{13}C NMR (75 MHz, $CDCl_3$) ppm: 17.67 (C-1); 21.73 (C-1′); 27.18 (C-5); 113.35 (C-8); 123.45 (C-3); 125.06 (C-14); 125.91 (C-9, C-10); 127.09 (C-13); 129.79 (C-15); 134.86 (C-11); 142.95 (C-12); 144.25 (C-6); 150.14 (C-7); 154.20 (C-2); 161.01 (C-4).

Chloro-{N′-[1-(1,3-dithiolan-2-yliden)]-N,N-diphenylhydrazone-C,N′S}-palladium(II) **2.2.** $C_{18}H_{17}ClN_2PdS_2$; MW 467.34 g/mol; orange solid; m.p. 201 °C_{dec}; 40 % yield. IR ($CHCl_3$) cm^{-1}; 1585 (C═N); 1489 (C = Car). MS (FAB^+), *m/z* (% ra): 468 [$M^+ + 1$(10)]; 391 [$M^+ - C_{12}H_{12}ClN_2PdS_2$ (30)]; 326 [$M^+ - PdCl$ (10)]; 168 [$M^+ - C_6H_8ClNPdS_2$ (55)]. ^{1}H NMR (300 MHz, $CDCl_3$) ppm: 2.15 (3H, s, H-5); 3.61 (2H, t, $J = 6.06$ Hz, H-1); 3.98 (2H, t, 6.06 Hz, H-1′); 6.18 (1H, s, H-3); 6.87-7.02 (3H, m, H-8, H-9, H-10); 7.16-7.21 (3H, m, H-13, H-15); 7.35 (2H, t, $J = 7.68$ Hz, H-14); 7.53 (1H, d, $J = 7.98$ Hz, H-11). ^{13}C NMR (75 MHz, $CDCl_3$) ppm: 24. 20 (C-5); 37.15 (C-1); 41. 57 (C-1′); 113.71 (C-8); 123.20 (C-3); 124.32 (C-14); 126.02 (C-9, C-10), 126.58 (C-13); 129.76 (C-15); 134.51 (C-11); 145.15 (C-6); 153.06 (C-7); 162.84 (C-4).

3.3. Reactivity with alkynes

3.3.1. Synthesis of *3.1*

One equivalent of **2.1** in 10 mL of anhydrous THF was dissolved under an atmosphere of N_2 at 0 °C, then one equivalent of lithium phenylacetylenide (1 M) was added. The mixture was stirred for 4 h. After this time, the solvent was removed and the product was purified by column chromatography over alumina by using a Hexane-CH_2Cl_2 solvent mixture as eluent.

N′-(1-Methyl-3,3-bis-methylsulfanylallyliden)-N,N-diphenylhydrazone-C, N′, S-(2-phenylethynyl) palladium (II) **3.1**. $C_{26}H_{24}N_2PdS_2$, MW 535.05 g/mol; yellow solid; m.p. 114–116 °C_{des}; yield 55%. IR ($CHCl_3$) cm^{-1}: 2108 (C≡C); 1588 (C═N); 1484 (C = Car). MS (FAB^+), *m/z* (% ra):535 [M^+ (25)]; 433 [$M^+ - C_8H_6$ (15)]; 328 [$M^+ - C_8H_5Pd$ (10)]; 267

Table 4
^{1}H and ^{13}C NMR data for complexes **3.1**, **4.1** and **4.2**

	H8 H9 H10	H11	H13	H14	H15	H18	H19	H20	H21
3.1	6.87–6.91 (3H, m)	8.11 (1H,d, J = 7.44)	7.14–7.25 (4H,m)	7.14–7.25 (4H,m)	7.32 (2H,t, J = 7.71)	–	7.14–7.25 (4H,m)	7.14–7.25 (4H,m)	7.32 (2H,t, J = 7.71)
4.1	6.83–6.89 (3H, m)	8.04 (1H,d, J = 7.14)	7.27 (2H,t, J = 7.14)	7.35 (2H,d, J = 7.68)	7.12 (1H,t, J = 7.14)	0.16 (9H,s)	–	–	–
4.2	6.84–7.03 (3H, m)	7.88 (1H,d, J = 8.52)	7.10–7.28 (3H,m)	7.41–7.53 (2H,m)	7.10–7.28 (3H,m)	0.17 (9H, s)	–	–	–7

	C6	C7′	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21
3.1	143.0	150.7	113.9	123.4	125.3	138.9	141.9	126.1	126.9	125.5	106.5	107.7	–	127.4	131.4	129.6
4.1	143.2	150.7	113.8	125.1	125.1	138.9	141.9	129.5	126.0	129.5	111.3	111.3	1.33	–	–	–
4.2	–	150.3	114.3	125.3	125.3	138.6	–	–	124.1	129.4	–	–	1.44	–	–	–

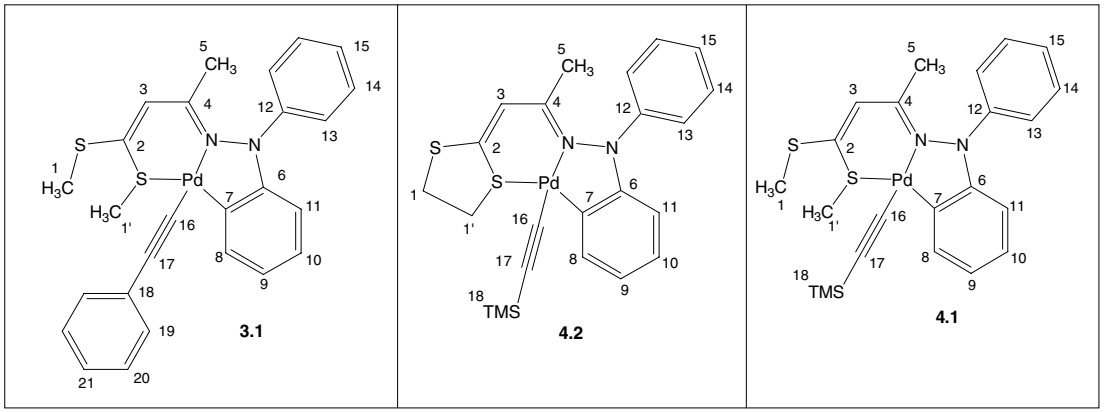


Table 5
Bond lengths (Å) and angles (°) for (*N*′-(1-methyl-3,3-bis-methylsulfanyl-allylidene)-*N*,*N*-diphenylhydrazine-C,*N*′,S)-(2-phenylethynyl)palladium(II) **(3.1)**

Bond lengths			
		S(2)–C(5)	1.758(15)
Pd(1)–C(25)	1.946(7)	S(2)–C(3)	1.792(8)
Pd(1)–C(7)	1.991(6)	S(2B)–C(3)	1.862(9)
Pd(1)–N(2)	2.036(5)	S(2B)–C(5B)	1.88(3)
Pd(1)–S(2B)	2.315(5)	N(1)–N(2)	1.420(7)
Pd(1)–S(2)	2.377(3)	N(I)–C(8)	1.446(8)
S(1)–C(3)	1.733(7)	N(1)–C(13)	1.460(8)
S(1)–C(6)	1.765(8)	N(2)–C(1)	1.310(8)
Bond angles			
C(25)–Pd(1)–C(7)	94.8(3)	C(5)–S(2)–C(3)	104.4(8)
C(25)–Pd(1)–N(2)	176.3(2)	C(5)–S(2)–Pd(1)	112.9(6)
C(7)–Pd(1)–N(2)	81.7(2)	C(3)–S(2)–Pd(1)	104.8(3)
C(25)–Pd(I)–S(2B)	84.5(3)	C(3)–S(2B)–C(5B)	93.1(11)
C(7)–Pd(1)–S(2B)	166.7(2)	C(3)– S(2B)–Pd(1)	104.9(3)
N(2)–Pd(1)–S(2B)	98.59(19)	C(5B)–S(2B)–Pd(1)	103.7(12)
C(25)– Pd(1)–S(2)	92.6(2)	N(2)–N(1)–C(8)	110.8(5)
C(7)– Pd(1)–S(2)	165.91(19)	N(2)–N(1)–C(13)	113.9(5)
N(2)–Pd(1)–S(2)	91.13(16)	C(8)–N(1)–C(13)	113.5(5)
C(3)–S(1)–C(6)	105.7(4)	C(1)–N(2)–N(1)	115.8(5)
C(1)–N(2)–Pd(1)	129.6(4)	N(2)–C(1)–C(2)	123.7(6)
N(1)–N(2)–Pd(1)	114.1(4)	N(2)–C(1)–C(4)	121.5(6)

$[M^+ - C_{10}H_{12}PdS$ (35)]; 167 $[M^+ - C_{12}H_9N$ (55)]. ^{1}H NMR (300 MHz, $CDCl_3$) ppm: 2.09 (3H, s, H-5); 2.45 (3H, s, H-1); 3.14 (3H, s, H-1′); 6.03 (1H, s, H-3); 6.87–6.91 (3H, m, H-8, H-9, H-10); 7.14–7.25 (4H, m, H-13, H-19); 7.32(2H, t, J = 7.71 Hz, H-15, H-21); 7.42–7.49 (4H, m, H-14, H-20); 8.11 (1H, d, J = 7.44 Hz, H-11). ^{13}C NMR (75 MHz, $CDCl_3$) ppm: 17.74 (C-1); 23.56 (C-1′); 26.86 (C-5); 106.50(C-16); 107.77 (C-17); 113.96 (C-8); 123.45 (C-9); 124.92 (C-3); 125.35 (C-10), 125.56 (C-15); 126.14 (C-13); 126.93 (C-14); 127.47 (C-19), 129.64 (C-21); 131.45 (C-20), 138.93 (C-11); 141.91 (C-12); 143.06 (C-6); 150.74 (C-7); 155.36 (C-2); 158.95 (C-4).

3.3.2. Synthesis of **4.1** and **4.2**

One equivalent of TMSC≡CH in 10 mL of dry THF was dissolved under an atmosphere of N_2 at −78 °C, then one equivalent of *n*-BuLi (1.3 M) was added. The mixture was allowed to warm to room temperature and then was transferred by cannula to a solution of **2.1** or **2.2** in 5 mL of dry THF at 0 °C. The mixture was stirred for 5 h at room temperature. The solvent was removed and the product was obtained as a solid.

N′*-(1-Methyl-3,3-bis-methylsufanyl-allilyden)-N,N-diphenylhydrazine-C,N*′*, S-(2-tetramethylsilylethynyl) palladium (II)* **4.1**. $C_{23}H_{28}N_2PdS_2Si$, MW 531.13 g/mol, green solid, m.p. 113–115 °C$_{dec}$, yield 45%. IR ($CHCl_3$) cm^{-1}; 2042 (C≡C); 1588 (C=N); 1488 (C = Car); 857 ($Si(CH_3)_3$). MS (FAB$^+$) *m*/*z* (% ra); 433 $[M^+ - C_5H_{10}Si$ (10)]; 387 $[M^+ - C_9H_8N_2$ (8)]; 221 $[M^+ - C_8H_{16}PdSi$ (50)]; 167 $[M^+ - C_{11}H_{20}PdS_2Si$ (75)]; 73 $[M^+ - C_{20}H_{19}N_2PdS_2$ (100)]. ^{1}H NMR (300 MHz, $CDCl_3$) ppm: 0.16 (9H, s, H-18); 2.04 (3H, s, H-5); 2.42 (3H, s, H-1); 3.09 (3H, s, H-1′); 5.97 (1H, s, H-3); 6.83-6.89 (3H, m, H-8, H-9, H-10); 7.12 (1H, t, J = 7.14 Hz, H-15); 7.27 (2H, t, J = 7.14 Hz, H-13); 7.35 (2H, d, J = 7.68 Hz, H-14); 8.04 (1H, d, J = 7.14 Hz, H-11). ^{13}C NMR (75 MHz, $CDCl_3$) ppm: 1.33 (C-18); 17.71 (C-1); 23.24 (C-1′); 26.70 (C-5); 111.33 (C-16, C-17); 113.88 (C-8); 124.78 (C-3); 125.18 (C-9, C-10); 126.08 (C-14); 129.55 (C-13, C-15); 138.95 (C-11); 141.91 (C-12); 143.21 (C-6); 150.72 (C-7); 155.19 (C-2); 158.95 (C-4).

N′*-[1-(1,3-dithiolan-2-ilyden)]-N,N-diphenyl-hydrazone-C,N*′*,S-(2-tetramethylsilyletynyl) palladium (II)* **4.2**. $C_{23}H_{26}N_2PdS_2Si$, MW 529.12 g/mol, brown solid, m.p. 170 °C$_{dec}$, yield 55%. IR ($CHCl_3$) cm^{-1}: 2041 (C≡C); 1588 (C=N); 1489 (C = Car); 856 ($Si(CH_3)_3$). MS (FAB$^+$) *m*/*z* (% ra); 529[M^+ (2)]; 326$[M^+ - C_5H_8PdSi$ (20)]; 221$[M^+ - C_8H_{13}PdS_2Si$ (60)]; 168$[M^+ - C_{21}H_{12}PdS_2Si$(75)]; 73$[M^+ - C_{20}H_{18}N_2PdS_2$ (100)]. ^{1}H NMR (300 MHz, $CDCl_3$) ppm: 0.17 (9H, s, H-18); 2.08 (3H, s, H-5); 3.61 (2H, t, H-1); 4.02 (2H, t, H-1′); 6.17 (1H, s, H-3); 6.84-7.03 (3H, m, H-8, H-9, H-10); 7.10-7.28 (3H, m, H-13, H-15); 7.41-7.53 (2H, m, H-14); 7.88 (1H, d, J = 8.52 Hz, H-11). ^{13}C NMR (75 MHz, $CDCl_3$) ppm: 1.44 (C-18); 24.18 (C-5); 36.2 (C-1); 42.64 (C-1′); 112.58 (C-16), 113.07 (C-17), 114.38 (C-8); 116.20 (C-3); 121.53 (C-15); 124.23 (C-14); 125.35 (C-9, C-10); 129.45 (C-13); 138.48 (C-11); 146.14 (C-12);147.85 (C6); 150. 33 (C-7); 154.06 (C-2); 163.24 (C-4).

3.4. X-ray crystal structure determination of compounds **2.1** and **3.1**

Data collection and refinement parameters are summarized in Table 2. The diffraction data for **2.1** was collected on a Siemens *P*4/*Pc* diffractometer, while the data for **3.1** was collected on a Bruker Smart Apex CCD diffractometer with Mo Kα radiation, λ = 0.71069 Å. Each data set was corrected for Lorentz and polarization effects. An empirical absorption corrections based on psi-scans were applied for the structure of **2.1**. The structures were solved by direct methods[23] and each structure was refined by full-matrix least-squares on F^2 using all data with all non-hydrogen atoms assigned anisotropic displacement parameters. The hydrogen atoms bound to carbon atoms were inserted at calculated positions with an isotropic temperature factor 1.2 times the U_{iso} of the parent carbon atom. The program used in the final refinements was SHELXL 97 [24].

3.5. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Centre CCDC No.247998 for complex **2.1**, No. 247999 for complex **3.1**. Copies of this information may be

obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.ukor www: http://www.cdcc.cam.ac.uk).

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