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# The unexpected case of reactions of halogens and interhalogens with halide substituted Pd(II) σ-butadienyl complexes†

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We have experimentally studied and theoretically interpreted the addition under stoichiometric conditions of halogens or interhalogens to σ-butadienyl palladium complexes bearing the heteroditopic thioquinolines as spectator ligands. The observed reactions do not involve the expected extrusion of the butadienyl fragment but rather the unpredictable substitution of the halide coordinated to palladium and in some cases also of that bound to the terminal butadienyl carbon. We have explained this peculiar reactivity with a mechanistic hypothesis based on a sequence of selective processes of oxidative addition and reductive elimination involving Pd(IV) intermediates.

## Introduction

Irrespective of the involved mechanism, the formation of aryl or alkyl Pd(II) species is comparatively easier and faster when aryl- or alkyl-iodide, instead of bromide and chloride derivatives are reacted with Pd(0) substrates.[1]

The product of the oxidative addition, *i.e.* complexes of the type $L_2PdIR$ are particularly stable and the substitution of $I^-$ with $Cl^-$ or $Br^-$ can be obtained by de-halogenation of the iodo-species followed by addition of an appropriate soluble halide,[2] which in the case of reactions carried out in nonprotic solvents can be an expensive compound.

The dehalogenation itself is a delicate process which usually takes a long time and can revert into massive decomposition if the temperature and the incident light are not controlled.

In the present paper we demonstrate that σ-butadienyl palladium complexes bearing thioquinoline or pyridylthioether as spectator ligands undergo substitution of the iodide bound to palladium(II) by bromide or chloride by a one pot reaction between the above complexes and the interhalogens IBr and ICl, respectively.

Probably the process above described is not of general importance since in the case of palladium complexes bearing phosphoquinoline[3] and bidentate nitrogen ligands,[4] a different behavior has been noticed. However, we think that any improvement leading to simplification of the halide metathesis could be of interest.

## Results and discussion

We first noticed the particularity of the reaction involving interhalogens in our attempt to extrude the substituted butadienes (1E,3E)-tetramethyl 1-bromo-4-chlorobuta-1,3-diene-1,2,3,4-tetracarboxylate (BCBD) or (1E,3E)-tetramethyl 1-bromo-4-iodobuta-1,3-diene-1,2,3,4-tetracarboxylate (BIBD) by reacting complex **1a** with a stoichiometric amount of ICl or IBr according to the well known and extensively used halogen addition and a subsequent elimination sequence liberating the organic fragments from the organopalladium complexes.[4,5] The almost instantaneously violet color assumed by the reaction mixture in both cases and the related NMR investigations indicate that the reaction products were instead molecular iodine and the complexes **1c** and **1d**, respectively (Scheme 1).

The σ-butadienyl complexes **1c** and **1d** are stable and isolable and their structure is inferred from the $^1H$ and $^{13}C$ NMR spectra (NMR spectra in Fig. S1, ESI†). In particular, the position of the pyridine proton $H^2$ in the case of complexes **1c** and **1d**[6] and that of the terminal butadienyl carbon coordinated to the halide in all the formed complexes is particularly diagnostic.[5i,j] Therefore, the structure of the complexes is immediately determined owing to the low-field resonance of the terminal butadienyl carbon C–I ($\delta \sim 100$ ppm), and the resonance of the quinolinic $H^2$ on the same side of the halide coordinated to

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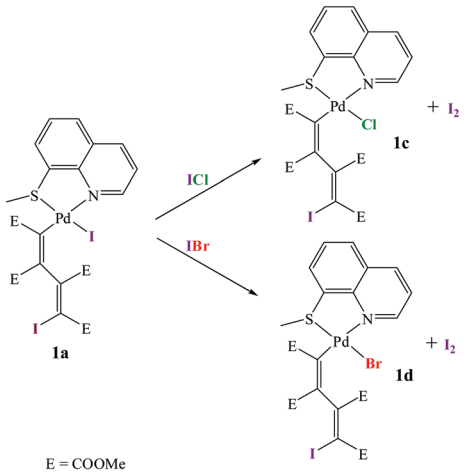



**Scheme 1** Studied complexes and products of the reaction between complex **1a** and the interhalogens ICl or IBr.

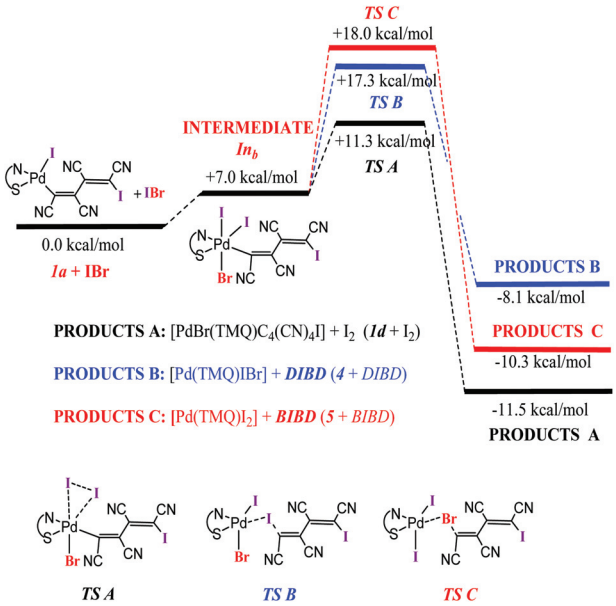



**Fig. 1** Computed energies for the reaction between complex **1a** and IBr.

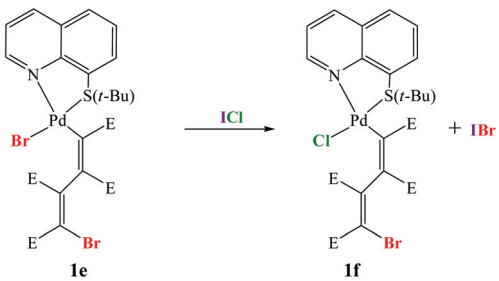
palladium, which resonates at 10.24 ppm in the case of the starting complex **2a** and at 9.74 and 9.95 ppm, in the case of complexes **1c** and **1d**.

As discussed in a previously published paper[5j] the complexes **1c** and **1d** can also be obtained by reacting ICl or IBr with a solution of the palladacyclopentadienyl complex [Pd(TMQ)($C_4(E)_4$)] (TMQ = 8-(methylthio)quinoline, E = COOMe). Furthermore, in the same paper it was shown that the formation of complexes **1c** and **1d** although less thermodynamically stable was kinetically driven. In fact, the energy of the transition states (TS) leading to the less stable isomer is considerably lower than that which should yield the thermodynamically favored reaction products, *i.e.* [Pd(TMQ)I(CE═CE–CE═CECl)] (**1c′**) and [Pd(TMQ)I(CE═CE–CE═CEBr)] (**1d′**).[5j]

Also in the present case, we resort to a computational study in order to give a correct interpretation to the observed phenomena (Scheme 1). To save computer time, COOMe was substituted with the less disordered CN group (the complexes computationally studied have been consequently indicated by the same labels as the original ones but written in italics).[7] In the case of the reaction between complex ***1a*** and IBr it is apparent from the computational output schematized in Fig. 1 that $I_2$ and complex ***1d***, among the probable ones represent the favored reaction products from both kinetic and thermodynamic points of view.

The formation and stabilization of the TS might be explained considering that the interhalogen IBr or ICl approaches palladium(II) *via* the more electronegative atom $Br^{\delta-}$ or $Cl^{\delta-}$. Thereafter, the hardness of the Pd(IV) in the intermediate and in TS favors the maintenance of the Pd–Br or Pd–Cl bond respectively, eventually collapsing into the experimentally observed compounds ***1d*** and $I_2$.

According to these observations, we surmise that the interhalogen ICl might also be exploited in the synthesis of complexes bearing chloride and bromide coordinated to palladium and to the terminal butadienyl carbon. Scheme 2 summarizes




**Scheme 2** Synthesis of complex **1f**.

the positive aspect of the synthetic approach to complex **1f**, as witnessed by the resonance of the pyridine $H^2$ shifting from 9.88 ppm of the starting **1e** derivative[5j] to 9.68 ppm of complex **1f**. Furthermore, such a result was confirmed by the solid state structure of the isolated complex whose ORTEP[8] representation is shown in Fig. 2 whereas the description of the structure and the table summarizing the selected bond distances and angles are reported in the crystal structure determination section. Also in this case the computational study is in agreement with the experimental result (Fig. S2, ESI†).

At this point it is worth noting that an alternative synthesis of complex **1f** *via* the highly unstable BrCl might be very difficult.

In the light of the above described results, we had the chance to explain the unexpected reactivity observed in the case of the reaction between **1a** and a stoichiometric amount of $Br_2$.

The occurring slow process (*ca.* 24 h), which can be verified from the change of color (from brown to violet) of the solution mixture and confirmed by the NMR spectra, consists in the

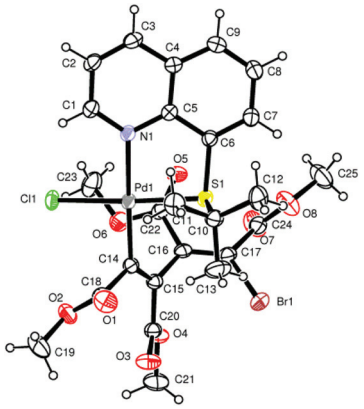
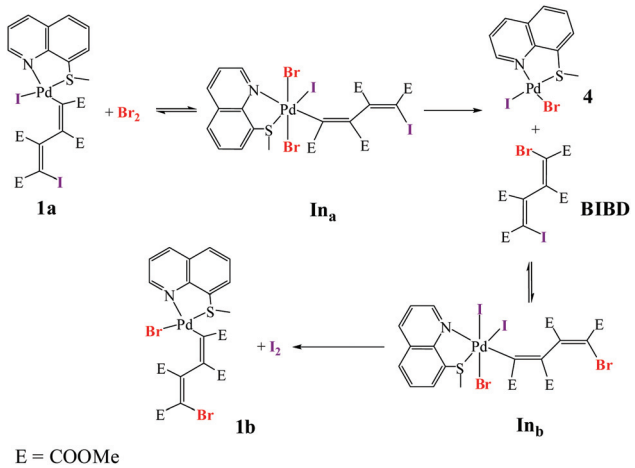



Fig. 2 ORTEP[8] view of complex **1f** showing the thermal ellipsoids at the 30% probability level.




Scheme 3 Proposed mechanism for the reaction **1a** + $Br_2$ → **1b** + $I_2$.

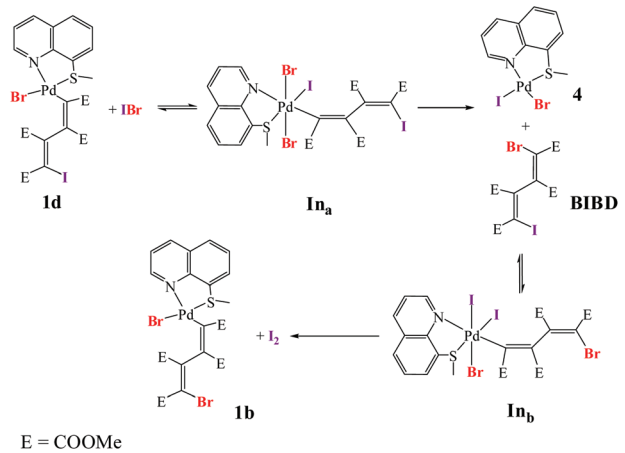
formation of molecular iodine and complex **1b** where two bromides have substituted both iodides of complex **1a**. Notably, no diene displacement is observed in this case either.[9] In order to maintain the internal consistency we therefore propose for such a reaction a sequence of elementary processes of oxidative addition and reductive elimination, as reported in the following Scheme 3 which is also in agreement with the dedicated computational study shown in Fig. 3.

The involvement of intermediates of the type described in Scheme 3 can also be reasonably cited in the case of the following reactions:

(a) the slow reaction between complex **1d** and a stoichiometric amount of IBr yields the derivative **1b** and $I_2$ and can be interpreted on the basis of the mechanism reported in Scheme 4 involving the same intermediates $\mathbf{In_a}$ and $\mathbf{In_b}$.

(b) The $^1$H NMR spectra immediately detected after the stoichiometric addition of IBr to **1d** or $Br_2$ to **1a** are identical. This fact can be interpreted on the basis of a fast equilibrium between **1a** and **1d** species *via* the common intermediate $\mathbf{In_a}$ (Scheme 5 and Fig. S3 in the ESI†).

(c) We have also studied the reaction between complex **1b** and IBr in excess. The result of this slow process (*ca.* 24 h) is summarized in Scheme 6.




Scheme 4 Proposed mechanism for the reaction **1d** + IBr → **1b** + $I_2$.

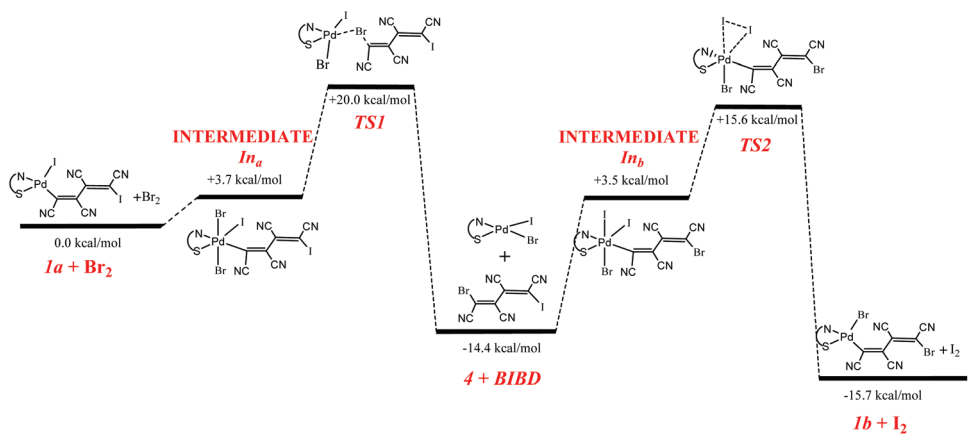
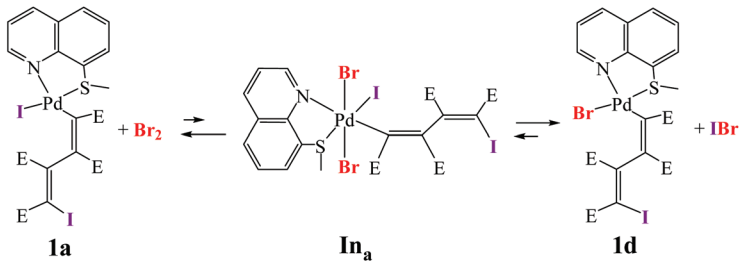
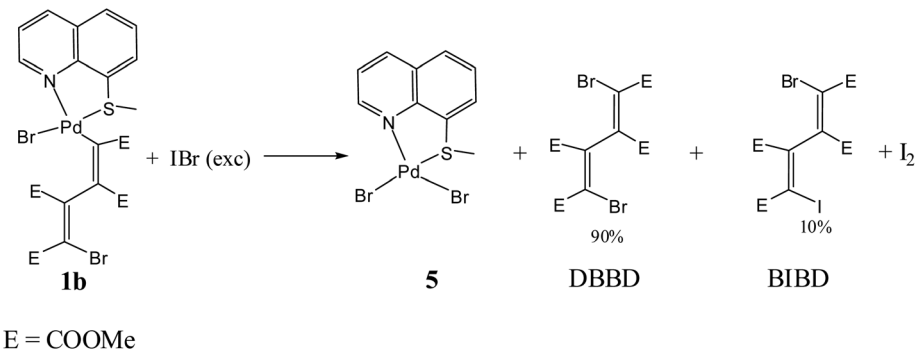



Fig. 3 Computed energies for the reaction between complex **1a** and $Br_2$.




**Scheme 5** Equilibria among **1a**, $Br_2$, **1d** and IBr.




**Scheme 6** Schematic representation of the reaction: **1b** + $IBr_{(exc)}$ → **5** + DBBD + BIBD + $I_2$.

As can be seen the reaction products are the low soluble complex **5** (detected from the $^1$H NMR spectrum of the inorganic fraction) and a 9 : 1 mixture of DBBD : BIBD (as shown in the GC-MS spectrum of the organic fraction extracted by diethylether (Fig. S4 in the ESI†)) and $I_2$.

Once again, the mechanism proposed for explaining the composition of the final mixture again takes into account the formation of Pd(IV) intermediates as can be seen in Scheme 7.

As a consequence of the attack of the interhalogen IBr to complex **1b** the formed intermediate $\mathbf{In_c}$ gives the derivatives **4** and **5** (Scheme 7(a)). Obviously, the relative amount of the formed complexes [**5**]/[**4**] in the earlier stage of the reaction is close to the $k_I/k_{Br}$ ratio. However, according to the previously described reaction (see Scheme 3) the BIBD diene reacts with complex **4** reforming complex **1b** (Scheme 7(b)) which again reacts with IBr in excess. From the detected final products it is also evident, also supported by the computational study (see Fig. 4), that $k_I > k_{Br}$ since complex **4** is the limiting reagent which is completely consumed at the end of the reaction.

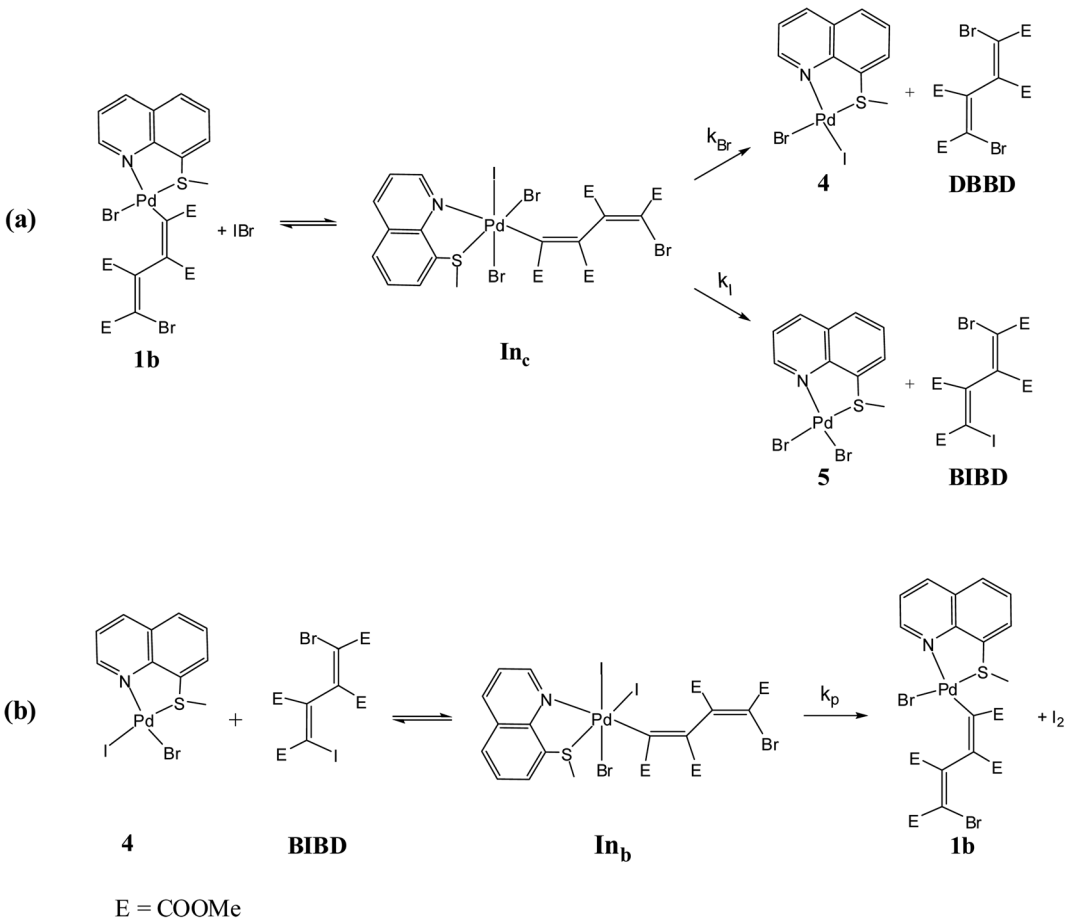
Finally, we have explored the possibility of using interhalogens for the replacement of the halide coordinated to the palladium centre in substrates different from the σ-butadienyl complexes. We have therefore reacted the palladium aryl derivatives **2** with IX (X = Br, Cl). In this case the easily and promptly obtained complex **3** confirms the specificity of the reaction which allows the otherwise difficult substitution of a $I^-$ coordinated to Pd with $Br^-$ or even with $Cl^-$ without preliminary de-halogenation (Scheme 6). However, it is noteworthy that in the case of the reaction of ICl a side reaction is observed (*ca.* 10%). Presumably, the partial displacement of the 1-iodo-4-trifluoromethylbenzene might also take place besides the main reaction yielding the complex **3b** (see Fig. S5, ESI†).

It is worth noting that complex **3a** can be directly synthesized by reacting 4-bromo-trifluoromethylbenzene with a Pd(0) derivative. However, at variance with the smooth and efficient method we propose, the direct synthesis is carried out under drastic conditions and often affected by significant decomposition (Scheme 8).

In conclusion we have experimentally and theoretically proved that addition of halogens or interhalogens to some organometallic palladium compounds induces the substitution of the halide coordinated to the metal and/or that bound to the organic residue instead of the expected extrusion of the organic fragment.

### Crystal structure determination of complex 1f

The geometry around the Pd center is slightly distorted square planar where the four positions are occupied by a halogen atom, Cl, the nitrogen, the sulphur of the (*tert*-butylsulfanyl) quinoline (TTBQ) ligand, and the carbon $C_\alpha$ of the 1,2,3,4 tetrakis(methoxycarbonyl)buta-1,3-diene-4-Br-1-yl ligand. The deviation of the Pd1 atom from the average basal plane is




**Scheme 7** Proposed mechanism for the reaction **1b** + IBr → **5** + DBBD + BIBD + $I_2$.

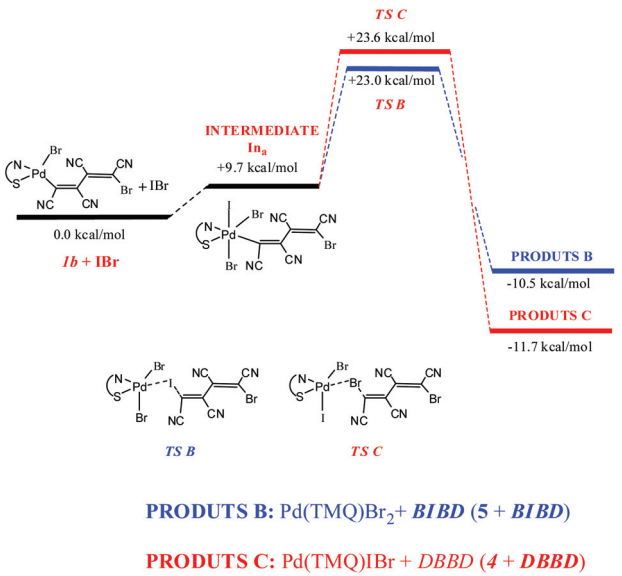
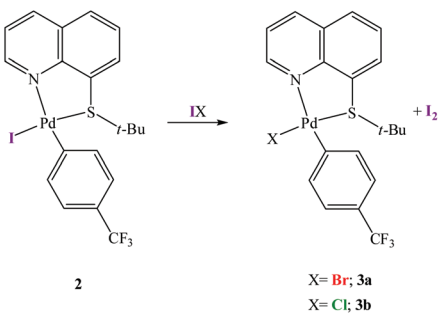



**Fig. 4** Computed energies for the reaction between complex **1b** and IBr.




**Scheme 8** Products of the reaction between complex **2** and the interhalogens IBr and ICl.

0.0872(2) Å, toward the C10 carbon. The C14═C15–C16═C17 buta-1,3-diene moiety adopts the *anti-clinal* conformation with a torsion angle of 119.1(3)°. The quinoline plane is rotated by 20.25(4)° with respect to the Pd coordination plane.

The selected bond distances and angles for complex **1f** are given in the following Table 1.

Table 1 Selected bond distances and angles for complex **1f** (Å and degrees)

| Distances | | Angles | |
|---|---|---|---|
| Pd1–Cl1 | 2.3244(6) | Cl1–Pd1–N1 | 93.56(5) |
| Pd1–S1 | 2.2922(6) | Cl1–Pd1–S1 | 174.97(3) |
| Pd1–N1 | 2.118(2) | Cl1-Pd1–C14 | 88.00(7) |
| Pd1–C14 | 1.995(3) | S1–Pd1–N1 | 84.68(5) |
| S1–C6 | 1.774(3) | S1–Pd1–C14 | 93.77(7) |
| S1–C10 | 1.897(3) | N1–Pd1–C14 | 178.44(6) |
| C14–C15 | 1.331(4) | Pd1–S1–C6 | 97.33(8) |
| C15–C16 | 1.491(3) | Pd1–S1–C10 | 108.10(9) |
| C16–C17 | 1.328(4) | Pd1–C14–C15 | 127.1(2) |
| C17–Br1 | 1.886(3) | Pd1–C14–C18 | 111.6(2) |

# Conclusions

The addition of the interhalogens ICl and IBr to the palladium butadienyl complex **1a** did not induce the expected extrusion of the butadiene moiety but rather the substitution of the strongly metal bound iodide with the less coordinating chloride or bromide and the displacement of $I_2$. The peculiarity of the observed reactivity drove us to investigate experimentally and theoretically the phenomenon and therefore we have carried out some further reactions and computational studies.

In one case we were able to substitute simultaneously the iodides bound to palladium and terminal butadienyl carbon with two bromides simply by adding bromine to complex **1a**.

All the results concur with the formulation of a general mechanism involving selective oxidative addition and reductive elimination *via* Pd(IV) intermediates which eventually gives the final products. In this respect, by reacting complex **1e** bearing the two coordinated bromides with ICl we were able to synthesize and resolve the solid state structure of the new complex **1f** bearing one chloride coordinated to palladium and one bromide on the final butadienyl carbon. Moreover, we have shown the versatility of this method by obtaining the complexes **3a** and **3b** through reaction of the aryl palladium species **2** with IBr and ICl, respectively.

# Experimental

### Solvents and reagents

All the distillation processes were carried out under an 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.

### IR, NMR, UV-Vis measurements and elemental analysis

The IR, $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively.

The $^1$H NMR reactivity tests were carried out by dissolving the complex under study in 0.8 ml of $CD_2Cl_2$ ([Complex] ≈ $1.2 \times 10^{-2}$ mol dm$^{-3}$) and adding microaliquots of a concentrated $CD_2Cl_2$ solution (*ca.* $1.2 \times 10^{-1}$ mol dm$^{-3}$) of $Br_2$, ICl or IBr and monitoring the signal for the disappearance of the starting complex and the appearance of the final products.

The ligands 8-(methylthio)quinoline (TMQ), and 8-(*t*-butylthio)quinoline[10] and complexes **1a** and **1e**[5j] were obtained according to published protocols.

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

### Synthesis and characterization of complex 1f

To 0.0492 g (0.064 mmol) of complex **1e** (prepared following a published procedure)[5j] dissolved in 10 ml of anhydrous $CH_2Cl_2$, 0.0114 g (0.070 mmol) of ICl dissolved in 5 ml of anhydrous $CH_2Cl_2$ was added under an inert atmosphere (Ar). The resulting mixture was stirred for further 10 min and then concentrated to a 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. 0.0454 g (yield 98%) of the title compound was obtained.

**$^1$H-NMR (300 MHz, $CDCl_3$, $T$ = 298 K, ppm)** $\delta$: 1.47 (s, 9H, $C(CH_3)_3$), 3.69 (bs, 6H, $OCH_3$), 3.73 (s, 3H, $OCH_3$), 3.89 (s, 3H, $OCH_3$), 7.61 (dd, 1H, $J$ = 8.0, 4.9 Hz, H$^3$), 7.76 (d, 1H, $J$ = 7.7 Hz, H$^6$), 8.07 (d, 2H, $J$ = 7.7 Hz, H$^5$, H$^7$), 8.44 (d, 1H, $J$ = 8.0 Hz, H$^4$), 9.68 (bd, 1H, H$^2$).

**$^{13}$C{$^1$H}-NMR ($CDCl_3$, $T$ = 298 K, ppm)** $\delta$: 30.2 ($CH_3$, $SC(CH_3)_3$), 51.9 ($CH_3$, $OCH_3$), 52.2 ($CH_3$, $OCH_3$), 53.2 ($CH_3$, $OCH_3$), 53.2 ($CH_3$, $OCH_3$), 59.2 (C, $C(CH_3)_3$), 123.0 (CH, C$^3$), 124.9 (C, C═CBr), 127.4 (CH, C$^6$), 129.4 (C, C$^8$), 129.9 (C, C$^{10}$), 131.1 (C, C═C), 131.3 (CH, C$^5$), 133.0 (C, C═C), 137.6 (CH, C$^7$), 139.3 (CH, C$^4$), 148.8 (C, C$^9$), 153.2 (CH, C$^2$), 156.8 (C, C═C), 161.4 (C, C═O), 164.5 (C, C═O), 166.5 (C, C═O), 172.2 (C, C═O). IR (KBr pellets): $\nu_{CO}$ = 1703, 1717, 1736 cm$^{-1}$.

### Characterization of complex 5

Complex 8-(methylthio)quinoline palladium dibromide (**5**) was separated as an insoluble product in the reaction between complex **1b** and IBr in excess[5j] and characterized by elemental analysis and $^1$H NMR.

**Anal. Calcd** for $C_{10}H_9NSBr_2Pd$: C, 27.21; H, 2.06; N, 3.17. Found C, 27.73; H 2.13; N, 3.09% (Elementar C H N "Cubo Micro Vario" Analyzer).

**$^1$H-NMR (300 MHz, $CDCl_3$, $T$ = 298 K, ppm)** $\delta$: 3.15 (s, 3H, $SCH_3$)), 7.71 (dd, 1H, $J$ = 8.2, 5.3 Hz, H$^3$), 7.84 (dd, 1H, $J$ = 8.1, 7.2 Hz, H$^6$), 8.09 (d, 2H, $J$ = 8.1 Hz, H$^7$), 8.15 (d, 1H, $J$ = 7.2 Hz, H$^5$), 8.52 (d, 1H, $J$ = 8.2 Hz, H$^4$), 10.26 (d, 1H, $J$ = 5.3 Hz, H$^2$) (Bruker 300 advance spectrometer).

### 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. In the following discussion the CN derivatives will maintain the same labels as the original complexes, albeit in italics (**4a** and **5a** become ***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,[7] and despite the implicit limitations ($\Delta\Delta G^\circ \approx \pm$ 2 kcal mol$^{-1}$ and the replacement of COOMe with CN), we have obtained 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 MO6,[11,12] in combination with polarized triple-ζ-quality basis sets (LAN2TZ(f))[13,14] and relativistic pseudopotential for the Pd atoms, a polarized double-ζ-quality basis sets (LANL2DZdp)[15] with diffuse functions for the halogen atoms and polarized double-ζ-quality basis sets (6-31G(d,p)) for the other elements. Solvent effects (acetonitrile, $\varepsilon$ = 37.5) were included using CPCM.[16,17]

The "restricted" formalism was applied in all the calculations. The zero-point vibrational energies and thermodynamic parameters were obtained[18] by means of the stationary points characterized by IR simulation.

All the computational work was carried out on Intel based ×86–64 workstations.

### Crystal structure determination

The crystal data of complex **1f** 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[19] and corrected for Lorentz, polarization and absorption effects (SORTAV).[20] The structure was solved by direct methods using the SIR97[21] 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. In this complex an illdefined region of residual electron density in the region around the inversion centre at 0.5, 0, 0.5 was found, probably containing a disordered molecule of diethyl ether. For this reason the program SQUEEZE was used to cancel out the effects of the disordered solvent. SQUEEZE is part of the PLATON program system which attempts to remove mathematically the effects of disordered solvent.[22]

All calculations were performed using PLATON,[22] SHELXL-97[23] and PARST[24] implemented in the WINGX[25] system of programs. The crystal data are given in Table S1.†

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1472780.

## Notes and references

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$Br_2$ to a solution of **1a** eventually yields DBDB, $I_2$ and [Pd(TMQ)$Br_2$](**5**) as the reaction products.

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