The addition of halogens and interhalogens on palladacyclopentadienyl complexes bearing quinolyl-thioether as spectator ligands. A kinetic and computational study

L. Canovese, F. Visentina, T. Scattolina, C. Santo, V. Bertolasi

A Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca’ Foscari, Venice, Italy
B Dipartimento di Chimica e Centro di Strutturistica Diffrattometrica, Università di Ferrara, Ferrara, Italy

Abstract

We have studied the oxidative addition of halogens (I₂ and Br₂) and interhalogens (ICl and IBr) on complexes of the type \[\text{[Pd(thioquinoline)C}_4\text{(COOMe)}_4]\], (thioquinoline = 8-(methylthio)quinoline, 8-(t-butylthio)quinoline, 2-methyl-8-(methylthio)quinoline, 2-methyl-8-(t-butylthio)quinoline).

The expected palladium/thioquinoline-\(\sigma\)-butadienyl derivatives have been obtained by the stoichiometric addition of I₂ and Br₂ to a solution of the starting palladacyclopentadienyl complexes. The bromine in excess induces the extrusion of the di-bromo-(E, E)-\(\sigma\)-butadiene and the formation of the thioquinoline palladium(II) di-bromide species. The kinetics and mechanism of these reactions have been determined.

Except for one case which was analyzed in detail by a computational study, the oxidative addition of the interhalogens ICl and IBr yields the species that is less predictable from the thermodynamic point of view. In general the computational approach justifies the reaction progress and allows an interpretative clue suggesting a kinetically governed path to the reaction products.

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

1. Introduction

Owing to their potential ability to give \(\sigma\)-butadienyl derivatives as the products of the oxidative addition of organic halides or halogens, palladacyclopentadienyl complexes have often been studied from the catalytic [1] and stoichiometric [2] point of view. The reaction entails the Pd(II)–Pd(IV)–Pd(II) conversion which was by far less studied than that involving the Pd(0)–Pd(II) process [3]. For such a reason we think that any attempts at shedding light on the still debated Pd(IV) intermediate should be of remarkable interest. Moreover, the possibility to obtain dienes with a Z–Z configuration by further addition of organic halides or halogens to the \(\sigma\)-butadienyl complexes extends the range of synthetic available methodologies based on acetylene coupling [4]. In this respect we have recently published three studies of the reactivity of some palladacyclopentadienyl complexes bearing isocyanides, phosphoquinolines and pyridylthioethers as ancillary ligands with halogens and interhalogens. In any case we have obtained interesting results. In the first study we have measured the rates of intramolecular conversion of the intermediate \(\text{trans-diiodo palladium(IV)}\) into the \(\text{cis-diisocyanide-tetramethyl pallada-1iodo-buta-1,3-diene-1,2,3,4-tetracarboxylate}\) and its subsequent isomerisation to the \(\text{trans-isomer}\) [2d]. The second investigation was characterized by the peculiar evolution of the initially formed \(\sigma\)-butadienyl complex, consisting in an intermolecular attack of the phosphorus originally coordinated to the metal on the \(\text{sp}^2\) carbon of the \(\sigma\)-butadienyl fragment with the consequent widening of the phosphoquinoline coordinating ring and the unexpected final formation of a zwitterionic species (Scheme 1) [2e].

Finally, we have studied the palladacyclopentadienyl complexes bearing pyridylthioethers as spectator ligands reacting with halogens and interhalogens to give the \(\sigma\)-butadienyl derivatives as final products. However, in the case of interhalogens the final product was not the predictable one but rather the less thermodynamically stable species [2h].

The intriguing aspects of these studies prompted us to undertake a further investigation on palladacyclopentadienyl complexes bearing thio-quinoline based spectator ligands reacting with halogens and interhalogens. In the present study, we tried to establish how the combination between the structure of the ancillary ligand...
and the sulfur atom might influence the overall reactivity of the complexes themselves and investigate whether the formation of the less stable σ-butaadienyl and/or zwitterionic species can be considered a general trend. Furthermore, we have studied the kinetics in detail and surmised a plausible mechanism for the reaction between the σ-butaadienyl complexes and Br₂ in excess leading to the extrusion of 1,4-dibromobuta-1,3-diene.

The ligands, the investigated complexes, the halogens, the intermediates and the products of the oxidative addition are reported in Scheme 2.

2. Results and discussion

2.1. General remarks

The ligands TMQ, TTQ [5], TMQ-Me [6], TTQ-Me [7], the polymer [PdC₄(COOMe)]ₙ [8] and complex 1c [6] were obtained according to published protocols. The complexes 1a, b, d are newly synthesized species and were obtained by adding a small excess of the appropriate ligand to the polymer [PdC₄(COOMe)]ₙ in inert atmosphere in anhydrous acetone. The formation of the complexes 1a–d is deduced from their NMR spectra which display all the signals of the ligands and carboxymethyl groups at different frequencies than those of the uncoordinated ones. In particular, owing to the ditopicity of the spectator ligands, the COOMe groups resonate as four distinct signals within 3.5–4.0 ppm (see Section 4 and Fig. 1 SM in Supplementary Material).

2.2. Reactivity of complexes 1a–d with I₂ and Br₂

Addition under inert atmosphere of a stoichiometric amount of I₂ or Br₂ to a solution of complexes 1a–c in anhydrous CH₂Cl₂ yields the (Z, Z)-σ-butaadienyl derivatives 2a–d or 3a–d, respectively. The reactions are fast and complete as can be seen from the immediate decolorization of the reaction mixture. A stoichiometric amount of halogens is crucial since an excess especially in the immediate decolorization of the reaction mixture. A stoichiometric amount of halogens is crucial since an excess of halogens and the products of the oxidative addition are reported in Scheme 2.

In summary, the thioquinoline palladacyclopentadienyl complexes behave very similarly to the analogous pyridyldithioether derivatives when reacting with halogens. In the Supplementary Material (Fig. 4 SM) we report the results of a computational study related to the energy involved in the above described reactions which parallels and confirms the results we and other authors have obtained in previously published articles [2b,2h]. In particular it is noteworthy that:

(i) The σ-butaadienyl derivatives are more stable than the starting reagents (Fig. 4a, b SM, [2b,2h]).

(ii) The reactions of the palladacyclopentadienyl complexes with Br₂ are thermodynamically favored with respect to those with I₂ (Fig. 4a, b SM, [2b,2h]).

(iii) Owing to the energy difference between the two possible isomers, the opening of the pentadienyl ring only occurs trans to the thioquinoline sulfur with the consequent formation of only one regioisomer (Fig. 4c, d SM, [2h]).

2.3. Reactivity of complexes 1a–d with ICl and IBr

The thioquinoline derivatives react with the interhalogens ICl and IBr to give selectively the isomers bearing Cl and Br, respectively coordinated to palladium, whereas I is in any case obviously bound to the terminal dienyl carbon. Remarkably, the displacement of pentadienyl ring again takes place trans to the thioquinoline sulfur (see Scheme 2). Therefore, only one of the four possible isomers is obtained in any case considered and these findings confirm the previously observed results obtained with the pyridyldithioether derivatives [2h].

The ¹H NMR spectra of the complexes 4 and 5 confirms the nature of the isomers since the resonance of the quinolyl H² in the interval 9.64–9.74 and 9.85–9.96 ppm is typical of a complex bearing a chlorine or bromide cis to quinoline ring, respectively. [[2h] and Refs. therein] (see also Section 4 and Fig. 6 SM in Supplementary Material section). Moreover the ¹³C low-field resonance of the terminal butadienyl carbon at ca. 100 ppm (≈C=I) is a further indication that the complexes with the bromide or chloride coordinated to palladium are formed.

In the case of complex 4a we were able to obtain crystals suitable for a diffractometric determination of its solid state structure which is reported in Fig. 2. Again, the structure will be discussed further on.

The regioisomers 4a–d are stable and isolable and a slow isomerization process is detectable only after different but in any case significant time intervals.

As for the derivatives obtained by adding IBr to 1a–d complexes, only the species 5a, b, d can be separated pure from the reaction mixture. However the latter display an enhanced tendency to isomerise to the most stable isomer (i.e. with 1
coordinated to palladium) with respect to that of the ICl derivatives. This tendency is particularly remarkable in the case of the reaction between $1c$ and IBr when, complex $5c$ cannot be separated pure.

We surmise that the formation of $4a$–$d$ and $5a$, $b$, $d$ is kinetically controlled as can be deduced from a detailed computational study whose results are shown in Fig. 3 and in Fig. 7 SM in Supplementary.

It is apparent that in these cases the formation of the less thermodynamically stable regioisomer is promoted by the smaller energy required to achieve the Transition State (TS), owing to the hardness of the Pd(IV) which favors the Pd–Cl (reaction with ICl) or the Pd–Br (reaction with IBr) bond. Remarkably, the energy gap required for the formation of the TS yielding the complex $4a$ is considerably higher than that required for the $5a$ derivative.

Notably, the lower stability of the isomers $4$ and $5$ justifies the successive slow rearrangement into the species $4$ and $5$ bearing iodide coordinated to palladium as experimentally observed in the case of the complexes $4$ and $5$.

2.4. Reactivity of type 1 complexes with Br₂ in excess

The extrusion of organic fragments coordinated to transition metals using molecular halogens is a well established synthetic strategy. In particular our and other research groups have been involved in the reaction between halogens and pallada-ơ-butadienyl complexes yielding di-halobutadiene species with Z–Z structure which are easily accessible for further synthetic strategy [2h,4]. In this respect, we have recently reported a hypothetical mechanism for the reaction between the pyridylthioether pallada-ơ-butadienyl bromide complexes and Br₂ yielding the extrusion of 1,4-dibromobuta-1,3-diene (DBBD) [2h]. In order to determine the intimate mechanism governing this sort of reactions, we have carried out a more detailed mechanistic investigation involving the thioquinoline derivatives reported in the present study. The reaction, the starting species, the reaction products and the suggested intermediates are represented in the following Scheme 3.

It is noteworthy that the DBBD compound can be easily separated by extraction with diethylether from the dried reaction
mixture, whereas the complexes 6a, c, d in the residual are easily characterized.

From a preliminary screening, complex 3c emerged as the most suitable complex for a detailed mechanistic study thank to the clearness of the \(^1\)H NMR signals and the measurable reaction rates recorded under variable bromine concentrations. (see Figs. 9 SM and 10 SM in Supplementary).

As can be deduced from the Figs. 9 SM and 10 SM the single reaction can be described by a first-order process of the type:

\[ \frac{d[3c]}{dt} = k_{II}[Br_2] \cdot (\text{obs}) \]

The dependence between the ensuing \( k_{\text{obs}} \) and \([Br_2]\) is linear with no statistically significant intercept and obeys to the equation:

\[ k_{\text{obs}} = k_{II}[Br_2] \]

Under the reasonable hypothesis that complexes 3a and 3d react analogously, in order to obtain a complete view of the problem we have carried out a kinetic analysis based on a single measurement by reacting the above cited complexes with a tenfold excess of \( Br_2 \) and calculated the \( k_{II} \) by dividing the fitted \( k_{\text{obs}} \) by the bromine concentration (see Fig. 11 SM in Supplementary). The resulting \( k_{II} \) values are reported in the following Table 1.

Furthermore, we have computed the energies involved in the process under study (see Fig. 12 SM in Supplementary). Since no intermediate is experimentally detectable and on the basis of the calculated energies, we surmise that the steady state approximation (\( k_r + k_2 \) \( \gg k_1 \)) can be applied to the process described in Scheme 2.

In this case the rate law becomes:

\[ \frac{d[3]}{dt} = k_{II}[Br_2] \cdot (\text{obs}) \]

The above suggested steady state approximation fits nicely with the experimental results summarized in Table 1. The bulky complex 3d reacts slower than 3a and 3c, the latter being the fastest. It is well known that the methyl substituent in position 2 of the pyridine ring in ligands of the type N–S or N–P induces a distortion on the main plane of the square planar complexes which favors the attack to the central metal [6,9]. Thus, the attack at the distorted complex 3c gives the less energetic intermediate and therefore 3c becomes the most reactive species. As similar conclusion is suggested by the reactivity of complex 3d since its measurable reaction rate, though the lowest, depends on the distortion of its spectator ligand TTBQ-Me. Remarkably, the reaction rate of the bulky but undistorted complex 3b is very low and complicated by incipient decomposition.

The computational results related to this sort of reaction are reported in Fig. 12 SM in Supplementary.

2.5. Reactivity of type 1 complexes with I\(_2\) in excess

The experimentally observed inertness of the complexes 2 toward oxidative addition of \( I_2 \) somehow matches with the computational results. As a matter of fact, only the most reactive complex 2c reacts with \( I_2 \) in excess to give in some days a reaction mixture in which some unreacted starting complex can still be detected. As can be deduced from the calculated energies, the gaps among the starting complexes, the intermediate and the TS are higher than those previously calculated for complexes 3 reacting with \( Br_2 \). Moreover, the small difference in energy between the starting complex and the reaction products justifies the experimentally observed final equilibrium mixture (see Fig. 13 SM in Supplementary).

2.6. Crystal structure determinations

ORTEP [10] views of the isostructural complexes 3a and 4a are shown in Figs. 1 and 2. A selection of bond distances and angles
is given in Table 1 SM (Supplementary Material). Both complexes adopt similar structures except for the presence of two Br atoms in complex 3a instead of a Cl atom bonded to a central Pd1 and an I atom on the butadiene substituted ligand in complex 4a.

The geometry around the Pd centers is slightly distorted square planar where the four positions are occupied by a halogen atom, Br in 3a or Cl in 4a, the nitrogen and the sulfur of the thio-methylquinoline ligand and the carbon C9 of the 1,2,3,4 tetrakis(methoxy-
carbonyl) buta-1,3-diene-4-Br(or I)-1-yl ligand. The C11=C12-C13=C14 buta-1,3-diene moieties display anti-clinal conformations with torsion angles of $-118.3(3)^\circ$ and $-109(1)^\circ$ in 3a and 4a, respectively. Both complexes, in the crystal packings, display short Halo-gen…Oxygen contacts [11–13]: Br2...O3 (x+1, y, z) = 3.209 Å in 3a and I1...O3 (1-x, 1-y, 2-z) = 2.965(8) Å in 4a.

3. Conclusion

We have synthesized some palladacyclopentadienyl derivatives bearing differently substituted thioquinolines as spectator ligands. The palladacyclopentadienyl complexes were reacted with halogens (I2 and Br2) and interhalogens (ICl and IBr) to give the thioquinolines as spectator ligands. Both complexes, in the crystal packings, display short Halo-gen…Oxygen contacts [11–13]: Br2...O3 (x+1, y, z) = 3.209 Å in 3a and I1...O3 (1-x, 1-y, 2-z) = 2.965(8) Å in 4a.

4. Experimental

4.1. Solvents and reagents

All the following distillation processes were carried out under inert atmosphere (Argon). Acetone and CH3Cl were distilled over 4 Å molecular sieves and CaH2, respectively. THF was carefully dried by distillation over Na/benzoquinone. All other chemicals were commercially available grade products and were used as purchased.

4.2. IR, NMR, UV–Vis measurements and elemental analysis

The IR, 1H, 13C and 31P 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

The reactions between complexes 3 and Br2 were studied by 1H NMR by dissolution the complex under study in 0.6 ml of CDCl3 ([Complex]0 $\approx 1.2 \times 10^{-2}$ mol dm$^{-3}$), adding microaliquots of a concentrated CDCl3 solution of bromine ([Br2] $\approx 1.2 \times 10^{-1}$ mol dm$^{-3}$) and monitoring the signal for the disappearance of the starting complex and the concomitant appearance of the final products.

4.4. Data analysis

Non linear regression analysis of the data related to kinetics measurements was performed by locally adapted routines written in the ORIGIN® 7.5 environment.

4.5. Crystal structure determinations

The crystal data of compounds 3a and 4a 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 [14] and corrected for Lorentz, polarization and absorption effects [SORTAV] [15]. The structures were solved by direct methods using SIR97 [16] 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. The crystal of 4a contains disordered molecules of solvent in the asymmetric unit: a molecule of CH3Cl which was refined with occupancy of 1/2 and a molecule of water which was split over two positions and refined with occupancy of 1/2 each.

All calculations were performed using SHELXL-97 [17] and PARST [18] implemented in WINGX [19] system of programs. The crystal data are given in Table 2 SM (Supplementary Material).

4.6. Computational details

In order to save computer time we have replaced the carboxymethyl group COOMe by the less disordered CN fragment in the complexes under study and in the following discussion the CN derivatives will maintain the same labels as the original complexes albeit in italics (4a, 5a becomes 4a and 5a, respectively). 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.

Remarkably, our experimental results were not in contrast with the computational study carried out by the GAUSSIAN 09 program [20] and despite the implicit limitations ($\Delta AG^0 \approx \pm 2$ kcal/mol and the replacement of COOMe with CN groups), we have obtained a confirmation and hence a possible explanation of the observed trend.

The geometrical optimization of the complexes was carried out without symmetry constraints, using the hyper-GGA functional M06 [21,22], in combination with polarized triple-$\zeta$-quality basis sets (LANZTZ(f)) [23,24] and relativistic pseudopotential for the Pd atoms, a polarized double-$\zeta$-quality basis sets (LANL2DZdp) [25] with diffuse functions for the halogen atoms and a polarized double-$\zeta$-quality basis sets (6-31G(d,p)) for the other elements. Solvent effects (acetonitrile, $\varepsilon = 37.5$) were included using PCM [26,27].

The “restricted” formalism was applied in all the calculations. The zero-point vibrational energies and thermodynamic parameters were obtained [28] by means of the stationary points characterized by IR simulation.

All the computational work was carried out on Intel based x86-64 workstations.

4.7. Synthesis of the complexes

As already stated the ligands TMQ, TTBQ [5], TMQ-Me [6], TTQB-Me [7], the polymer [Pd4(COOMe)4]In [8] and the complex 1c [6] have been synthesized according to published procedures. The synthesis and characterization of all the other complexes are reported in the following experimental part. The atom numbering
scheme related to the complexes described in this section is established in Scheme 2.

4.7.1. Synthesis of complex 1a

A solution of 0.20 g (0.51 mmol) of complex [PdC6(COOME)4]n and 0.0999 g (0.57 mmol) of TMQ in 20 ml of anhydrous acetone were stirred under inert atmosphere (Ar) for 1 h. The solution was then evaporated to small volume (ca. 5 ml) under vacuum.

Complex 1a was precipitated by slow addition of diethylether, filtered off on a gooch, washed with diethylether and n-pentane and dried under vacuum. 0.2498 g (yield 83%) of the title complex was obtained as yellow microcrystalline solid.

\[ \text{IR (KBr pellets): } \nu_{C=O} 1728, 1700, 1683 \text{ cm}^{-1}. \]

4.10. Synthesis of complex 2a

To 0.10 g (0.177 mmol) of complex 1a dissolved in 10 ml of anhydrous CH3Cl2, 0.0559 g (0.022 mmol) of I2 dissolved in 5 ml of anhydrous CH3Cl2 was added under inert atmosphere (Ar). The resulting mixture instantaneously decolorized, was stirred for further 10 min and then concentrated to small volume under vacuum. Addition of diethyl ether induces the precipitation of a yellow solid which was filtered off on a gooch, washed with diethyl ether and n-pentane and dried under vacuum at RT. 0.1429 g (yield 99%) of the title compound was obtained.

4.8. Synthesis of complex 1b

Dark yellow microcrystals. Yield 79%.

4.11. Synthesis of complex 2b

Yellow microcrystals. Yield 81%.

4.9. Synthesis of complex 1d

Yellow microcrystals. Yield 80%.

4.12. Synthesis of complex 2c

Yellow microcrystals. Yield 89%.

\[ \text{IR (KBr pellets): } \nu_{C=O} 1728, 1700, 1683 \text{ cm}^{-1}. \]


The synthesis of the complexes 1b, d was carried out following a procedure similar to that described for complex 1a.

IR (KBr pellets): \( \nu_{C=O} \) 1728, 1710, 1694 cm\(^{-1}\).

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

IR (KBr pellets): \( \nu_{C=O} \) 1724, 1714, 1704 cm\(^{-1}\).

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

IR (KBr pellets): \( \nu_{C=O} \) 1724, 1714, 1704 cm\(^{-1}\).

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

IR (KBr pellets): \( \nu_{C=O} \) 1728, 1700, 1683 cm\(^{-1}\).

\[ \text{IR (KBr pellets): } \nu_{C=O} 1728, 1700, 1683 \text{ cm}^{-1}. \]

\[ \text{Anal. Calc. for C22H21NO8PdS: C, 46.69; H, 3.74; N, 2.48. Found: C, 46.81; H, 3.62; N, 2.33.} \]

The synthesis of the complexes 1b, d was carried out following a procedure similar to that described for complex 1a.

IR (KBr pellets): \( \nu_{C=O} \) 1728, 1710, 1694 cm\(^{-1}\).

\[ \text{IR (KBr pellets): } \nu_{C=O} 1728, 1700, 1683 \text{ cm}^{-1}. \]

\[ \text{Anal. Calc. for C22H21NO8PdS: C, 46.69; H, 3.74; N, 2.48. Found: C, 46.81; H, 3.62; N, 2.33.} \]
C=C), 147.8 (C, 9-qui), 154.5 (C, C=C), 159.4 (C, C=C), 165.1 (C, C=C), 166.1 (C, C=C), 167.4 (CH, 2-Pyr), 171.6 (C, C=C).

IR (KBr pellets): \(v_{C=0} = 1725\) cm\(^{-1}\).

**Anál. Calc. for C\(_{23}\)H\(_{23}\)I\(_2\)NO\(_8\)PdS: C, 33.13; H, 3.54; N, 1.82. Found: C, 38.98; H, 3.67; N, 1.71.**

### 4.13. Synthesis of complex 2d

Yellow microcrystals. Yield 87%.

\(^1\)H NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm): \(\delta = 1.37\) (s, 9H, C(CH\(_3\))\(_3\)), 3.25 (s, 3H, quinoline-CH\(_3\)), 3.53 (bs, 3H, OCH\(_3\)), 3.72 (s, 6H, OCH\(_3\)), 3.88 (s, 3H, OCH\(_3\)), 7.39 (dd, 1H, \(J = 8.4\) Hz, \(H^3\)), 7.59 (dd, 1H, \(J = 8.2, 7.1\) Hz, \(H^4\)), 7.90 (dd, 1H, \(J = 8.2, 1.3\) Hz, \(H^5\)), 8.01 (dd, 1H, \(J = 7.1, H^6\)), 8.17 (dd, 1H, \(J = 8.4\) Hz, \(H^7\)).

IR (KBr pellets): \(v_{C=0} = 1721\) cm\(^{-1}\).

**Anál. Calc. for C\(_{23}\)H\(_{23}\)I\(_2\)NO\(_8\)PdS: C, 35.66; H, 3.34; N, 1.60. Found: C, 35.66; H, 3.34; N, 1.60.**

### 4.14. Synthesis of complex 3a

To 0.089 g (0.157 mmol) of complex 1a dissolved in 10 ml of anhydrous CHCl\(_3\), 0.0301 g (0.188 mmol) of Br\(_2\) dissolved in 5 ml of anhydrous CHCl\(_3\) was added under inert atmosphere (Ar). The resulting mixture, which instantaneously decolorizes was stirred for 5 min. The solution was concentrated to small volume under vacuum and the title complex was precipitated as yellow solid by addition of diethyl ether. The solid was filtered off on a gooch, washed with diethyl ether and n-pentane and dried under vacuum at RT. 0.1128 g (yield 96%) of the title complex was obtained.

IR (KBr pellets): \(v_{C=0} = 1721\) cm\(^{-1}\).

**Anál. Calc. for C\(_{23}\)H\(_{23}\)I\(_2\)NO\(_8\)PdS: C, 35.66; H, 3.34; N, 1.60. Found: C, 35.53; H, 3.19; N, 1.48.**

### 4.15. Synthesis of complex 3b-d

Yellow microcrystals. Yield 93%.

\(^1\)H NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm): \(\delta = 1.47\) (s, 9H, C(CH\(_3\))\(_3\)), 3.68 (bs, 6H, OCH\(_3\)), 3.73 (s, 3H, OCH\(_3\)), 3.87 (s, 3H, OCH\(_3\)), 7.61 (dd, 1H, \(J = 8.3, 5.0\) Hz, \(H^3\)), 7.75 (dd, 1H, \(J = 8.1, 7.3\) Hz, \(H^4\)), 8.04–8.08 (m, 2H, \(H^5, H^6\)), 8.42 (dd, 1H, \(J = 8.3, 1.5\) Hz, \(H^7\)), 9.88 (bd, 1H, \(H^8\)).

IR (KBr pellets): \(v_{C=0} = 1709\) cm\(^{-1}\).

**Anál. Calc. for C\(_{23}\)H\(_{23}\)I\(_2\)NO\(_8\)PdS: C, 35.66; H, 3.34; N, 1.60. Found: C, 35.66; H, 3.34; N, 1.60.**

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

### 4.16. Synthesis of complex 3c

Yellow microcrystals. Yield 88%.

\(^1\)H NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm): \(\delta = 2.89\) (s, 3H, S(CH\(_3\))), 3.26 (s, 3H, qui-CH\(_3\)), 3.74 (s, 3H, OCH\(_3\)), 3.80 (s, 3H, OCH\(_3\)), 3.85 (bs, 6H, OCH\(_3\)), 7.43 (d, 1H, \(J = 8.4\) Hz, \(H^3\)), 7.58 (dd, 1H, \(J = 8.1, 7.2\) Hz, \(H^6\)), 7.87 (dd, 1H, \(J = 8.1, H^7\)), 7.92 (dd, 1H, \(J = 7.2, H^8\)), 8.18 (dd, 1H, \(J = 8.4\) Hz, \(H^9\)).

**Anál. Calc. for C\(_{26}\)H\(_{29}\)I\(_2\)NO\(_8\)PdS: C, 35.66; H, 3.34; N, 1.60. Found: C, 35.53; H, 3.19; N, 1.48.**

### 4.17. Synthesis of complex 3d

Yellow microcrystals. Yield 90%.

\(^1\)H NMR (300 MHz, CDCl\(_3\), \(T = 298\) K, ppm): \(\delta = 1.37\) (s, 9H, C(CH\(_3\))\(_3\)), 3.22 (s, 3H, quinoline-CH\(_3\)), 3.55 (s, 3H, OCH\(_3\)), 3.71 (s, 3H, OCH\(_3\)), 3.72 (s, 3H, OCH\(_3\)), 3.90 (s, 3H, OCH\(_3\)), 7.39 (d, 1H, \(J = 8.4\) Hz, \(H^3\)), 7.61 (dd, 1H, \(J = 8.1, 7.2\) Hz, \(H^6\)), 7.94 (dd, 1H, \(J = 8.1, 1.3\) Hz, \(H^7\)), 7.98 (dd, 1H, \(J = 7.2, H^8\)), 8.19 (dd, 1H, \(J = 8.4\) Hz, \(H^9\)).

**Anál. Calc. for C\(_{26}\)H\(_{29}\)I\(_2\)NO\(_8\)PdS: C, 35.66; H, 3.34; N, 1.60. Found: C, 35.53; H, 3.19; N, 1.48.**

### 4.18. Synthesis of complex 4a

To 0.0913 g (0.161 mmol) of complex 1a dissolved in 10 ml of anhydrous CHCl\(_3\), 0.0288 g (0.177 mmol) of ICl dissolved in 5 ml of anhydrous CHCl\(_3\) was added under inert atmosphere (Ar). The resulting mixture which instantaneously turned from dark red to yellow, was stirred for 5 min. The solution was concentrated to small volume under vacuum and the title complex was precipitated as yellow solid by addition of diethyl ether. The solid was filtered off on a gooch, washed with diethyl ether and n-pentane and dried under vacuum at RT. 0.1128 g (yield 96%) of the title complex was obtained.

IR (KBr pellets): \(v_{C=0} = 1718\) cm\(^{-1}\).

**Anál. Calc. for C\(_{23}\)H\(_{23}\)Br\(_2\)NO\(_8\)PdS: C, 39.94; H, 3.74; N, 1.79. Found: C, 39.79; H, 3.21; N, 1.77.**

**Anál. Calc. for C\(_{24}\)H\(_{26}\)Br\(_2\)NO\(_8\)PdS: C, 39.94; H, 3.74; N, 1.79. Found: C, 39.79; H, 3.21; N, 1.77.**
13C{1H}-NMR (CDCl3, T = 298 K, ppm) δ: 29.0 (CH2, SCH2), 52.1 (CH3, OCH3), 52.2 (CH3, OCH3), 53.2 (CH3, OCH3), 53.3 (CH3, OCH3), 103.9 (C, C=Cl), 123.1 (CH, C3), 128.1 (CH, C6), 130.2 (C, C10), 130.5 (CH, C13), 133.1 (C, C3), 133.3 (C, C=Cl), 134.7 (CH, C7), 139.4 (CH, C4), 145.0 (C, C=C), 147.0 (CH, C8), 152.9 (CH, C2), 158.8 (C, C=C), 159.8 (C, C=Cl), 161.5 (C, C=O), 166.1 (C, C=O), 172.1 (C, C=O).

IR (KBr pellets): ν(C=O) 1711 cm⁻¹.

Found: C, 39.97; H, 3.62; N, 1.84.

4.2.2. Synthesis of complex 5a

To 0.090 g (0.159 mmol) of complex 1a dissolved in 10 ml of anhydrous CH2Cl2, 0.0393 g (0.190 mmol) of IBr dissolved in 5 ml of anhydrous CH2Cl2, was added under inert atmosphere (Ar). The resulting mixture which instantaneously turned from red to yellow, was stirred for 5 min. The solution was concentrated to small volume under vacuum and The title complex was precipitated as yellow solid by addition of diethyl ether. The solid was filtered off on a gouch, washed with diethyl ether and n-pentane and dried under vacuum at RT. 0.1104 g (yield 90%) of the title complex was obtained.

13C{1H}-NMR (CDCl3, T = 298 K, ppm) δ: 3.09 (s, 9H, SCH3), 3.74 (s, 3H, OCH3), 3.75 (s, 3H, OCH3), 3.85 (s, 3H, OCH3), 3.89 (s, 3H, OCH3), 7.63 (dd, 1H, J = 8.3, 5.0 Hz, H5), 7.76 (dd, 1H, J = 8.2, 7.4 Hz, H8), 8.02 (dd, 1H, J = 8.2, 1.1 Hz, H7), 8.13 (dd, 1H, J = 7.4, 1.1 Hz, H4), 8.93 (dd, 1H, J = 8.3, 1.6 Hz, H5), 9.95 (dd, 1H, J = 5.0, 1.6 Hz, H6).

IR (KBr pellets): ν(C=O) 1721 cm⁻¹.

Found: C, 39.13; H, 3.61; N, 1.79.

4.2.3. Synthesis of complex 5b

Yellow microcrystals. Yield 92%.

IR (KBr pellets): ν(C=O) 1718 cm⁻¹.

Found: C, 39.20; H, 3.74; N, 1.81.

The synthesis of the complexes 5b, d was carried out following a procedure similar to that described for complex 4a.

4.2.4. Synthesis of complex 5d

Yellow microcrystals. Yield 96%.

IR (KBr pellets): ν(C=O) 1718 cm⁻¹.

Found: C, 36.97; H, 3.19; N, 1.56.

The synthesis of the complexes 5b, d was carried out following a procedure similar to that described for complex 5a.

4.2.4. Synthesis of complex 5d

Yellow microcrystals. Yield 96%.

IR (KBr pellets): ν(C=O) 1718 cm⁻¹.

Found: C, 36.85; H, 3.34; N, 1.72.

The synthesis of the complexes 5b, d was carried out following a procedure similar to that described for complex 5a.
130.9 (CH, C\(^5\)), 133.5 (C=C), 136.7 (CH, C\(^6\)), 138.5 (CH, C\(^4\)), 146.0 (C, C=C), 149.1 (C, C\(^6\)), 155.5 (C=C), 160.1 (C, C=O), 165.4 (C, C=O), 166.0 (C, C=O), 166.7 (CH, C\(^3\)), 171.5 (C, C=O).

IR (KBr pellets): \(\nu_{\text{C=C}} = 1714 \text{ cm}^{-1}\).

**Analy. Calc. for C\(_{26}\)H\(_{29}\)BrIINO\(_8\)PdS:** C, 37.68; H, 3.53; N, 1.69.

**Found:** C, 37.51; H, 3.42; N, 1.58.

**Appendix A. Supplementary data**

CCDC 1449188 and 1449189 contains the supplementary crystallographic data for this article. 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.04.008.

**References**


