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Addition of halogens and interhalogens on palladacyclopentadienyl complexes stabilized by pyridyl–thioether N–S spectator ligands

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ABSTRACT

We have studied from the experimental and theoretical point of view the oxidative addition of halogens (I_2 and Br_2) and interhalogens (ICl and IBr) on palladiumcyclopentadienyl complexes bearing heteroditopic pyridyl–thioether spectator ligands.

Addition of I_2 or of a stoichiometric amount of Br_2 to a $CDCl_3$ solution of the starting palladacyclopentadienyl complexes yields the expected palladium–σ–butadienyl derivatives. The bromide derivative in the presence of a further excess of Br_2 gives the wanted dibromo–(E, E)–σ–butadienyl and the pyridylthioether palladium(II) dibromide species. The rates of these reactions have been determined.

When the interhalogens are used as oxidizing agents the thermodynamically hampered species is formed at first. Only in the case of the reaction of IBr is the formation of the energetically hampered derivative followed by partial isomerization to the most stable complex. The rate of isomerization and the related equilibrium constant between isomers have been measured. On the basis of the experimental evidence and the computational approach we have proposed a plausible energetic path yielding the first formed unexpected species.

Finally, the solid state structures of two reaction products were resolved and reported.

1. Introduction

The ease and versatility characterizing the Pd(0)/Pd(II) catalyzed cross coupling reactions have promoted in the past decade a number of studies, as witnessed by the available vast literature [1]. Conversely, the redox reactions involving the Pd(II)–Pd(IV)–Pd(II) conversions have been less investigated and are usually limited to the addition of halogens or organic halides in catalytic [2] or stoichiometric [3] processes often yielding conjugated dienes as their final products.

The conjugated dienes are important compounds contained in many natural and bioactive products. In this respect, some synthetic approaches based on catalytic protocols involving palladium complexes have been developed [4]. We are deeply interested in the mechanistic features of reactions involving Pd(IV) intermediates which in our opinion still represent a promising field worth of detailed investigations [3d-e]. As a matter of fact, a thorough knowledge on the nature of the cited elusive intermediates can give a marked impulse to the design of new Pd(II)/Pd(IV) catalytic cycles [2c], although from the original articles of Canty [5] new advances in the isolation of stable Pd(IV) species were achieved [2c and Refs. therein].

Palladacyclopentadienyl derivatives bearing different spectator ligands have been often studied owing to their potential capability to give σ–butadienyl derivatives and thence conjugated dienes [2–3,6]. In particular, our group has recently focused its interest on the oxidative attack of di–halogens on palladacyclopentadienyl complexes with monodentate isocyanides [3d] and phosphoquinoline [3e] as ancillary ligands. In the latter case, the peculiarity of the reaction course resulting in an unexpected widening of the coordinative ring drove us to extend our investigation to the oxidative reactions of halogens and inter-halogens on palladacyclopentadienyl derivatives bearing pyridylthioethers as spectator ligands. Moreover, for the sake of completeness, we have investigated the displacement of the halide-substituted conjugated dienes by exhaustive oxidative elimination of the starting complexes with

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bromine in excess. We have therefore tried to determine how the structure of the well known pyridylthioether ancillary ligands could affect the reaction rate since it was often shown that the overall reactivity of the pyridylthioether derivatives is strongly influenced by the electronic and steric properties imparted by the substituents to the ancillary ligands themselves [6g,7]. The ligands, the complexes and the reactions described in the present paper are reported in the following Scheme 1.

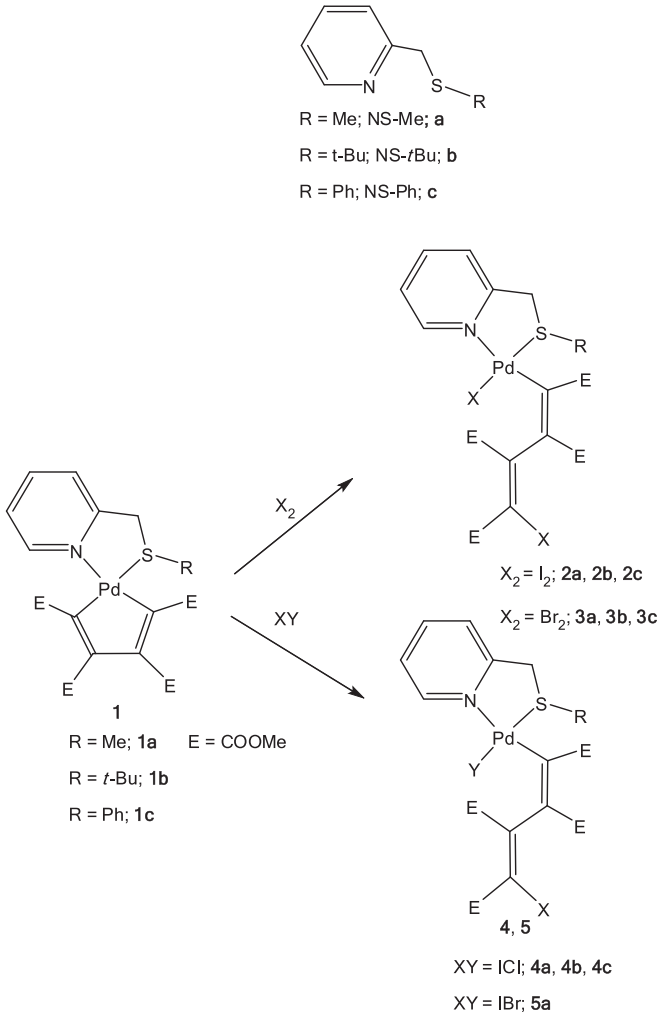
2. Results and discussion

2.1. General considerations

The ligands NS-R (R = Me, *t*-Bu, Ph) [7] and the complexes **1a**–**c** [8], were obtained according to published protocols by adding the appropriate ligand to the polymer $[PdC_4(COOMe)_4]_n$ [9]. The complexes **2a**–**c**, **3a**–**c**, **4a**–**c** and **5a** are newly synthesized compounds.

2.2. Reactions of complexes *1a–c* with I_2

Addition under inert atmosphere (Ar) of a slight excess of I_2 to a solution of complexes **1a**–**c** in anhydrous CH_2Cl_2 yields the (E, E)–σ–butadienyl derivatives **2a**–**c**. The reactions are fast and complete and proceed through two steps consisting in the formation of the Pd(IV) intermediate bearing two apical iodides followed by reductive elimination with the consequent opening of the cyclopentadienyl ring and formation of the σ–butadienyl derivatives [3b]. All the σ–butadienyl complexes are stable and isolable, although in the presence of excess iodine ([**2a**–**c**]/[I_2] = 1/10) a further and very slow reaction yielding the free 1,4–diiodobuta–1,3–diene (DIBD) and the [Pd(NS-R)I_2] complexes occurs ($t_{1/2} \approx 4$ months).



Scheme 1. Ligands, starting complexes, halogens, interhalogens and reaction products.

The structure of complexes **2a**–**c** can be deduced on the basis of their ^1H and ^{13}C NMR spectra and from analogy with the spectra of similar σ-butadienyl derivatives [3e,7c]. In particular, the σ–coordinated butadienyl fragment is identified by the presence of four signals ascribable to $COOCH_3$ protons resonating at different frequencies of the same groups of the original palladacyclopentadienyl species (Fig. 1SI in Supplementary). Moreover, the iodide coordinated to palladium induces a remarkable down-field shift of the *ortho* proton of the pyridine ring of the pyridylthioether ligands which resonates at ca. 9.6 ppm.

The structure of complexes **2a**–**c** was also identified by the ^{13}C NMR spectra recorded at RT since the four different carbons of the $-OCH_3$, CO and C=C groups resonate at very different frequencies from those of the cyclopalladate derivative precursors. Moreover, the terminal butadienyl carbon bound to iodide is particularly diagnostic owing to its low field resonance (ca. 100 ppm) (See Experimental and Fig. 2 SM in Supplementary material).

The resonance of the *ortho* pyridine proton (9.6 ppm) represents a marker identifying the structure of only one of the two possible geometric isomers. It is worth noting that a similar chemical shift was always detected in all the palladium complexes bearing a halide *cis* to the pyridine nitrogen of the ancillary ligands [6g,7a]. The formation of the uniquely observable isomer is strictly correlated to the sulfur *trans*–influence which is higher than that of nitrogen. The sulfur *trans*–influence determines the position of the cyclopentadienyl ring opening and consequently the formation of only the derivatives **2a**–**c** (see Scheme 1). The displacement of the carbon *trans* to sulfur by iodide is also responsible for the observed diastereotopicity at RT of the CH_2–S protons of the complexes **2a** and **2b**. The reduced *trans*–influence of iodide with respect to carbon renders the Pd–S bond of complexes **2a** and **2b** stronger than that of complexes **1a**–**c**. Consequently the rate of inversion of the sulfur absolute configuration [10] slows down [7c] (Fig. 1 SM in Supplementary material). An exception is represented by the CH_2S protons of the complex **2c**. This complex, bearing an electron-withdrawing phenyl group coordinated to sulfur, does not display similar behavior owing to the reduced strength of the Pd–S bond. Therefore complex **2c** behaves as complexes **1a**–**c** and its CH_2S protons resonate as a singlet at RT.

The low temperature NMR spectra of complexes **2** deserve a further comment. Owing to the perpendicular position of the σ–butadienyl fragment and that of the sulfur substituents which can be on the same or opposite side with respect to the main coordination plane [7c], the presence in solution of the *endo* and *exo* isomers can be detected from the splitting of the several signals at low temperature (Fig. 1).

The isomeric distribution of complex **2b** is strongly unbalanced (15/1), the *exo* being the less hindered and therefore the most probable isomer, owing to the steric interference exerted by the bulky *t*–Bu group.

2.3. Reactions of complexes *1a–c* with Br_2

Addition of a stoichiometric amount of bromine to complexes **1a**–**c** yields derivatives **3a**–**c**. In this case, however, the concentration of bromine is crucial since an excess causes a further reaction of the complexes **3a**–**c** (see later).

The ^1H and ^{13}C NMR spectra of the complexes **3a**–**c** are easily

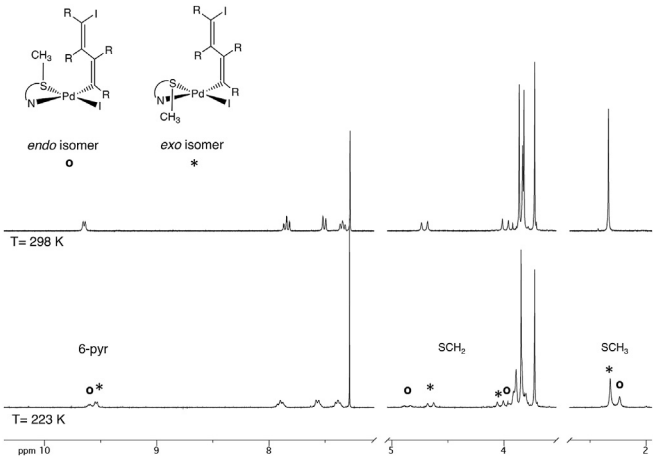


Fig. 1. ^{1}H NMR spectra of complex **2a** at 298 and 223 K in $CDCl_3$.

traceable back to those of the corresponding iodide derivatives **2a**–**c**. The $-OCH_3$ proton signals resonate at different frequencies from those of the original palladacyclopentadienyl and the 6–Py proton is detected at 9.40 ppm ca. testifying the *cis* nature of the isomer (see Scheme 1). The ^{13}C spectra display all the expected resonances (see Experimental) and in particular the resonance at ca. 125 ppm ascribable to the terminal butadienyl carbon suggests that the shielding contribution of the bromide is higher than that of iodide.

In this case the reduced *trans*–influence of bromide (with respect to iodide) is apparent since the diastereotopicity of the $-CH_2-$S protons due to the increased strength of the Pd–S bond is detected in all the complexes **3a**–**c** synthesized (Fig. 3SM in Supplementary material).

As a decisive confirmation of the nature of the type **3** complexes we report in the following Fig. 2 the resolved solid state structure of complex **3b**, whose details will be discussed later. (See section *2.5*).

2.4. Reactions of complexes *1a–c* with ICl

Addition of the interhalogen ICl to complexes **1 a**–**c** immediately yields the derivatives **4 a**–**c**. Interestingly, only the isomers bearing the chloride coordinated to palladium *trans* to sulfur and the iodide bound to the terminal butadienyl carbon are obtained. (See Scheme 2).

Complexes **4a**–**c** again are identified on the basis of the different distribution of the $-OCH_3$ protons with respect to that of the starting palladacyclopentadienyl species and the resonance of the 6–Py proton at ca. 9.20 ppm. Such a peculiar downfield shift of the 6–Py proton is typical of the complexes bearing a chloride coordinated palladium *cis* to the pyridine ring [7c]. As a matter of fact, if complexes **4′a**–**c** were formed, the above mentioned resonance should be at ca. 9.60 ppm owing to the de-shielding effect exerted by the iodide (*vide supra*). This conclusion is also confirmed by the position of the terminal carbon bearing the coordinated iodide resonating at the typical frequency of C=C–I carbon at ca. 100 ppm in the ^{13}C NMR spectra (*vide supra*; see also Fig. 4a SM and 4b SM in Supplementary material) and by the resolved structure of complex **4b** (see Fig. 3; the structural details will be discussed in the further dedicated section).

Since complexes **4′a**–**c** probably represent the most stable species from the thermodynamic point of view, we surmise that the formation of complexes **4a**–**c** is kinetically controlled and proceeds *via* the an octrahedral intermediate whose formation is triggered by the initial attack of the electronegative chlorine to the metal

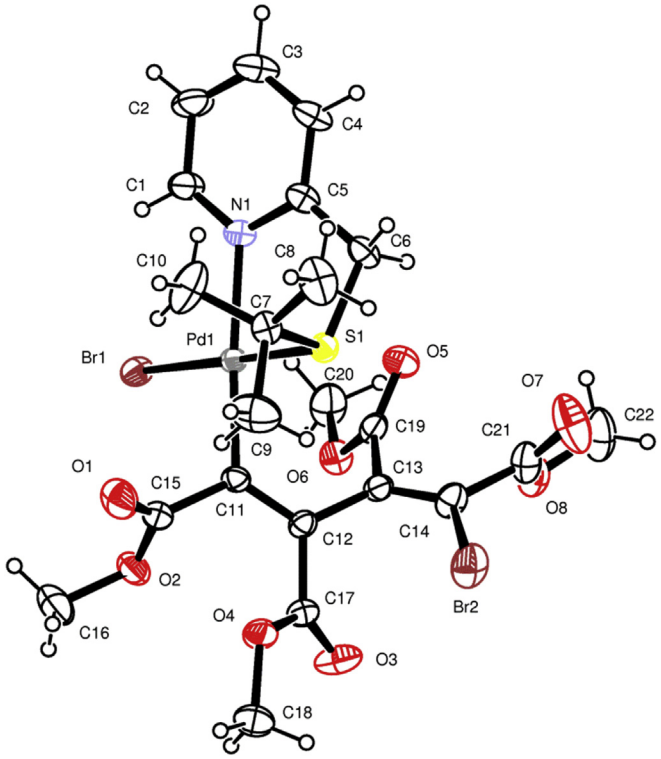
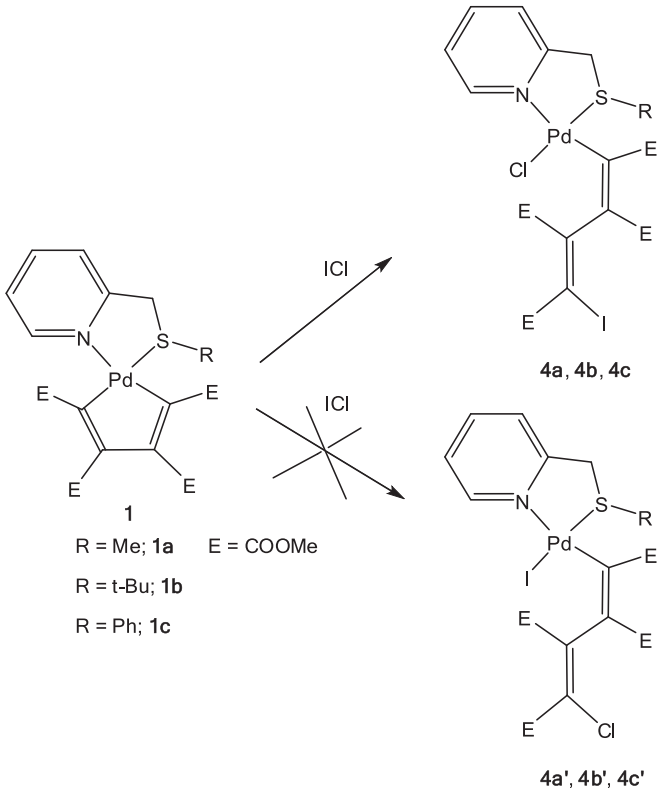


Fig. 2. ORTEP view of complex 3b showing the thermal ellipsoids at 30% probability level.



Scheme 2. Reaction products in the reaction of complexes **1** with the interhalogen ICl.

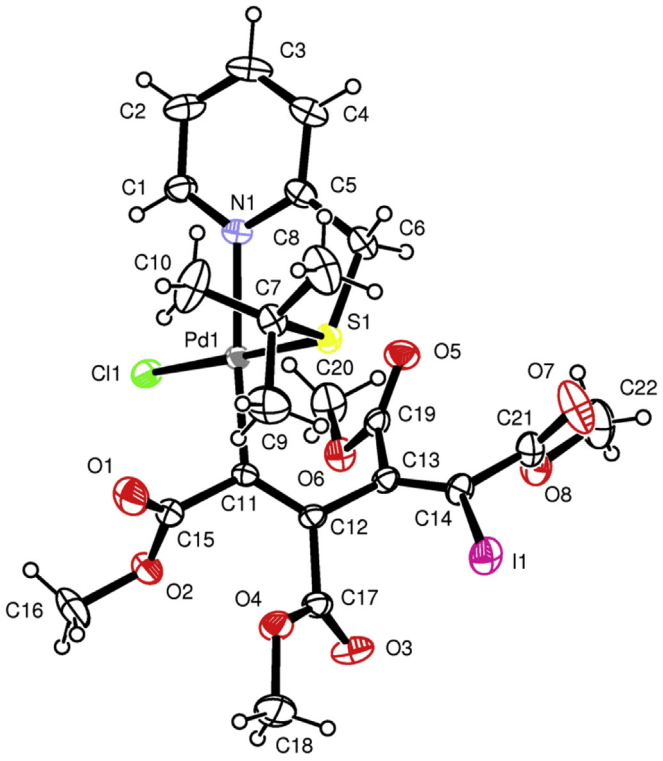


Fig. 3. ORTEP view of complex **4b** showing the thermal ellipsoids at 30% probability level.

centre. It is worth noting that the isomers **4a**–**c** display no tendency to isomerize and no hint of complexes **4′a**–**c** is detected in solution. On the other hand, the *endo* and *exo* isomers are observable also in this case by recording the NMR spectra at low temperature (223 K). Notably, Complex **4b,** thanks to its bulky *t*–Bu substituent, freezes already at 253 K displaying a ratio between the *exo* and *endo* rotamers of ca.1: 2. (See Fig. 5 SI in Supplementary material).

2.5. X–ray structure of complexes *3b* and *4b*

ORTEP [11] views of the isostructural complexes **3b** and **4b** are shown in Figs. 2 and 3. A selection of bond distances and angles is given in Table 1. Both complexes adopt the same structure except for the presence of two Br atoms in complex **3b** instead of a Cl atom bonded to a central Pd1 and an I atom on the butadiene substituted ligand in complex **4b**. The geometry around the Pd centers is slightly distorted square planar where the four positions are occupied by a halogen atom, Cl in **4b** or Br in **3b**, the pyridine nitrogen and the sulphur of the 2–[(*tert*–butylsulfanyl)methyl] pyridine (NS–*t*Bu) ligand, and the carbon C_α of the 1,2,3,4–tetrakis(methoxycarbonyl) buta–1,3–diene–4–I ligand. The deviations of Pd1 atoms from the average basal planes are 0.0280(2) Å in complex **4b**, and 0.0045(2) Å in complex **3b**, toward C7 carbon.

The C11 = C12–C13 = C14 buta-1,3-diene moieties display *anti-clinal* conformations with torsion angles of 135.4(4)° and 135.0(4) in **4b** and **3b**, respectively.

Both complexes in the crystal packings display short Halogen …. Halogen contacts [12-14]: Cl1 … I1 (x,y,z+1) = 3.4254(9) Å in **4b** and Br1 … Br1(x,y,z+1) = 3.5191(6) Å in **3b**.

Table 1
Crystallographic data.

Compound	**4b**	**3b**
Formula	$C_{22}H_{27}ClINO_8PdS$	$C_{22}H_{27}Br_2NO_8PdS$
M	734.26	731.73
Space group	$Pna2_1$	$Pna2_1$
Crystal system	Orthorhombic	Orthorhombic
a/Å	17.1622 (2)	17.4379 (3)
b/Å	16.3702 (5)	16.4679 (4)
c/Å	9.8937 (6)	9.7139 (2)
U/Å^3	2779.6 (2)	2789.5 (1)
Z	4	4
T/K	295	295
D_c/g cm^{-3}	1.755	1.742
F(000)	1448	1448
μ(Mo-Kα)/mm^{-1}	1.993	3.648
Measured Reflections	20,892	25,641
Unique Reflections	7792	6602
R_{int}	0.0407	0.0456
Obs. Refl.ns [I ≥ 2σ(I)]	6430	5518
θ_{min}– θ_{max}/°	2.76–30.00	3.37–30.00
hkl ranges	−24,18;−22,22;−13,13	−23,24;−23,323; −13,13
R(F^2) (Obs.Refl.ns)	0.0323	0.0302
wR(F^2) (All Refl.ns)	0.0709	0.0736
No. Variables	323	323
Goodness of fit	1.016	1.069
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e Å^{-3}	1.175; −0.847	0.517; −0.638
CCDC Deposition N.	1437242	1437243

2.6. Reaction of complexes *1a* with IBr

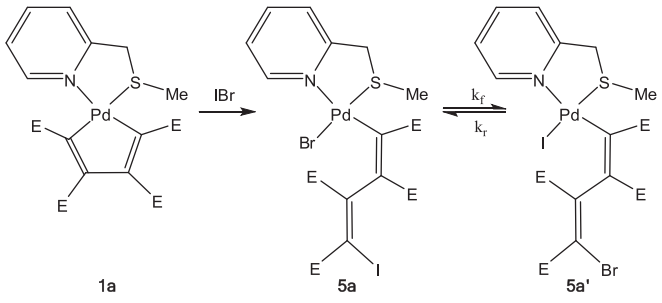
A nice confirmation that the formation of complexes **4′** might be kinetically controlled is inferred from the reactivity of complex **1a** with IBr. Again the addition of IBr to a solution of **1a** at RT yields instantaneously the complex **5a**. However, the reaction proceeds slowly further to give an equilibrium mixture of **5a** and **5a′** in a 2: 3 ratio, respectively (Scheme 3).

In this case it is also possible to measure the isomerisation rate. As reported in Fig. 4 the reaction follows a first-order process with a rate constant $k_e = (k_f + k_r) = (3.71 \pm 0.07) \times 10^{-5}$ s^{-1}. From the experimentally estimated equilibrium constant (Ke ≈ 1.5) and from the value of k_e it is possible to calculate the forward (k_f) and reverse (k_r) rate constants which are 2.22×10^{-5} and 1.48×10^{-5} s^{-1}, respectively.

It is worth noting that the forward isomerisation **5a** –> **5a′** is characterized by a partial *cis*/*trans* isomerization of the double bonds of the products.

2.7. Computational study

We have undertaken a detailed computational study in order to verify the consistency, if any, between the calculated results and our experimental observations in the case of complexes **4a**/**4a′** and **5a**/**5a′**.



Scheme 3. Attack of the interhalogen IBr to complex **5a**, reaction products.

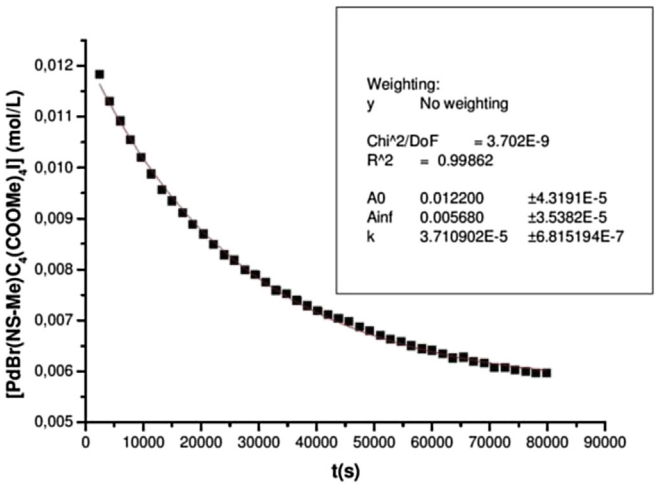


Fig. 4. Concentration vs. time data and related non-linear regression analysis of the reaction **5a**⇌**5a**′ carried out by ^{1}H NMR in $CDCl_3$ at 298 K.

In order to save computer time we have replaced the carboxymethyl group COOMe by the less disordered CN fragment and in the following discussion the CN derivatives will maintain the same labels as the original complexes albeit marked with an asterisk.

Remarkably, our experimental results were not in contrast with the computational study carried out by the Gaussian 09 program [15] and despite the implicit limitations ($\Delta\Delta G^\circ \approx \pm 2$ kcal/mol and the replacement of COOMe with CN groups), we have obtained a confirmation and hence a possible explanation of the observed trend.

Elsevier and co-workers have carried out a similar, exhaustive computational approach taking into account all the steps involved in the reaction of palladacyclopentadiene complexes bearing bidentate nitrogen ligands as ancillary ligands with Br_2 [3b]. Remarkably, the TSs we have proposed have similar structures and energies of the same order of magnitude as those suggested in the above cited paper. However, our investigations with interhalogens were mainly focused on the part of the whole process that is responsible for the peculiar regioselectivity yielding the less thermodynamically stable derivatives as reaction products. In this respect we have put much emphasis on the shape and energy of the TS of the reductive elimination step, omitting the different rotamers and van der Waals adducts involved in the overall reaction progress.

As can be seen in the schematic representations of the energies involved (see Fig. 5) the prominent emerging computational data for complexes **4a***, **4a***′ and **5a*** and **5a***′ can be summarized as follows:

i) As expected complex **4a***′ is thermodynamically more stable than **4a*** by ca. 1.6 kcal/mol. Therefore, the formation of complex **4a*** is confirmed as being governed kinetically. The stability of **4a*** probably depends on the remarkable difference between the energies of the two transition states involved in the isomerization process ($\Delta\Delta G^\circ_{(TS)} = 5.9$ kcal/mol) which renders the reaction yielding complex **4a*** about 5 orders of magnitude faster than that giving **4a***′.

ii) The data related to complexes **5a*** and **5a***′ are in line with the former results and the complex **5a*** is again the first species formed. However its partial isomerization is now feasible since the difference between the transition state energy ($\Delta\Delta G^\circ_{(TS)} = 1.8$ kcal/mol) is considerably smaller than that calculated for complexes **4a***/**4a***′ (*vide supra*). The related difference in reaction rates differs by only one order of magnitude. Remarkably (and fortunately), the calculated equilibrium constant Ke ≈ 2.3 is quite comparable with that measured experimentally (Ke ≈ 1.5).

2.8. Reaction of complexes **3a**–**c** with Br_2 in excess

As mentioned before, the formation of complexes **3** can be achieved only by addition of a stoichiometric amount of Br_2 since its excess promotes the further progress of the reaction yielding the complete extrusion of 1,4–dibromobuta–1,3–diene (DBBD) and complexes **6** (Scheme 4).

Therefore, we have studied the reactivity of complexes **3** in the presence of bromine in excess by ^{1}H NMR technique and the half-time of the single reaction, taken as a reactivity index, is reported in the following Table 2:

As an internal check of consistency in order to validate all the data in Table 1, we have carried out and kinetically monitored the reaction between complex **3a** and Br_2 which is the most practicable from the experimental point of view. From the k_{obs} value ($k_{obs} = 2.36 \pm 0.04$ min^{-1}) determined by non linear regression analysis of the monoexponential decay of the concentration of complex **3a** as a function of time (s) we have estimated $t_{1/2} = 29$ min. This $t_{1/2}$ is in good agreement with the previously determined one and reported in Table 1 (30 min) (See Fig. 6a SM in Supplementary).

As can be seen in Table 1, the $t_{1/2}$ of the reactions markedly depends on the nature of the complex under study, since the steric hindrance of the complexes strongly influences the rate of reaction.

We therefore think that the rate determining step is the slow associative formation of a Pd(IV) octahedral intermediate bearing two bromides in its axial position, although no hints of its formation can be detected experimentally. (See NMR spectra of the progress of reaction and the reaction products in Fig. 6b SM in Supplementary material). The fast reductive elimination giving complexes **6** (which partially precipitates within the NMR test tube) and DBBD suggests a steady state control of the overall reaction rate.

3. Conclusion

We have carried out the syntheses of some novel σ–butadienyl derivatives of Pd(II) by adding di–halogens (I_2 or Br_2) or interhalogens (ICl or IBr) to three cyclopalladate complexes bearing differently substituted pyridylthioethers as spectator ligands. In any case we obtained the (E, E)–σ–butadienyl derivatives, but the reaction with the interhalogens surprisingly gave the less thermodynamically stable products. We have surmised that the formation of the less stable species was kinetically controlled and supported the hypothesis by an adequate computational approach.

In the case of the thermodynamic unstable complex **5a** which isomerizes to **5a**′ in a reasonable time it was possible to study the isomerization process.

The solid state structures of two derivatives were also carried out, confirming the suggested nature of the isomers.

We have also followed the kinetics of the extrusion of 1,4–dibromobuta–1,3–diene from the type **3** complexes with Br_2 in excess and proposed a mechanism involving the slow associative formation of a Pd(IV) octahedral intermediate bearing two bromides in its axial position.

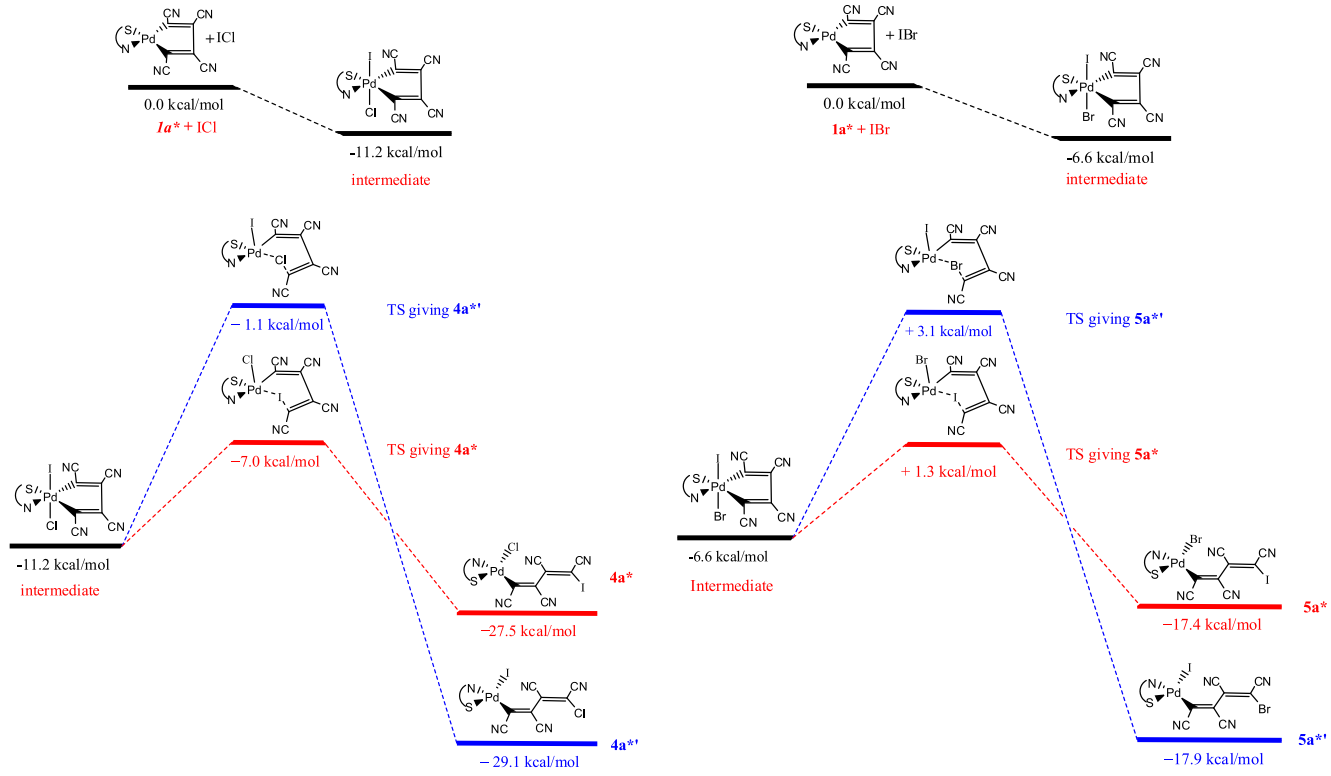
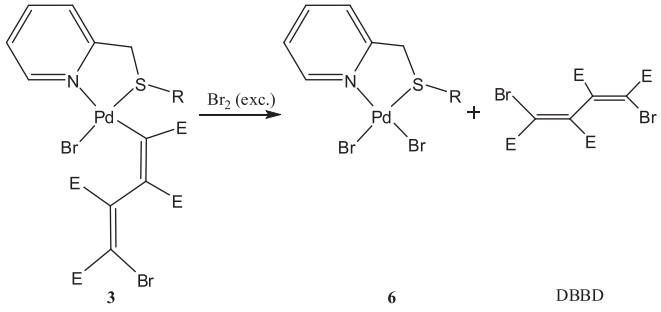


Fig. 5. Schematic computational energies computed for complexes **4a***, **4a***′ (left) and **5a***, **5a***′(right).



E = COOMe

DBBD = (1E,2E)-tetramethyl-1,4-dibromobuta-1,3diene-1,2,3,4-tetracarboxylate

Scheme 4. Reaction of complexes **3** with Br_2 in excess.

4. Experimental

4.1. Solvents and reagents

All the following distillation processes were carried out under inert atmosphere (Argon). Acetone and CH_2Cl_2 were distilled over 4 Å molecular sieves and CaH_2, respectively. All other chemicals were commercially available grade products and were used as purchased.

Table 2
Measured half-times for the reaction **3** + Br_2 → **6** + DBBD.

Complex	$t_{1/2}$
3a	30′
3b	12h
3c	15′

4.2. IR, NMR, and UV-Vis measurements

The IR, ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively. UV-Vis spectra were taken on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Perkin-Elmer PTP6 (Peltier temperature programmer) apparatus.

The elemental analysis of the synthesized complexes was carried out using an Elementar CHN "CUBO micro Vario" analyzer.

4.3. Kinetic measurements by ^1H NMR technique

The isomerisation reaction was studied by ^1H NMR by dissolving the complex **1a** in 0.6 ml of $CDCl_3$ ($[Complex]_0 \approx 1.22 \times 10^{-2}$ mol dm^{-3}), adding a stoichiomeric amount of IBr ([**1a**]/[IBr] = 1/1.05) at 298 K and monitoring the signal for the disappearance of the starting complex.

The reactions between complexes **3** and Br_2 were studied by ^1H NMR by dissolving the complex under study in 0.6 ml of $CDCl_3$ ($[Complex]_0 \approx 1.2 \times 10^{-2}$ mol dm^{-3}), adding microaliquots of a concentrated $CDCl_3$ solution of bromine ($[Br_2] \approx 1.18 \times 10^{-1}$ mol dm^{-3}) and monitoring the signal for the disappearance of the starting complex and the concomitant appearance of the final products. The halftime of each reaction ($t_{1/2}$) was detected and taken as a measure of reactivity.

4.4. Data analysis

Non linear analysis of the data related to equilibrium and

kinetics measurements was performed by locally adapted routines written in ORIGIN® 7.5 environments.

4.5. Synthesis of the complexes

As already stated the ligands [7] and the complexes **1** [8] were synthesized according to published procedures.

4.6. Crystal structure determinations

The crystal data of compounds **4b** and **3b** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation. The data sets were integrated with the Denzo-SMN package [16] and corrected for Lorentz, polarization and absorption effects (SORTAV) [17]. The structures were solved by direct methods using SIR97 [18] system of programs and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms.

All calculations were performed using SHELXL-97 [19] and PARST [20] implemented in WINGX [21] system of programs.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1437243 and 1437243. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, Union Road, Cambridge, CB2 1EZ, UK [fax (+44) 1223-336033, e-mail: deposit@ccdc.cam.ac.uk]:

4.7. Computational details

The geometrical optimization of the complexes was carried out without symmetry constraints, using the hyper-GGA functional MO6 [22,23], in combination with polarized triple-ζ-quality basis sets (LAN2TZ(f)) [24,25] and relativistic pseudopotential for the Pd atoms, a polarized double-ζ-quality basis sets (LANL2DZdp) [26] with diffuse functions for the halogen atoms and a polarized double-ζ-quality basis sets (6-31G(d,p)) for the other elements. Solvent effects (acetonitrile, $\varepsilon = 37.5$) were included using CPCM [27,28].

The "restricted" formalism was applied in all the calculations. By means of the stationary points characterized by IR simulation, the zero-point vibrational energies and thermodynamic parameters were obtained [29].

The software used was Gaussian '09 [11] and all the computational work was carried out on Intel based x 86-64 workstations. The cartesian coordinates of the computed species are reported in Table 1 SM (Supplementary material).

4.8. Synthesis of complex *2a*

To 10 ml solution of 0.10 g (0.19 mmol) of complex **1a** in anhydrous CH_2Cl_2, 0.0592 g (0.23 mmol) of I_2 dissolved in 5 ml of anhydrous CH_2Cl_2 was added under inert atmosphere (Ar). The resulting solution was stirred for 10 min and evaporated to small volume (ca 5 ml) under vacuum.

The title complex was precipitated by diethylether, filtered off on a gooch, washed with diethylether and *n*−pentane and dried under vacuum. 0.1428 g (yield 97%) of complex **2a** was obtained as yellow microcrystalline solid.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.31 (s, 3H, SCH_3), 3.72 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.03 (d, J = 16.1, 1H, SCH_2), 4.63 (d, J = 16.1, 1H, SCH_2), 7.40 (dd, 1H, J = 7.8, 5.4 Hz, 5-pyr), 7.55 (d, J = 7.8 Hz, 1H, 3-pyr), 7.89 (td, J = 7.7, 1.7 Hz, 1H, 4-pyr), 9.61 (d, J = 5.4 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.2 (CH_3, SCH_3), 45.3 (CH_2, SCH_2), 52.5 (CH_3, OCH_3), 52.5 (CH_3, OCH_3), 53.2 (CH_3, OCH_3), 53.9 (CH_3, OCH_3), 103.2 (C, C═CI), 124.2 (CH, 3-Pyr), 125.0 (CH, 5-Pyr), 132.1 (C, C═C), 139.3 (CH, 4-Pyr), 145.3 (C, C═C), 155.5 (C, 6-Pyr), 157.1 (C, C═C), 158.2 (CH, 2-Pyr), 159.6 (C, C═O), 165.8 (C, C═O), 167.1 (C, C═O), 172.8 (C, C═O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1725 cm^{-1}.

Anal. Calcd for $C_{19}H_{21}I_2NO_8PdS$: C, 29.12; H, 2.70; N, 1.79. Found: C, 29.22; H, 2.63; N, 1.81.

The synthesis of the complexes **2b** and **2c** was carried out following a procedure similar to that described for complex **2a**.

4.9. Synthesis of complex *2b*

Yellow microcrystals. Yield 92%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 1.37 (s, 9H, $C(CH_3)_3$) 3.72 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.08 (d, J = 16.9, 1H, SCH_2), 4.88 (d, J = 16.9, 1H, SCH_2), 7.30 (dd, 1H, J = 7.8, 5.1 Hz, 5-pyr), 7.46 (d, J = 7.8 Hz, 1H, 3-pyr), 7.81 (td, J = 7.7, 1.7 Hz, 1H, 4-pyr), 9.61 (d, J = 5.1 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.4 (CH_3, $C(CH_3)_3$), 41.7 (CH_2, SCH_2), 51.5 (CH_3, OCH_3), 52.1 (CH_3, OCH_3), 52.2 (CH_3, OCH_3), 53.5 (CH_3, OCH_3), 54.0 (C, $C(CH_3)_3$), 103.3 (C, C═CI), 121.9 (CH, 3-Pyr), 124.1 (CH, 5-Pyr), 133.8 (C, C═C), 138.8 (CH, 4-Pyr), 145.2 (C, C═C), 154.7 (C, 6-Pyr), 155.1 (C, C═C), 159.6 (CH, 2-Pyr), 159.9 (C, C═O), 164.4 (C, C═O), 166.7 (C, C═O), 172.2 (C, C═O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1717 cm^{-1}.

Anal. Calcd for $C_{22}H_{27}I_2NO_8PdS$: C, 32.00; H, 3.30; N, 1.70. Found: C, 32.13; H, 3.21; N, 1.78.

4.10. Synthesis of complex *2c*

Yellow microcrystals. Yield 70%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 3.61 (bs, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.26 (d, J = 16.7, 1H, SCH_2), 5.07 (d, J = 16.7, 1H, SCH_2), 7.26–7.38 (m, 5H, 5-pyr, 3-pyr, Ph), 7.67–7.75 (m, 3H, 4-pyr, Ph), 9.64 (d, J = 5.2 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 48.3 (CH_2, SCH_2), 51.6 (CH_3, OCH_3), 52.1 (CH_3, OCH_3), 53.5 (CH_3, OCH_3), 53.6 (CH_3, OCH_3), 103.1 (C, C═CI), 123.1 (CH, 3-Pyr), 124.4 (CH, 5-Pyr), 129.5 (CH, Ph), 130.0 (C, Ph), 130.2 (CH, Ph), 131.7 (CH, Ph), 132.3 (C, C═C), 138.7 (CH, 4-Pyr), 154.6 (C, 6-Pyr), 155.5 (C, C═C), 157.8 (CH, 2-Pyr), 159.1 (C, C═O), 165.4 (C, C═O), 166.3 (C, C═O), 171.2 (C, C═O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1718 cm^{-1}.

Anal. Calcd for $C_{24}H_{23}I_2NO_8PdS$: C, 34.08; H, 2.74; N, 1.66. Found: C, 33.96; H, 2.78; N, 1.62.

4.11. Synthesis of complex *3a*

To 10 ml of refrigerated solution (273 K) of 0.0932 g (0.17 mmol) of complex **1a** in anhydrous CH_2Cl_2, 0.0367 g (0.23 mmol) of Br_2 dissolved in 5 ml of anhydrous CH_2Cl_2 was added under inert atmosphere (Ar). The resulting solution was stirred for 5 min and evaporated to small volume (ca 5 ml) under vacuum.

The title complex was precipitated by diethylether, filtered off on a gooch, washed with diethylether and *n*−pentane and dried under vacuum. 0.1105 g (yield 91%) of complex **3a** was obtained as yellow microcrystalline solid.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.40 (s, 3H, SCH_3), 3.73 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.98 (d, J = 16.9, 1H, SCH_2), 4.67 (d, J = 16.9, 1H, SCH_2), 7.39 (dd, 1H, J = 7.7, 5.1 Hz, 5-pyr), 7.51 (d, J = 7.7 Hz, 1H, 3-pyr), 7.86 (td, J = 7.7, 1.6 Hz, 1H, 4-pyr), 9.38 (d, J = 5.1 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.6 (CH_3, SCH_3), 45.6 (CH_2, SCH_2), 52.6 (CH_3, OCH_3), 52.6 (CH_3, OCH_3), 53.8 (CH_3, OCH_3), 53.9 (CH_3, OCH_3), 124.0 (CH, 3-Pyr), 124.3 (C, C═CBr), 124.7 (CH, 5-Pyr), 129.4 (C, C═C), 139.5 (CH, 4-Pyr), 139.7 (C, C═C), 152.9 (C, 6-

Pyr), 157.9 (CH, 2-Pyr), 159.3 (C, C=C), 160.2 (C, C=O), 165.3 (C, C=O), 166.5 (C, C=O), 172.6 (C, C=O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1727 cm^{-1}.

Anal. Calcd for $C_{19}H_{21}Br_2NO_8PdS$: C, 33.09; H, 3.07; N, 2.03. Found: C, 33.22; H, 3.01; N, 1.95.

The synthesis of the complexes **3b** and **3c** was carried out following a procedure similar to that described for complex **3a**.

4.12. Synthesis of complex *3b*

Yellow microcrystals. Yield 84%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 1.38 (s, 9H, C(CH_3)$_3$) 3.71 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.07 (d, J = 16.9, 1H, SCH_2), 4.84 (d, J = 16.9, 1H, SCH_2), 7.34 (dd, 1H, J = 7.8, 5.1 Hz, 5-pyr), 7.47 (d, J = 7.8 Hz, 1H, 3-pyr), 7.83 (td, J = 7.7, 1.7 Hz, 1H, 4-pyr), 9.37 (d, J = 5.1 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.3 (CH_3, C(CH_3)$_3$), 41.7 (CH_2, SCH_2), 51.7 (CH_3, OCH_3), 52.1 (CH_3, OCH_3), 52.3 (C, *C*(CH_3)$_3$), 53.4 (CH_3, OCH_3), 53.6 (CH_3, OCH_3), 121.7 (CH, 3-Pyr), 123.9 (CH, 5-Pyr), 124.1 (C, C=CBr), 131.5 (C, C=C), 139.1 (CH, 4-Pyr), 139.2 (C, C=C), 152.2 (C, 6-Pyr), 156.4 (C, C=C), 159.3 (CH, 2-Pyr), 160.7 (C, C=O), 165.0 (C, C=O), 167.0 (C, C=O), 172.0 (C, C=O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1715; 1740 cm^{-1}.

Anal. Calcd for $C_{22}H_{27}Br_2NO_8PdS$: C, 36.11; H, 3.72; N, 1.91. Found: C, 35.97; H, 3.81; N, 1.83.

4.13. Synthesis of complex *3c*

Yellow microcrystals. Yield 86%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 3.60 (bs, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.88 (s, 6H, OCH_3), 4.23 (d, J = 16.3, 1H, SCH_2), 5.02 (d, J = 16.3, 1H, SCH_2), 7.29–7.40 (m, 5H, 5-pyr, 3-pyr, Ph), 7.68–7.79 (m, 3H, 4-pyr, Ph), 9.40 (d, J = 5.3 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 49.0 (CH_2, SCH_2), 51.7 (CH_3, OCH_3), 52.1 (CH_3, OCH_3), 53.5 (CH_3, OCH_3), 53.5 (CH_3, OCH_3), 123.1 (CH, 3-Pyr), 124.1 (C, C=CBr), 124.2 (CH, 5-Pyr), 129.4 (C, C=C), 129.6 (CH, Ph), 129.8 (C, Ph), 130.5 (CH, Ph), 132.0 (CH, Ph), 139.1 (CH, 4-Pyr), 139.4 (C, C=C), 152.1 (C, 6-Pyr), 157.5 (CH, 2-Pyr), 157.7 (C, C=C), 159.7 (C, C=O), 165.0 (C, C=O), 166.4 (C, C=O), 171.0 (C, C=O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1717 cm^{-1}.

Anal. Calcd for $C_{24}H_{23}Br_2NO_8PdS$: C, 38.35; H, 3.08; N, 1.86. Found: C, 38.44; H, 3.12; N, 1.71.

4.14. Synthesis of complex *4a*

To 10 ml solution of 0.0803 g (0.15 mmol) of complex **1a** in anhydrous CH_2Cl_2, 1.039 μl (0.17 mmol) of a solution prepared by dissolving 0.0519 g (0.32 mmol) of ICl in 2 ml of anhydrous CH_2Cl_2 was added under inert atmosphere (Ar). The resulting solution was stirred for 5 min and evaporated to small volume (ca 5 ml) under vacuum.

The title complex was precipitated by diethylether, filtered off on a gooch, washed with diethylether and *n*–pentane and dried under vacuum. 0.0862 g (yield 82%) of complex **4a** was obtained as yellow microcrystalline solid.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.43 (s, 3H, SCH_3), 3.73 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.97 (d, J = 16.3, 1H, SCH_2), 4.64 (d, J = 16.3, 1H, SCH_2), 7.41 (dd, 1H, J = 7.7, 5.5 Hz, 5-pyr), 7.51 (d, J = 7.7 Hz, 1H, 3-pyr), 7.88 (td, J = 7.7, 1.6 Hz, 1H, 4-pyr), 9.20 (d, J = 5.5 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.5 (CH_3, SCH_3), 45.2 (CH_2, SCH_2), 52.1 (CH_3, OCH_3), 52.2 (CH_3, OCH_3), 53.2 (CH_3, OCH_3), 53.4 (CH_3, OCH_3), 103.1 (C, C=CI), 123.4 (CH, 3-Pyr), 124.0 (CH, 5-Pyr), 132.0 (C, C=C), 138.8 (C, C=C), 139.1 (CH, 4-Pyr), 151.0 (C, 6-Pyr), 155.0 (C, C=C), 157.1 (CH, 2-Pyr), 159.5(C, C=O), 165.3 (C, C=O), 166.8 (C, C=O), 172.0 (C, C=O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1730 cm^{-1}.

Anal. Calcd for $C_{19}H_{21}ClINO_8PdS$: C, 32.97; H, 3.06; N, 2.02. Found: C, 33.12; H, 3.18; N, 1.88.

The synthesis of the complexes **4b** and **4c** was carried out following a procedure similar to that described for complex **4a**.

4.15. Synthesis of complex *4b*

Yellow microcrystals. Yield 86%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 1.39 (s, 9H, C(CH_3)$_3$) 3.72 (s, 3H, OCH_3), 3.81 (bs, 3H, OCH_3), 3.86 (bs, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.05 (d, J = 16.9, 1H, SCH_2), 4.83 (d, J = 16.9, 1H, SCH_2), 7.38 (dd, 1H, J = 7.7, 5.1 Hz, 5-pyr), 7.47 (d, J = 7.8 Hz, 1H, 3-pyr), 7.85 (td, J = 7.7, 1.7 Hz, 1H, 4-pyr), 9.16 (bs, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.3 (CH_3, C(CH_3)$_3$), 41.7 (CH_2, SCH_2), 51.8 (CH_3, OCH_3), 52.1 (CH_3, OCH_3), 52.3 (C, *C*(CH_3)$_3$), 53.4 (CH_3, OCH_3), 53.4 (CH_3, OCH_3), 103.1 (C, C=CI), 121.7 (CH, 3-Pyr), 123.7 (CH, 5-Pyr), 134.0 (C, C=C), 139.2 (CH, 4-Pyr), 139.4 (C, C=C), 150.8 (C, 6-Pyr), 151.0 (C, C=C), 159.0 (CH, 2-Pyr), 160.2 (C, C=O), 164.3 (C, C=O), 165.2 (C, C=O), 167.3 (C, C=O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1713, 1733 cm^{-1}.

Anal. Calcd for $C_{22}H_{27}ClINO_8PdS$: C, 35.98; H, 3.71; N, 1.91. Found: C, 35.87; H, 3.79; N, 1.74.

4.16. Synthesis of complex *4c*

Pale yellow microcrystals. Yield 90%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 3.65 (bs, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.85 (bs, 6H, OCH_3), 4.23 (d, J = 16.1, 1H, SCH_2), 4.98 (d, J = 16.1, 1H, SCH_2), 7.28–7.41 (m, 5H, 5-pyr, 3-pyr, Ph), 7.67–7.70 (m, 2H, Ph), 7.79 (td, J = 7.7, 1.6 Hz, 1H, 4-pyr), 9.22 (d, J = 5.5 Hz, 1H, 6-pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 48.9 (CH_2, SCH_2), 51.7 (CH_3, OCH_3), 52.1 (CH_3, OCH_3), 53.3 (CH_3, OCH_3), 53.4 (CH_3, OCH_3), 103.6 (C, C=CI), 122.9 (CH, 3-Pyr), 124.0 (CH, 5-Pyr), 129.6 (CH, Ph), 129.8 (C, Ph), 130.5 (CH, Ph), 131.9 (CH, Ph), 132.5 (C, C=C), 138.7 (C, C=C), 139.1 (CH, 4-Pyr), 150.8 (C, 6-Pyr), 157.2 (CH, 2-Pyr), 158.7 (C, C=C), 159.5 (C, C=O), 165.6 (C, C=O), 167.0 (C, C=O), 170.9 (C, C=O).

IR (KBr, pellet): $\nu_{C\equiv O}$ = 1705 cm^{-1}.

Anal. Calcd for $C_{24}H_{23}ClINO_8PdS$: C, 38.22; H, 3.07; N, 1.86. Found: C, 38.37; H, 2.91; N, 1.83.

4.17. Synthesis of complex *5a*

To 10 ml solution of 0.0730 g (0.138 mmol) of complex **1a** in anhydrous CH_2Cl_2, 0.0342 g (0.165 mmol) of IBr dissolved in 5 ml of anhydrous CH_2Cl_2 was added under inert atmosphere (Ar). The resulting solution was stirred for 5 min and evaporated to small volume (ca 5 ml) under vacuum. The title complex was precipitated by diethylether, filtered off on a gooch, washed with diethylether and *n*–pentane and dried under vacuum. 0.0991 g (yield 98%) of complex **5a** was obtained as yellow microcrystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 2.40 (s, 3H, SCH_3), 3.73 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.98 (d, J = 16.2 Hz, SCH_2), 4.67 (d, J = 16.2 Hz, SCH_2), 7.39 (dd, 1H, J = 7.7, 4.9 Hz, H^5), 7.52 (d, 1H, J = 7.7, Hz, H^3), 7.86 (dd, 1H, J = 7.7, 1.6 Hz, H^4), 9.38 (d, 1H, J = 4.9 Hz, H^6).

^{13}C{^{1}H}-NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.1 (CH_3, SCH_3), 45.0 (CH_2, SCH_2), 52.1 (CH_3, OCH_3), 53.4 (CH_3, OCH_3), 123.5 (CH, C^3), 124.2 (CH, C^5), 139.0 (CH, C^4), 152.4 (CH, C^6), 157.4 (CH, C^2), 159.4 (C, C=O), 164.7 (C, C=O), 165.3 (C, C=O), 172.1 (C, C=O); the fours signals C, (C=C) not detectable.

IR (KBr, pellet): $\nu_{C\equiv O} = 1725\ cm^{-1}$.

Anal. Calcd for $C_{19}H_{21}BrINO_8PdS$: C, 30.98; H, 2.87; N, 1.90. Found: C, 31.11; H, 2.99; N, 1.74.

The diene (1E,2E)−tetramethyl−1,4−dibromobuta−1,3−diene −1,2,3,4−tetracarboxylate (DBBD) was extracted from the dried reaction mixture using diethylether and identified from its ^1H NMR spectrum in $CDCl_3$ (See Fig. 6b SM in Supplementary).

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 3.81 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3).

Complex **5a**′ was not isolated from the equilibrium mixture.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.02.011.

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