Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 12386

www.rsc.org/dalton

PAPER

Synthesis and catalytic application of palladium imidazol(in)ium-2-dithiocarboxylate complexes†‡

Martin J. D. Champion,[a] Riten Solanki,[a] Lionel Delaude,[b] Andrew J. P. White[a] and James D. E. T. Wilton-Ely*[a]

Received 29th June 2012, Accepted 15th August 2012
DOI: 10.1039/c2dt31413d

The palladium(II) dimer, $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)Cl]_2$ reacts with two equivalents of the NHC·CS_2 zwitterionic ligands [NHC = IPr (1,3-diisopropylimidazol-2-ylidene), ICy (1,3-dicyclohexylimidazol-2-ylidene), IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), IDip (1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), SIMes (1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene)] in the presence of NH_4PF_6, to yield the cationic products $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)(S_2C\cdot NHC)]^+$. In a similar fashion, the compounds $[Pd(C,N\text{-bzq})(S_2C\cdot NHC)]^+$ (bzq = benzo[*h*]quinolinyl, NHC = ICy, IMes, IDip) are obtained from the corresponding dimer $[Pd(C,N\text{-bzq})Cl]_2$. The bis(phosphine) compounds $[Pd(S_2C\cdot NHC)(PPh_3)_2]^{2+}$ (NHC = ICy, IMes, IDip, SIMes) are obtained on treatment of $[PdCl_2(PPh_3)_2]$ with NHC·CS_2 zwitterions in the presence of NH_4PF_6. The reaction of $[PdCl_2(dppf)]$ with IMes·CS_2 and NH_4PF_6 provides the complex $[Pd(S_2C\cdot IMes)(dppf)]^{2+}$. The complexes $[Pd(S_2C\cdot NHC)(PPh_3)_2](PF_6)_2$ (NHC = IMes, IDip) were active pre-catalysts (1 mol% loading) for the conversion of benzo[*h*]quinoline to 10-methoxybenzo[*h*]quinoline in the presence of $PhI(OAc)_2$ and methanol. The intermediacy of $[Pd(C,N\text{-bzq})(S_2C\cdot NHC)]^+$ was supported by the high yield of 10-methoxybenzo[*h*]quinoline using $[Pd(C,N\text{-bzq})(S_2C\cdot IDip)]^+$ to promote the same reaction. Small amounts of 2,10-dimethoxybenzo[*h*]quinoline were also isolated from these reactions. Using $[Pd(C,N\text{-bzq})(S_2C\cdot IDip)]^+$ and *N*-chlorosuccinimide as the oxidant led to the formation of 10-chlorobenzo[*h*]quinoline in moderate yield from benzo[*h*]quinoline. The molecular structures of $[Pd(S_2C\cdot IMes)(PPh_3)_2](PF_6)_2$ and $[Pd(S_2C\cdot IMes)(dppf)](PF_6)_2$ were determined crystallographically.

Introduction

A huge number of complexes bearing 1,1-dithio ligands are known in the literature.[1–5] Amongst them, compounds with dithiocarbamate ($R_2NCS_2^-$)[1–4] or xanthate functional groups ($ROCS_2^-$)[1,2,5] dominate. This is not surprising given the great synthetic ease with which these anions are obtained from the reaction of carbon disulfide with amines under basic conditions or alkoxides and aryloxides, respectively. In order to expand the potential of these ligands beyond simple alkyl or aryl substituents, we have been involved in a programme to introduce additional functional groups on their substituents.[6] More recently, our attention has turned to another class of 1,1-dithio ligands which are often neglected, the dithiocarboxylates (RCS_2^-, where R is a carbon-based substituent). Due to the synthetic difficulties encountered in their preparation, they have been employed only sporadically in the preparation of sulfur chelates.[1,7]

N-Heterocyclic carbenes (NHCs)[8,9] are another class of ligands which have acquired a prominent position in organometallic chemistry and homogeneous catalysis as robust, electron-rich alternatives to phosphines.[10,11] Archetypal examples of NHC-based catalyst precursors include the Grubbs second generation metathesis initiator $[Ru(=CHPh)Cl_2(SIMes)(PCy_3)]$[12] (SIMes is 1,3-dimesitylimidazolin-2-ylidene) and the copper(I) compounds [CuX(NHC)] (X = halide) used extensively in 'click' chemistry.[13] Moreover, the potential of NHCs extends well beyond their use as monodentate carbon-bonded ligands. This has been demonstrated in the abundance of ligand systems in which pendant donors available for coordination have been added to a central carbene unit. Versions with sulfur arms have been explored in a variety of palladium-catalysed carbon–carbon coupling reactions.[14,15] Braunstein and co-workers recently reported an interesting variation on NHC pincer complexes with two thioether donors, which were catalytically active in Suzuki–Miyaura cross-coupling reactions.[14n] Conventional 1,1-dithio ligands are rarely found in catalysis, though some disulfur

[a]*Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, UK. E-mail: j.wilton-ely@imperial.ac.uk*
[b]*Laboratory of Organometallic Chemistry and Homogeneous Catalysis, Institut de Chimie (B6a), Université de Liège, Sart-Tilman par 4000 Liège, Belgium*

† Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

‡ Electronic supplementary information (ESI) available. CCDC 880366 (**2**) and 880367 (**5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31413d

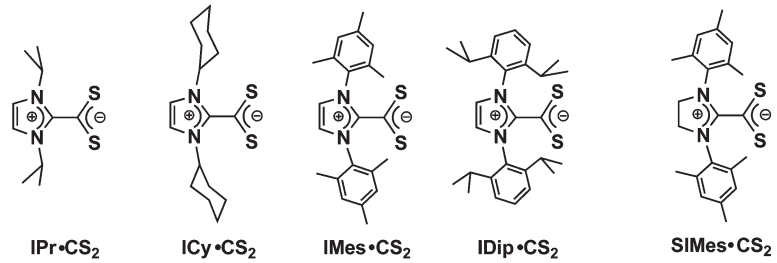


Fig. 1 *N*-Heterocyclic carbene-derived dithiocarboxylate ligands used in this research.

(but not 1,1-dithio) examples are known in the field of asymmetric catalysis.[16] This is perhaps surprising given that an important industrial process – the promotion of cross-linking in rubber vulcanisation – involves catalysis performed by zinc dithiocarbamate complexes.[17]

In addition to the huge impact of *N*-heterocyclic carbenes[8,9] as ligands of choice for many transition metal catalysts,[10,11] the potential of these divalent carbon species to generate other ligand systems has been explored sporadically.[18] One such avenue of investigation is the facile reaction of NHCs with the heteroallenes COS, CS_2 and RNCS to afford the corresponding betaines NHC·C(A)S (where A = S, O, NPh).[19] The dithiocarboxylate adducts of NHCs display arguably the greatest potential for coordination chemistry. Early work carried out in 1986 demonstrated that 1,3-dimethylimidazolium-2-dithiocarboxylate formed stable complexes with a number of transition metal halides or nitrates.[20] The precise structure of these compounds remained unclear for many years, possibly contributing to their relative obscurity. In 2009, ruthenium–arene complexes bearing NHC·CS_2 ligands were prepared and fully characterized in a thorough, systematic study of the coordination chemistry of these zwitterions.[21] This initiated our interest in further exploring the potential of NHC·C(A)S ligands for coordination to a range of metals.[22] One of us has also investigated the catalytic activity of ruthenium–arene complexes bearing NHC·C(A)S ligands in various reactions (olefin metathesis, atom transfer radical reactions, enol ester synthesis). Stable Ru(S_2C·NHC) chelates were found to be devoid of any significant activity in these transformations,[21a] except under forcing conditions.[21b] Monodentate Ru(SOC·NHC) compounds performed better, but this was most likely due to their rapid dethiocarboxylation under the experimental conditions adopted to generate active Ru–NHC species.[23] Although metal-based catalysis has been disappointing so far, NHC·CS_2 betaines[24a] and their thiocarboxylate analogues[24b] have recently been employed in organocatalysis.

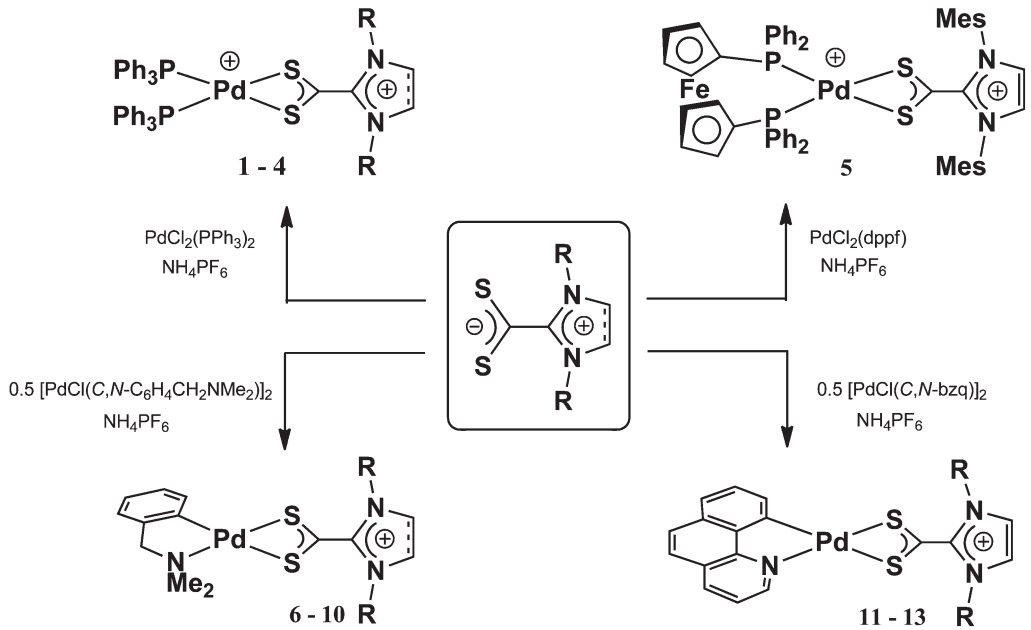
An earlier study exploring the coordination chemistry of NHC-derived dithiocarboxylate ligands with ruthenium(II) carbonyl compounds showed that variations to the steric profile of the NHC did not result in changes to the ν_{CO} frequency.[22d] This suggests that, unlike phosphines, the steric bulk of the NHC·CS_2 ligands can be varied without changing their electronic properties – a potentially useful attribute. In other 1,1-dithio ligands, such as dithiocarbamates ($R_2NCS_2^-$) and xanthates ($ROCS_2^-$), the bulk of the substitutents (R) is too remote to affect the metal centre. This is not the case for NHC·CS_2 betaines, which have been shown to induce the adoption of a *cis*-arrangement in bis(phosphine) systems when the NHC is bulky.[25] Thus, we sought to explore a catalytic reaction in which the suitability of complexes bearing a range of NHC·CS_2 ligands could be compared.

In this contribution, we report the synthesis and characterisation of the first palladium imidazol(in)ium-2-dithiocarboxylate complexes that extend beyond the simple homoleptic examples reported by Borer and co-workers.[20] For this purpose, five representative NHC·CS_2 zwitterions bearing alkyl or aryl groups on their nitrogen atoms were used as ligands (Fig. 1). The association of these ligands to ruthenium–arene complexes[21] did not lead to catalytically active species due to the strong chelate effect and the coordinative saturation of the metal centre. From this point of view, the 16-electron compounds described here are more promising candidates for use in a catalytic setting, particularly in terms of the tuneable steric bulk of the substituents on their nitrogen atoms. Therefore, we have investigated their catalytic potential in the oxidative C–H functionalization of benzo[*h*]-quinoline.

Results and discussion

In the presence of an excess of NH_4PF_6, the reaction of $[PdCl_2(PPh_3)_2]$ with ICy·CS_2 in dichloromethane and methanol led to the formation of $[Pd(S_2C{\cdot}ICy)(PPh_3)_2](PF_6)_2$ (**1**) (Scheme 1). The dark yellow product was isolated in 64% yield after recrystallisation. ^{31}P NMR analysis revealed the formation of a new compound with a singlet resonance at 32.3 ppm. The incorporation of the zwitterionic ligand was evident from the ^{1}H NMR spectrum with a singlet at 7.60 ppm for the imidazolium backbone and a multiplet at 4.53 ppm for the NCH protons of the cyclohexyl substituents. The remaining aliphatic protons appeared as multiplets between 1.23 and 2.07 ppm, while further aromatic signals located between 7.39 and 7.55 ppm were assigned to triphenylphosphine. Little change was observed in the solid-state infrared spectrum of the complex compared to the uncoordinated ligand apart from the presence of additional features associated with the PPh_3 units. The overall formulation of **1** was confirmed by a molecular ion in the mass spectrum at *m*/*z* 938 and a good agreement of elemental analysis with the calculated values.

The red mesityl derivative $[Pd(S_2C{\cdot}IMes)(PPh_3)_2](PF_6)_2$ (**2**) was prepared in a similar manner to **1** in 81% yield. Recrystallisation of this compound by slow diffusion of petroleum ether into a dichloromethane solution afforded large red blocky needles suitable for X-ray diffraction analysis (Fig. 2, see also the following section). Likewise, the SIMes·CS_2 ligand featuring a saturated imidazolinium backbone was employed to prepare



Scheme 1 Formation of palladium imidazol(in)ium-2-dithiocarboxylate complexes **1–13**. Hexafluorophosphate counteranions are present in all complexes.

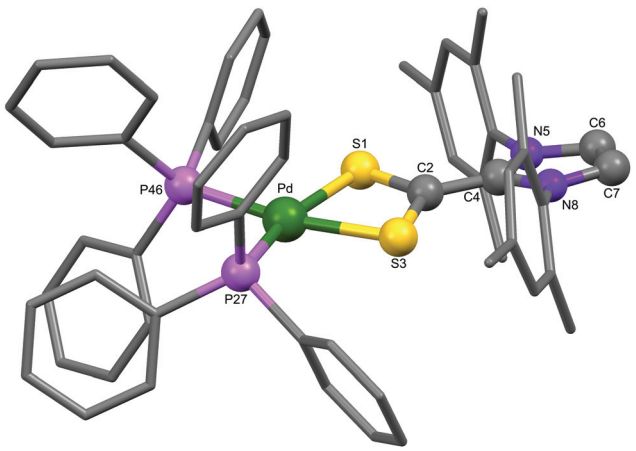


Fig. 2 Molecular structure of $[Pd(S_2C{\cdot}IMes)(PPh_3)_2](PF_6)_2$ (**2**). Hydrogen atoms, hexafluorophosphate counteranions, and co-crystallised solvent molecules were omitted for clarity. Selected bond distances (Å) and angles (°): Pd–P(46) 2.3099(6), Pd–P(27) 2.3202(5), Pd–S(3) 2.3340(6), Pd–S(1) 2.3724(6), S(1)–C(2) 1.683(2), C(2)–C(4) 1.452(3), C(2)–S(3) 1.692(2), C(4)–N(8) 1.350(3), C(4)–N(5) 1.352(3), C(6)–C(7) 1.346(4), S(3)–Pd–S(1) 73.71(2), S(1)–C(2)–S(3) 113.50(12), P(27)–Pd–P(46) 100.97(2).

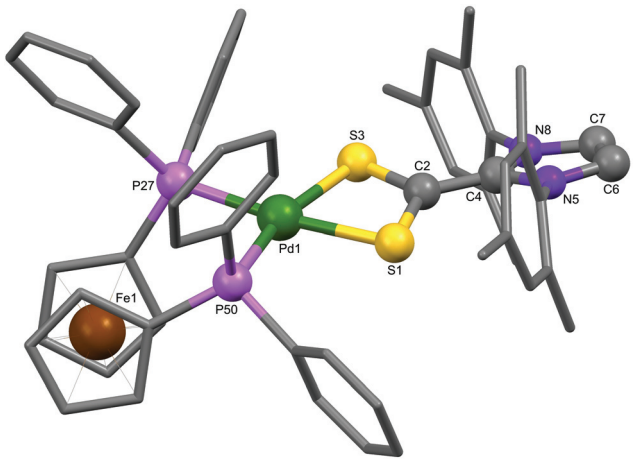


Fig. 3 Molecular structure of $[Pd(S_2C{\cdot}IMes)(dppf)](PF_6)_2$ (**5**). Hydrogen atoms, hexafluorophosphate counteranions, and co-crystallised solvent molecules were omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–P(50) 2.2931(6), Pd(1)–P(27) 2.3035(7), Pd(1)–S(1) 2.3391(7), Pd(1)–S(3) 2.3681(7), S(1)–C(2) 1.685(3), C(2)–C(4) 1.461(3), C(2)–S(3) 1.684(3), C(4)–N(8) 1.347(3), C(4)–N(5) 1.354(3), C(6)–C(7) 1.345(4), S(1)–Pd(1)–S(3) 73.89(2), S(3)–C(2)–S(1) 114.25(14), P(27)–Pd–P(50) 98.24(2).

the deep red compound $[Pd(S_2C{\cdot}SIMes)(PPh_3)_2](PF_6)_2$ (**3**). The main spectroscopic difference between this product and the IMes·CS_2 derivative (**2**) was the presence of a singlet at 4.49 ppm in the ^{1}H NMR spectrum corresponding to the methylene bridging units of the heterocycle. Last but not least, the most bulky of the dithiocarboxylate betaines shown in Fig. 1, IDip·CS_2, was used to prepare $[Pd(S_2C{\cdot}SIDip)(PPh_3)_2](PF_6)_2$ (**4**) in an identical fashion to compounds **1–3**.

In order to extend the scope of our methodology, we prepared the compound $[Pd(S_2C{\cdot}IMes)(dppf)](PF_6)_2$ (**5**) from $[PdCl_2(dppf)]$ (dppf is 1,1′-bis(diphenylphosphino)ferrocene) (Scheme 1). With its chelating diphosphine ligand in place of two triphenylphosphine ligands, this complex would also serve as a comparison point for the catalytic investigations to come (*vide infra*). Spectral data recorded for **5** were similar to those observed for **2** apart from the resonances associated with the ferrocene moiety at 4.47 and 4.63 ppm in the ^{1}H NMR spectrum. Single crystals of this heterobimetallic compound were also obtained and a structural study undertaken (Fig. 3 and following section).

Palladium is known to undergo cyclometallation reactions readily, often resulting in halide bridged compounds.[26] These dimers are useful precursors for the synthesis of organometallic complexes bearing bidentate chelates.[6b,d,h] A representative starting compound, $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)Cl]_2$, was employed to prepare the first organopalladium examples with an NHC·CS_2 ligand (Scheme 1). The dimer was treated with two equivalents of IPr·CS_2 in the presence of excess ammonium hexafluorophosphate to provide an orange solid in 76% yield after work up. Retention of the cyclometallated ligand was confirmed by the presence of singlets at 3.06 (NMe_2) and 4.14 (CH_2N) ppm in the ^{1}H NMR spectrum, while the IPr ligand gave rise to resonances at 7.61 (CH═CH), 4.94 (exocyclic NCH) and 1.65 (CH_3) ppm. The overall formulation was confirmed as $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)(S_2C\cdot IPr)]PF_6$ (**6**) by mass spectrometry (*m*/*z* 468) and good agreement of the elemental analysis with calculated values. The slightly bulkier ICy derivative, $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)(S_2C\cdot ICy)]PF_6$ (**7**), was prepared in the same manner. The spectroscopic data pertaining to the NHC·CS_2 ligand for $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)(S_2C\cdot IMes)]PF_6$ (**8**) and $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)(S_2C\cdot SIMes)]PF_6$ (**9**) were found to be similar to those observed for **2** and **3**, respectively. An example bearing the most bulky ligand shown in Fig. 1, $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)(S_2C\cdot IDip)]PF_6$ (**10**) was also synthesised in good yield.

Structural analysis

The structures of both complex **2** and **5** are based on a distorted square planar arrangement with *cis*-interligand angles in the range 73.71(2)–100.97(2)° and 73.89–98.24(2)°, respectively. In each case, the smallest of these angles is the S–Pd–S bite angle of the NHC·CS_2 ligand. In both structures the chelates are asymmetric (the Pd–S bond lengths being 2.3340(6) and 2.3724(6) Å in **2**, and 2.3391(7) and 2.3681(7) Å in **5**), though this asymmetry does not extend to the C–S bonds, which range between 1.683(2) and 1.692(2) Å across the two structures. The C–S distances recorded in this study along with some related literature data are collected in Table 1. Multiple bond character is clearly present in all the compounds under scrutiny with values approaching typical C═S double bond lengths (1.67 Å) rather than C–S single bonds (1.75 Å).[27] The S–C–S bond angles of 113.50(12)° for **2** and 114.25(14)° for **5** are clearly different, but vary relatively little in the context of related bidentate ruthenium complexes shown in Table 1. In acyclic carbenium dithiocarboxylates[28] and imidazol(in)ium-2-dithiocarboxylates,[29] the anionic and cationic units usually have almost orthogonal orientations in the crystal structures, and this conformation is largely retained upon complexation, as exemplified by the ruthenium and gold complexes listed in Table 1. In the structures of **2** and **5**, conversely, the two units are approximately coplanar, the torsion angles about the linking C–C bond being *ca.* 11° and 17°, respectively. A tendency towards orthogonality in free dithiocarboxylate betaines is often attributed to coulombic interactions.[29f] In the compounds investigated here, it is unclear whether steric or crystal packing effects are preventing this from occurring. The bond lengths of the N_2C^+ motif in **2** [1.350(3) Å, 1.352(3) Å] and **5** [1.347(3) Å, 1.354(3) Å] are the same. They are also shorter than typical C–N single bonds (1.47 Å),[27] indicating significant C═N double bond character due to electronic conjugation.

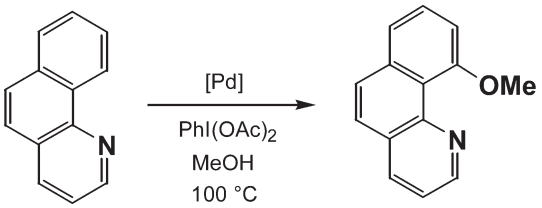
Catalytic studies

Palladium-catalysed coupling reactions are now some of the most useful and widely employed tools in synthetic organic chemistry. The majority of these reactions are thought to involve zerovalent palladium species in the catalytic cycle, even if divalent pre-catalysts, such as $[PdCl_2(PPh_3)_2]$ are often employed. Sanford and co-workers have shown that a range of oxidative C–H functionalization reactions are catalysed by palladium(II) compounds, often using palladium acetate as the pre-catalyst.[30] This prompted us to use the conversion of benzo[*h*]quinoline to 10-methoxybenzo[*h*]quinoline as a benchmark reaction to

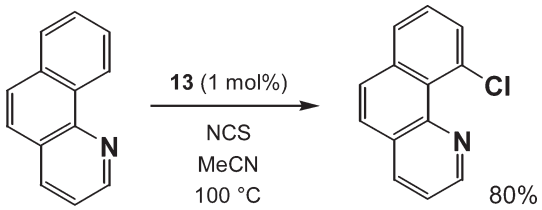
Table 1 Bond data for various transition metal complexes featuring NHC·CS_2 ligands

Complex	Reference	C–S (Å)	S–C–S (°)	S–C–C–N (°)
$[Pd(S_2C\cdot IMes)(PPh_3)_2]^+$ (**2**)	This work	1.683(2) 1.692(2)	113.50(12)	12.0
$[Pd(S_2C\cdot IMes)(dppf)]^+$ (**5**)	This work	1.684(3) 1.685(3)	114.25(14)	17.4
$[Ru(CH{=}CHC_6H_4Me\text{-}4)(S_2C\cdot ICy)(CO)(PPh_3)_2]^+$	22*b*	1.685(3) 1.691(3)	113.26(17)	38.5
$[Ru(C(C{\equiv}CPh){=}CHPh)(S_2C\cdot ICy)(CO)(PPh_3)_2]^+$	22*c*	1.663(7) 1.690(7)	114.7(4)	46.4
$[RuCl(p\text{-cymene})(S_2C\cdot IMes)]^+$	21*a*	1.680(3) 1.673(2)	112.3(2)	48.1
$[(Ph_3P)Au(S_2C\cdot IMes)]^+$	22*a*	1.640(3) 1.708(3)	128.26(15)[a]	57.4
$[(Ph_3P)Au(S_2C\cdot IDip)]^+$	22*a*	1.6420(16) 1.7027(14)	129.63(9)[a]	73.1
$[(IDip)Au(S_2C\cdot IPr)]^+$	22*a*	1.639(4) 1.701(4)	130.1(2)[a]	77.0
$[(IDip)Au(S_2C\cdot IMes)]^+$	22*a*	1.643(4) 1.702(5)	128.3(2)[a]	54.7

[a] Monodentate coordination.



Scheme 2 Selective C–H oxidative functionalization of benzo[*h*]-quinoline.



Scheme 3 Selective C–H oxidative chlorination of benzo[*h*]quinoline.

explore the catalytic potential of the compounds prepared in this study. Sanford reported that this transformation proceeded in 94% yield in methanol using 1.2 mol% $Pd(OAc)_2$ and a sacrificial oxidant at 100 °C for 22 h (Scheme 2).[30a] When the reaction was performed using a 1 mol% loading of $[Pd(S_2C{\cdot}ICy)(PPh_3)_2](PF_6)_2$ (**1**), the desired product was isolated in 86% yield after column chromatography. The use of complex **2** featuring the $IMes{\cdot}CS_2$ zwitterion resulted in a higher yield (95%), while the more bulky IDip version (**4**) gave the highest conversion (96%). Thus, changes in the steric profile of imidazolium-2-dithiocarboxylate ligands bearing aromatic substituents on their nitrogen atoms play only a modest role in this particular setting.

In order to ascertain whether lability of the phosphines was important, the transformation was attempted using the diphosphine derivative $[Pd(S_2C{\cdot}IMes)(dppf)](PF_6)_2$ (**5**). No significant conversion was observed, which was ascribed to the lack of lability of the dppf chelate. To further probe the nature of the active species, the residue at the end of the catalytic transformation performed with **2** was analysed and found to display characteristic resonances for the methyl substituents of the $IMes{\cdot}CS_2$ ligand at 2.12 and 2.40 ppm in the ^1H NMR spectrum, slightly shifted from their positions in precursor **2** (2.00 and 2.31 ppm) and quite different to those of the free ligand (2.36 and 2.38 ppm). These signals are likely due to a solvent-stabilised complex as the reaction is performed in air and triphenylphosphine oxide is identified by ^{31}P NMR spectroscopy.

Sanford and co-workers showed that the cyclometallated benzo[*h*]quinolinyl complex, $[Pd(C,N\text{-bzq})(OAc)]_2$, was also an active (pre)catalyst for the reaction shown in Scheme 2.[30] This observation is in line with a mechanism involving cyclometallation of benzo[*h*]quinoline followed by attack of methanol at the Pd–C bond. Accordingly, the series of benzo[*h*]quinolinyl compounds $[Pd(C,N\text{-bzq})(S_2C{\cdot}NHC)]PF_6$ (NHC = ICy **11**, IMes **12**, IDip **13**) was prepared (Scheme 1). Compound **13** was investigated in the conversion of benzo[*h*]quinoline to 10-methoxybenzo[*h*]quinoline under the same conditions as used previously, giving a 69% yield with a 1 mol% catalyst loading. Shortening the reaction time from 22 h to 17 h led only to a minor drop of yield from 69% to 67%. Lower catalyst loadings for the reaction were also explored. Hence, after 22 h, a 41% yield of 10-methoxybenzo[*h*]quinoline was obtained with 0.1 mol% of **2**.

In an unexpected development, it was discovered that a small amount of 2,10-dimethoxybenzo[*h*]quinoline (3%) was also formed in the reaction using 1 mol% of **4** under literature conditions. Separation of this by-product from the main 10-methoxybenzo[*h*]quinoline product (96%) was achieved by column chromatography. This suggests that, although selectivity for the 10-position is very high, it is not exclusive, and the dithiocarboxylate complexes reported here are capable of forming disubstituted products. The mechanism by which this reaction takes place is difficult to surmise as the cyclometallation of the substrate, which leads to the high selectivity for the 10-position in benzo[*h*]quinoline, is unlikely to take place at the 2-position. Instead, a bimetallic, intermolecular activation pathway could be responsible for the second methoxylation.

Using *N*-chlorosuccinimide as oxidant in place of $PhI(OAc)_2$, an acetonitrile solution of benzo[*h*]quinoline was converted to 10-chlorobenzo[*h*]quinoline in 80% yield in the presence of 1 mol% of **13** (Scheme 3). Sanford *et al.* reported that the same reaction with palladium acetate was sluggish[30a] and this was found to be the case in this study with the reaction mixture being heated at 100 °C for 44 h. Under these conditions, the yield obtained was lower than the 95% value reported by Sanford after 3 days of reaction and in both cases column chromatography was required to purify the product. More importantly, this result provides additional support for the active catalytic species being a palladium dithiocarboxylate unit. Given the literature precedent for the use of $Pd(OAc)_2$ in these transformations, it is possible that the acetate released from the $PhI(OAc)_2$ sacrificial oxidant would displace the dithiocarboxylate ligand, forming a palladium acetate complex *in situ*, which could then perform the catalysis. However, the performance of $[Pd(C,N\text{-bzq})(S_2C{\cdot}Dip)]PF_6$ (**13**) with *N*-chlorosuccinimide as oxidant provides evidence that high catalytic activity is also maintained in the absence of acetate, supporting the involvement of a $Pd(S_2C{\cdot}NHC)$ species in the catalytic cycle. This is not surprising as the $NHC{\cdot}CS_2$ adducts are very robust in both free[31] and coordinated[21] forms, in contrast to the carboxylate analogues.[32]

Conclusion

Previous to this report, the only examples of palladium complexes bearing $NHC{\cdot}CS_2$ ligands were simple homoleptic compounds. Thus, the organopalladium and phosphine-based complexes described here substantially broaden this class of compounds. Moreover, for the first time, complexes bearing imidazol(in)ium-2-dithiocarboxylate units were shown to be effective pre-catalysts for an important and selective transformation, namely oxidative C–H functionalisation. They were able to achieve this both at a similar level of performance and catalyst loading to the pre-eminent examples from the literature. These results will help dispel the notion that 1,1-dithio ligands offer little in the design of highly active catalytic species.

Experimental section

General comments

All experiments were carried out under aerobic conditions and the products obtained appear indefinitely stable towards the atmosphere, whether in solution or in the solid state. The complexes $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)Cl]_2$,[26] $[Pd(C,N\text{-bzq})(OAc)]_2$ [30a] *cis*-$[PdCl_2(PPh_3)_2]$[33] and $[PdCl_2(dppf)]$[34] were prepared according to literature. The betaines IPr·CS_2, ICy·CS_2, IMes·CS_2, IDip·CS_2 and SIMes·CS_2 were prepared using an established procedure.[31] Solvents and other reagents were used as received from commercial suppliers. Petroleum ether refers to the fraction boiling in the 40–60 °C range. Electrospray mass spectra were obtained using a Micromass LCT Premier instrument. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Characteristic triphenylphosphine-associated infrared data are not reported. Unless otherwise indicated, NMR spectroscopy was performed at 25 °C using a Varian Mercury 300 spectrometer. All couplings are reported in Hertz. The resonance for the hexafluorophosphate anion was observed in all cases but is omitted from the NMR data below for reasons of brevity. Elemental analyses were provided by London Metropolitan University.

Synthesis of $[Pd(S_2C{\cdot}NHC)(PPh_3)_2](PF_6)_2$ complexes

$[PdCl_2(PPh_3)_2]$ (27 mg, 0.038 mmol) and a NHC·CS_2 ligand (0.042 mmol) were dissolved in chloroform (20 mL) and methanol (10 mL). NH_4PF_6 (25 mg, 0.153 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. The solvents were then removed under reduced pressure with a rotary evaporator and a minimum amount of dichloromethane was added to dissolve the residue. The resulting suspension was filtered through Celite to remove NH_4Cl and excess NH_4PF_6. The filtrate was concentrated to *ca.* 2 mL and layered with hexane to precipitate the product overnight. The final compound was washed with hexane (10 mL) and dried.

$[Pd(S_2C{\cdot}ICy)(PPh_3)_2](PF_6)_2$ (1). Yellow-brown solid (32 mg, 69%). IR (solid): 3173, 2939, 2862, 1481, 1452, 1436, 1313, 1276, 1192, 1046, 1015, 946, 875, 828 (ν_{PF}), 780, 710 cm^{-1}. ^{31}P NMR (CD_2Cl_2): 32.3 (s, PPh_3) ppm. ^1H NMR (CD_2Cl_2): 1.23, 1.58–1.66, 1.72, 1.84, 2.04, 2.07 (6 m, 20H, cyclohexyl), 4.53 (tt, 2H, NC*H*-cyclohexyl, J_{HH} = 6.6 Hz), 7.39–7.42, 7.46–7.55 (2 m, 30H, PPh_3), 7.60 (s, 2H, HC═CH) ppm. MS (FAB +ve) *m*/*z* (abundance): 938 (4) $[M]^+$, 676 (14) $[M - PPh_3]^+$. Analysis: Calculated for $C_{52}H_{54}F_{12}N_2P_4PdS_2$ (1229.43): C 50.8, H 4.4, N 2.3%; Found C 50.8, H 4.4, N 2.2%.

$[Pd(S_2C{\cdot}IMes)(PPh_3)_2](PF_6)_2$ (2). Red solid (40 mg, 81%). IR (solid): 3164, 2921, 1606, 1481, 1437, 1404, 1387, 1233, 1000, 905, 827 (ν_{PF}), 774, 739 cm^{-1}. ^{31}P NMR (CD_2Cl_2): 31.4 (s, PPh_3) ppm. ^1H NMR (CD_2Cl_2): 2.00 (s, 12H, *o*-CH_3) 2.31 (s, 6H, *p*-CH_3), 6.91 (s, 4H, *m*-C_6H_2), 7.18–7.22, 7.29–7.32, 7.49–7.52 (3 m, 30H, PPh_3), 7.77 (s, 2H, HC═CH) ppm. MS (FAB +ve) *m*/*z* (abundance): 1155 (6) $[M + PF_6]^+$, 1010 (13) $[M]^+$, 748 (23) $[M - PPh_3]^+$. Analysis: Calculated for $C_{58}H_{54}F_{12}N_2P_4PdS_2$ (1301.49): C 53.5, H 4.2, N 2.2%; Found C 53.6, H 4.3, N 2.1%.

$[Pd(S_2C{\cdot}SIMes)(PPh_3)_2](PF_6)_2$ (3). Dark red solid (28 mg, 57%). IR (solid): 2938, 1608, 1560, 1383, 1288, 1192, 879, 830 (ν_{PF}) cm^{-1}. ^{31}P NMR (CD_2Cl_2): 32.4 (s, PPh_3) ppm. ^1H NMR (CD_2Cl_2): 2.22 (s, 12H, *o*-CH_3), 2.37 (s, 6H, *p*-CH_3), 4.49 (s, 4H, H_2CCH_2), 6.98 (s, 4H, *m*-C_6H_2), 7.12–7.16, 7.32–7.35, 7.53–7.57 (3 m, 30H, PPh_3) ppm. MS (FAB +ve) *m*/*z* (abundance): *m*/*z* 1157 (8) $[M + PF_6]^+$, 1012 (15) $[M]^+$. Analysis: Calculated for $C_{58}H_{56}F_{12}N_2P_4PdS_2$ (1303.51): C 53.4, H 4.3, N 2.2%; Found C 53.6, H 4.2, N 2.1%.

$[Pd(S_2C{\cdot}IDip)(PPh_3)_2](PF_6)_2$ (4). Dark red-brown solid (38 mg, 72%). IR (solid): 3161, 2969, 2931, 1543, 1437, 1395, 1218, 1187, 1164, 998, 912, 877, 829 (ν_{PF}), 745 cm^{-1}. ^{31}P NMR (CD_2Cl_2): 31.5 (s, PPh_3) ppm. ^1H NMR (CD_2Cl_2): 1.11 (d, 12H, CH_3CHCH_3, J_{HH} = 6.8 Hz), 1.23 (d, 12H, CH_3CHCH_3, J_{HH} = 6.8 Hz), 2.17 (sept, 4H, CH_3CHCH_3, J_{HH} = 6.6 Hz), 7.09–7.13, 7.23–7.30, 7.49–7.53 (3 m, 36H, PPh_3 + C_6H_3), 7.97 (s, 2H, HC═CH) ppm. MS (FAB +ve) *m*/*z* (abundance): 1157 (8) $[M + PF_6]^+$, 1012 (15) $[M]^+$. Analysis: Calculated for $C_{64}H_{68}F_{12}N_2P_4PdS_2$ (1385.65): C 55.5, H 4.8, N 2.0%; Found C 55.6, H 4.9, N 1.9%.

Synthesis of $[Pd(S_2C{\cdot}IMes)(dppf)](PF_6)_2$ (5)

$[PdCl_2(dppf)]$ (27.5 mg, 0.038 mmol) and IMes·CS_2 (15.7 mg, 0.041 mmol) were dissolved in chloroform (20 mL) and methanol (10 mL). NH_4PF_6 (25 mg, 0.153 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. The solvents were then removed under reduced pressure with a rotary evaporator and a minimum amount of dichloromethane was added to dissolve the residue. The resulting suspension was filtered through Celite to remove NH_4Cl and excess NH_4PF_6. The filtrate was concentrated to *ca.* 2 mL and layered with hexane to precipitate the deep red product overnight. The final compound was washed with hexane (10 mL) and dried. Yield: 27 mg (53%). IR (solid state): 3175, 2925, 1480, 1435, 1401, 1386, 1308, 1229, 1168, 1097, 1031, 998, 904, 825 (ν_{PF}), 747 cm^{-1}. ^{31}P NMR (CD_2Cl_2): 37.2 (s, dppf) ppm. ^1H NMR (CD_2Cl_2): 1.98 (s, 12H, *o*-CH_3), 2.32 (s, 6H, *p*-CH_3), 4.47, 4.63 (2 m, 8H, C_5H_4), 6.92 (s, 4H, *m*-C_6H_2), 7.42–7.49, 7.63–7.67 (3 m, 20H, C_6H_5), 7.75 (s, 2H, HC═CH) ppm. MS (FAB +ve) *m*/*z* (abundance): 1185 (6) $[M + PF_6]^+$, 1040 (20) $[M]^+$. Analysis: Calculated for $C_{56}H_{52}F_{12}FeN_2P_4PdS_2$ (1333.30): C 50.5, H 3.9, N 2.1%; Found C 50.4, H 3.9, N 2.1%.

Synthesis of $[Pd(C,N\text{-}C_6H_4CH_2NMe_2)(S_2C{\cdot}NHC)]PF_6$ complexes

$[Pd(C,N\text{-}C_6H_4CH_2NMe_2)Cl]_2$ (20 mg, 0.036 mmol) and a NHC·CS_2 ligand (0.072 mmol) were dissolved in dichloromethane (20 mL) and a solution of NH_4PF_6 (24 mg, 0.147 mmol) in methanol (10 mL) was added. The reaction mixture was stirred for 2 h at room temperature. The solvents were removed under reduced pressure with a rotary evaporator and a minimum amount of dichloromethane was added to dissolve the residue. The resulting suspension was filtered through Celite to remove NH_4Cl and excess NH_4PF_6. The solvent was

again removed and the residue was triturated ultrasonically in diethyl ether (10 mL) to afford the product. The final compound was washed with diethyl ether (10 mL) and dried.

[Pd(*C*,*N*-$C_6H_4CH_2NMe_2$)(S_2C·IPr)]PF_6 (6). Orange solid (33 mg, 75%). IR (solid): 3067, 2917, 2849, 1515, 1453, 1425, 1366, 1202, 1073, 911, 805 (ν_{PF}), 757, 722 cm^{-1}. ^1H NMR ($CDCl_3$): 1.65 (d, 12H, CH_3CHCH_3, J_{HH} = 6.7 Hz), 3.06 (s, 6H, NMe_2), 4.14 (s, 2H, CH_2), 4.94 (s, 2H, CH_3CHCH_3, J_{HH} = 6.4 Hz), 7.02–7.19 (m, 4H, C_6H_4), 7.61 (s, 2H, HC=CH) ppm. MS (ES +ve) *m*/*z* (abundance): 468 (100) $[M]^+$. Analysis: Calculated for $C_{19}H_{28}F_6N_3PPdS_2$ (613.96): C 37.2, H 4.6, N 6.8%; Found C 37.3, H 4.5, N 6.7%.

[Pd(*C*,*N*-$C_6H_4CH_2NMe_2$)(S_2C·ICy)]PF_6 (7). Brown solid (34 mg, 68%). IR (solid): 3171, 2933, 2858, 1564, 1451, 1199, 1053, 833 (ν_{PF}), 750, 710 cm^{-1}. ^1H NMR ($CDCl_3$): 1.33–1.41, 1.71–1.74, 1.92–1.95, 2.15–2.17 (4 m, 20H, cyclohexyl), 3.02 (s, 6H, NMe_2), 4.10 (s, 2H, CH_2NMe_2), 4.44 (m, 2H, NCH-Cy), 7.00–7.15 (m, 4H, C_6H_4), 7.53 (s, 2H, HC=CH) ppm. MS (ES +ve) *m*/*z* (abundance): 548 (22) $[M]^+$. Analysis: Calculated for $C_{25}H_{36}F_6N_3PPdS_2$ (694.09): C 43.3, H 5.2, N 6.1%; Found C 43.4, H 5.2, N 5.9%.

[Pd(*C*,*N*-$C_6H_4CH_2NMe_2$)(S_2C·IMes)]PF_6 (8). Orange solid (32 mg, 58%). IR (solid): 3165, 2921, 1607, 1579, 1556, 1484, 1452, 1383, 1230, 1119, 1061, 1020, 831 (ν_{PF}), 742, 723 cm^{-1}. ^1H NMR (CD_2Cl_2): 2.19 (s, 12H, *o*-CH_3), 2.39 (s, 6H, *p*-CH_3), 2.79 (s, 6H, NMe_2), 3.94 (s, 2H, CH_2), 6.68–6.70, 6.89–6.92, 7.01–7.04 (3 m, 4H, C_6H_4), 7.10 (s, 4H, C_6H_2), 7.61 (s, 2H, HC=CH) ppm. MS (ES +ve) *m*/*z* (abundance): 620 (23) $[M]^+$. Analysis: Calculated for $C_{31}H_{36}F_6N_3PPdS_2$ (766.15): C 48.6, H 4.7, N, 5.5%; Found C 48.6, H 4.7, N 5.6%.

[Pd(*C*,*N*-$C_6H_4CH_2NMe_2$)(S_2C·SIMes)]PF_6 (9). Dark red solid (49 mg, 89%). IR (solid): 2922, 1609, 1561, 1453, 1287, 1212, 1098, 1023, 831 (ν_{PF}), 741 cm^{-1}. ^1H NMR ($CDCl_3$): 2.31 (s, 6H, *p*-CH_3), 2.44 (s, 12H, *o*-CH_3), 2.79 (s, 6H, NMe_2), 3.91 (s, 2H, CH_2), 4.51 (s, 4H CH_2CH_2), 6.75–6.77, 6.87–6.90, 6.93–6.98, 7.02–7.07 (4 m, 10H, C_6H_4 + C_6H_2) ppm. MS (ES +ve) *m*/*z* (abundance): 622 (33) $[M]^+$. Analysis: Calculated for $C_{31}H_{38}F_6N_3PPdS_2$ (768.15): C 48.5, H 5.0, N 5.5%; Found C 48.6, H 4.9, N 5.4%.

[Pd(*C*,*N*-$C_6H_4CH_2NMe_2$)(S_2C·IDip)]PF_6 (10). Dark brown solid (47 mg, 77%). IR (solid): 3149, 2966, 2927, 2871, 1545, 1469, 1390, 1220, 1100, 1063, 1046, 1000, 833 (ν_{PF}), 801, 730 cm^{-1}. ^1H NMR ($CDCl_3$): 1.28 (d, 12H, CH_3CHCH_3, J_{HH} = 6.8 Hz), 1.30 (d, 12H, CH_3CHCH_3, J_{HH} = 6.9 Hz), 2.43 (sept, 4H, CH_3CHCH_3, J_{HH} = 6.8 Hz), 2.77 (s, 6H, NMe_2), 3.92 (s, 2H, CH_2), 6.58–6.60, 6.91–6.97, 7.03–7.06 (3 m, 4H, C_6H_4), 7.34 (d, 4H, *m*-C_6H_3, J_{HH} = 7.9 Hz), 7.59 (t, 2H, *p*-C_6H_3, J_{HH} = 7.8 Hz), 7.89 (s, 2H, HC=CH) ppm. MS (ES +ve) *m*/*z* (abundance): 704 (32) $[M]^+$. Analysis: Calculated for $C_{37}H_{48}F_6N_3PPdS_2$ (850.31): C 52.3, H 5.7, N 4.9%; Found C 52.5, H 5.7, N 4.8%.

Synthesis of [Pd(*C*,*N*-bzq)(S_2C·NHC)]PF_6 complexes

$[Pd(C,N\text{-bzq})Cl]_2$ (40 mg, 0.063 mmol) and a NHC·CS_2 ligand (0.126 mmol) were dissolved in dichloromethane (20 mL) and a solution of NH_4PF_6 (41 mg, 0.252 mmol) in methanol (10 mL) was added. The reaction mixture was stirred for 2 h at room temperature. The solvents were removed under reduced pressure with a rotary evaporator and the residue was dissolved in a minimum amount of dichloromethane before filtration through Celite and removal of the dichloromethane under vacuum (rotary evaporator). The residue was triturated with diethyl ether (10 mL), filtered and dried in the air.

[Pd(*C*,*N*-bzq)(S_2C·ICy)]PF_6 (11). Brown solid (49 mg, 53%). IR (solid state): 3654, 2932, 2858, 2079, 1739, 1622, 1566, 1450, 1403, 1325, 1199, 1143, 1058, 831 (ν_{PF}), 754, 707 cm^{-1}. ^1H NMR (CD_2Cl_2): 1.30–1.49, 1.73–1.85, 1.90–2.08, 2.24–2.37 (4 m, 20H, Cy), 4.59–4.73 (m, 2H, NCH-Cy), 7.22–7.29, 7.41–7.44, 7.53–7.57, 7.77, 7.86–7.92, 8.07–8.12, 8.48–8.54, 8.86–8.89 (8 m, 10H, HC=CH + bzq) ppm; MS (FAB +ve) *m*/*z* (abundance): 592 (19) $[M]^+$. Calculated for $C_{29}H_{32}F_6N_3PPdS_2$·OEt_2 (812.22): C 48.8, H 5.2, N 5.2%; Found: C 48.8, H 4.6, N 5.7%.

[Pd(*C*,*N*-bzq)(S_2C·IMes)]PF_6 (12). Brown solid (80 mg, 78%). IR (solid state): 3668, 3158, 2931, 1608, 1556, 1483, 1452, 1405, 1326, 1228, 1118, 1053, 832 (ν_{PF}), 720, 705 cm^{-1}. ^1H NMR (CD_2Cl_2): 2.25 (s, *o*-CH_3, 6H), 2.38 (s, *o*-CH_3, 6H), 2.46 (s, *p*-CH_3, 6H), 6.37, 6.65, 6.95, 7.13 (4 m, 4H, *m*-C_6H_2), 7.76 (s, HC=CH, 2H), 7.22–7.27, 7.32, 7.45–7.49, 7.57–7.61, 7.85, 7.99, 8.44–8.47, 8.59–8.61 (8 m, 8H, bzq) ppm. MS (FAB +ve) *m*/*z* (abundance): 663 (35) $[M]^+$. Calculated for $C_{35}H_{32}F_6N_3PPdS_2$ (810.17): C 51.9, H 4.0, N 5.2%; Found: C 51.8, H 4.0, N 5.1%.

[Pd(*C*,*N*-bzq)(S_2C·IDip)]PF_6 (13). Brown solid (82 mg, 73%). IR (solid state): 3169, 2966, 2930, 1571, 1554, 1465, 1404, 1389, 1368, 1325, 1213, 1106, 1061, 1024, 915, 835 (ν_{PF}), 754, 724 cm^{-1}. ^1H NMR (CD_2Cl_2): 1.35, 1.42 (2 d, 24H, CH_3, J_{HH} = 6.8 Hz), 2.56 (sept, 4H, $CHMe_2$, J_{HH} = 6.7 Hz), 7.78 (s, HC=CH, 2H), 7.03, 7.45–7.50, 7.57–7.61, 7.70–7.74, 7.85, 8.44–8.47, 8.56–8.58 (7 m, 14H, C_6H_3 + bzq) ppm. MS (FAB +ve) *m*/*z* (abundance): 748 (100) $[M]^+$. Calculated for $C_{41}H_{44}F_6N_3PPdS_2$·$0.25CH_2Cl_2$ (915.56): C 54.1, H 4.9, N 4.6%; Found: C 53.8, H 5.0, N 4.5%.

Synthesis of 10-methoxybenzo[*h*]quinoline

Methanol (7.5 mL) was added to a mixture of benzo[*h*]quinoline (151 mg, 0.843 mmol), $PhI(OAc)_2$ (541 mg, 1.680 mmol) and the palladium complex (1 mol%, 0.0084 mmol) in a 20 mL vial. The vial was sealed with a screw cap lined with Teflon and the solution was heated with stirring to 100 °C for 22 h. The solvent was then removed with a rotary evaporator and the crude solid was purified by column chromatography on silica gel (eluent: 3 : 2 v/v ethyl acetate–*n*-hexane). The desired yellow-orange product was the last fraction eluted. All the solvents were removed and the pale yellow product was dried under vacuum. Spectroscopic and analytical data agreed well with the values reported in the literature.[30a] Yields for the 22 h runs using catalyst **1**: 151 mg, 86%; **2**: 167 mg, 95%; **4**: 169 mg, 96%; **13**: 121 mg, 69% (1 mol% in all cases). Yield for the 17 h run using catalyst **13** (1 mol%): 118 mg, 67%. Yield for the 22 h run using catalyst **2** (0.1 mol%): 71 mg, 40%.

Synthesis of 2,10-dimethoxybenzo[*h*]quinoline

The same procedure was used as above for 10-methoxybenzo[*h*]-quinoline using benzo[*h*]quinoline (151 mg, 0.843 mmol) with $[Pd(S_2C{\cdot}IDip)(PPh_3)_2](PF_6)_2$ (**4**, 11.6 mg, 0.0084 mmol) as catalyst. Using a 1 : 1 v/v ethyl acetate–*n*-hexane mixture, the second eluted compound was collected. All the solvents were removed and the yellow oil was dried under vacuum (6 mg, 3%). 169 mg (96%) of 10-methoxybenzo[*h*]quinoline was also isolated. IR (solid): 2937, 2857, 1717, 1592, 1562, 1453, 1433, 1385, 1317, 1260 (ν_{CO}), 1194, 1122, 1072, 1030, 964 cm^{-1}. ^1H NMR ($CDCl_3$): 4.15 (s, 3H, CH_3), 4.28 (s, 3H, CH_3), 7.33 (dd, 1H, bzq-H, J_{HH} = 8.0, 1.1 Hz), 7.60 (dd, 1H, bzq-H, J_{HH} = 7.9, 1.1 Hz), 7.71 (t, 1H, bzq-H, J_{HH} = 7.9 Hz), 7.75 (d, 1H, bzq-H, J_{HH} = 8.8 Hz), 7.92 (d, 1H, bzq-H, J_{HH} = 8.8 Hz), 8.34 (d, 1H, bzq-H, J_{HH} = 8.2 Hz), 8.39 (d, 1H, bzq-H, J_{HH} = 8.2 Hz) ppm. ^{13}C NMR ($CDCl_3$): 166.3 (s), 159.3 (s), 146.8 (s), 145.9 (s), 137.5 (s), 136.8 (s), 130.9 (s), 130.3 (s), 129.1 (s), 125.8 (s), 121.4 (s), 121.3 (s), 110.6 (s), 56.8 (s), 53.1 (s) ppm. MS (FAB) *m*/*z* (abundance): 239 $[M]^+$. Calculated for $C_{15}H_{13}NO_2$ (239.27): C 75.3, H 5.5, N 5.9%; Found: C 75.1, H 5.3, N 5.9%.

Synthesis of 10-chlorobenzo[*h*]quinoline

Acetonitrile (7.5 mL) was added to a mixture of benzo[*h*]-quinoline (159 mg, 0.887 mmol), *N*-chlorosuccinimide (137 mg, 1.026 mmol) and $[Pd(C,N\text{-bzq})(S_2C{\cdot}IDip)]PF_6$ (**13**, 8 mg, 0.0089 mmol) in a 20 mL vial. The vial was sealed with a screw cap lined with Teflon and the solution was heated with stirring to 100 °C for 44 h. The solvent was removed with a rotary evaporator and the crude solid was purified by column chromatography on silica gel (eluent: 1 : 4 v/v ethyl acetate–*n*-hexane). After unreacted benzo[*h*]quinoline was eluted, the second fraction was carefully collected and the solvents removed. The colourless solid was dried under vacuum to afford the product (152 mg, 80%). Spectroscopic and analytical data agreed well with the values reported in the literature.[30a]

Crystallography

Crystals of compounds **2** and **5** were grown by slow diffusion of petroleum ether (bp 40–60 °C) into a dichloromethane solution.

Crystal data for 2. $[C_{58}H_{54}N_2P_2PdS_2](PF_6)_2{\cdot}1.5(CH_2Cl_2)$, M = 1428.82, triclinic, $P\bar{1}$ (no. 2), a = 11.1014(4), b = 14.2330(2), c = 20.2200(5) Å, α = 79.2326(18), β = 82.282(2), γ = 84.242(2)°, V = 3100.90(14) $Å^3$, Z = 2, D_c = 1.530 g cm^{-3}, μ(Mo-Kα) = 0.676 mm^{-1}, T = 173 K, orange tabular needles, Oxford Diffraction Xcalibur 3 diffractometer; 14 425 independent measured reflections (R_{int} = 0.0202), F^2 refinement,[35] R_1(obs) = 0.0359, wR_2(all) = 0.0863, 11 951 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 59°], 783 parameters. CCDC 880366.

Crystal data for 5. $[C_{56}H_{52}FeN_2P_2PdS_2](PF_6)_2{\cdot}CH_2Cl_2$, M = 1416.17, monoclinic, $P2_1/c$ (no. 14), a = 10.6623(3), b = 20.1267(5), c = 27.4186(6) Å, β = 96.124(2)°, V = 5850.4(3) $Å^3$, Z = 4, D_c = 1.608 g cm^{-3}, μ(Mo-Kα) = 0.906 mm^{-1}, T = 173 K, red blocky needles, Oxford Diffraction Xcalibur 3 diffractometer; 13 549 independent measured reflections (R_{int} = 0.0289), F^2 refinement,[35] R_1(obs) = 0.0396, wR_2(all) = 0.0895, 10 406 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 59°], 736 parameters. CCDC 880367.

Acknowledgements

We thank Johnson Matthey Ltd for a generous loan of palladium salts.

References

1 (*a*) D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11**, 233–371; (*b*) D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301–469.
2 R. P. Burns, F. P. McCullough and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1980, **23**, 211–280.
3 G. Hogarth, *Prog. Inorg. Chem.*, 2005, **53**, 71–561.
4 J. Cookson and P. D. Beer, *Dalton Trans.*, 2007, 1459–1472.
5 E. R. T. Tiekink and I. Haiduc, *Prog. Inorg. Chem.*, 2005, **54**, 127–319.
6 (*a*) J. D. E. T. Wilton-Ely, D. Solanki and G. Hogarth, *Eur. J. Inorg. Chem.*, 2005, 4027–4030; (*b*) E. R. Knight, D. Solanki, G. Hogarth, K. B. Holt, A. L. Thompson and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 2008, **47**, 9642–9653; (*c*) E. R. Knight, A. R. Cowley, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2009, 607–609; (*d*) E. R. Knight, N. H. Leung, Y. H. Lin, A. R. Cowley, D. J. Watkin, A. L. Thompson, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2009, 3688–3697; (*e*) E. R. Knight, N. H. Leung, A. L. Thompson, G. Hogarth and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 2009, **48**, 3866–3874; (*f*) M. J. Macgregor, G. Hogarth, A. L. Thompson and J. D. E. T. Wilton-Ely, *Organometallics*, 2009, **28**, 197–208; (*g*) S. Naeem, E. Ogilvie, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2010, **39**, 4080–4089; (*h*) S. Naeem, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Organometallics*, 2010, **29**, 2547–2556; (*i*) Y. H. Lin, N. H. Leung, K. B. Holt, A. L. Thompson and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2009, 7891–7901.
7 N. Kano and T. Kawashima, *Top. Curr. Chem.*, 2005, **251**, 141–180.
8 (*a*) A. Igau, H. Grutzmacher, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.*, 1988, **110**, 6463–6466; (*b*) A. Igau, A. Baceiredo, G. Trinquier and G. Bertrand, *Angew. Chem., Int. Ed.*, 1989, **28**, 621–622; (*c*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39–92.
9 (*a*) A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361–363; (*b*) A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 2801; (*c*) A. J. Arduengo III, *Acc. Chem. Res.*, 1999, **32**, 913–921.
10 For monographs, see: (*a*) *N-Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, 2006; (*b*) *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Topics in Organometallic Chemistry, ed. F. Glorius, Springer, Berlin, 2007, vol. 21; (*c*) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, RSC Catalysis Series, ed. S. Díez-González, Royal Society of Chemistry, Cambridge, 2010, vol. 6; (*d*) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, Catalysis by Metal Complexes, ed. C. S. J. Cazin, Springer, Dordrecht, 2011, vol. 32.
11 For recent reviews, see: (*a*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172; (*b*) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561–3598; (*c*) P. L. Arnold and I. J. Casely, *Chem. Rev.*, 2009, **109**, 3599–3611; (*d*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676; (*e*) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677–3707; (*f*) C. Samojłowicz, M. Bieniek and K. Grela, *Chem. Rev.*, 2009, **109**, 3708–3742; (*g*) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746–1787.
12 (*a*) J. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2674–2678; (*b*) M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953–956.
13 S. Díez-González, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 7595–7606.
14 (*a*) D. E. Bergbreiter, P. L. Osburn and Y.-S. Liu, *J. Am. Chem. Soc.*, 1999, **121**, 9531–9538; (*b*) A. S. Gruber, D. Zim, G. Ebeling,

A. L. Monteiro and J. Dupont, *Org. Lett.*, 2000, **2**, 1287–1290; (*c*) D. Zim, A. S. Gruber, G. Ebeling, J. Dupont and A. L. Monteiro, *Org. Lett.*, 2000, **2**, 2881–2884; (*d*) J. Dupont, A. S. Gruber, G. S. Fonseca, A. L. Monteiro and G. Ebeling, *Organometallics*, 2001, **20**, 171–176; (*e*) P. B. Silveira, V. R. Lando, J. Dupont and A. L. Monteiro, *Tetrahedron Lett.*, 2002, **43**, 2327–2329; (*f*) C. S. Consorti, G. Ebeling, F. R. Flores, F. Rominger and J. Dupont, *Adv. Synth. Catal.*, 2004, **346**, 617–624; (*g*) V. V. Thakur, N. S. C. R. Kumar and A. Sudalai, *Tetrahedron Lett.*, 2004, **45**, 2915–2918; (*h*) Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen and Z. Yang, *Org. Lett.*, 2004, **6**, 3337–3340; (*i*) R. B. Bedford, C. S. J. Cazin, M. B. Hursthouse, M. E. Light and V. J. M. Scordia, *Dalton Trans.*, 2004, 3864–3868; (*j*) K. Yu, W. Sommer, J. M. Richardson, M. Weck and C. W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161–171; (*k*) J. Spencer, D. P. Sharratt, J. Dupont, A. L. Monteiro, V. I. Reis, M. P. Stracke, F. Rominger and I. M. McDonald, *Organometallics*, 2005, **24**, 5665–5672; (*l*) M.-T. Chen, C.-A. Huang and C.-T. Chen, *Eur. J. Inorg. Chem.*, 2006, 4642–4648; (*m*) H. V. Huynh, C. H. Yeo and Y. X. Chew, *Organometallics*, 2010, **29**, 1479–1486; (*n*) C. Fliedel, A. Sabbatini and P. Braunstein, *Dalton Trans.*, 2010, **39**, 8820–8828; (*o*) W.-C. Wang, K.-F. Peng, M.-T. Chen and C.-T. Chen, *Dalton Trans.*, 2012, **41**, 3022–3029; (*p*) A. F. Hill and J. D. E. T. Wilton-Ely, *Organometallics*, 1997, **16**, 4517–4518.

15 H. M. Lee, C. C. Lee and P. Y. Cheng, *Curr. Org. Chem.*, 2007, **11**, 1491–1524.

16 M. Mellah, A. Voituriez and E. Schultz, *Chem. Rev.*, 2007, **107**, 5133–5209.

17 P. J. Nieuwenhuizen, A. W. Ehlers, J. G. Haasnoot, S. R. Janse, J. Reedijk and E. J. Baerends, *J. Am. Chem. Soc.*, 1999, **121**, 163–168.

18 (*a*) M. Azouri, J. Andrieu, M. Picquet, P. Richard, B. Hanquet and I. Tkatchenko, *Eur. J. Inorg. Chem.*, 2007, 4877–4883; (*b*) O. Kaufhold and F. E. Hahn, *Angew. Chem., Int. Ed.*, 2008, **47**, 4057–4061; (*c*) M. Azouri, J. Andrieu, M. Picquet and H. Cattey, *Inorg. Chem.*, 2009, **48**, 1236–1242; (*d*) M. Alcarazo, *Dalton Trans.*, 2011, **40**, 1839–1845.

19 For a review, see: L. Delaude, *Eur. J. Inorg. Chem.*, 2009, 1681–1699.

20 (*a*) L. L. Borer, J. V. Kong and E. Sinn, *Inorg. Chim. Acta*, 1986, **122**, 145–148; (*b*) L. L. Borer, J. V. Kong, P. A. Keihl and D. M. Forkey, *Inorg. Chim. Acta*, 1987, **129**, 223–226; see also: (*c*) T. Sugaya, T. Fujihara, A. Nagasawa and K. Unoura, *Inorg. Chim. Acta*, 2009, **362**, 4813–4822.

21 (*a*) L. Delaude, X. Sauvage, A. Demonceau and J. Wouters, *Organometallics*, 2009, **28**, 4056–4064; (*b*) Q. Willem, F. Nicks, X. Sauvage, L. Delaude and A. Demonceau, *J. Organomet. Chem.*, 2009, **694**, 4049–4055.

22 (*a*) S. Naeem, L. Delaude, A. J. P. White and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 2010, **49**, 1784–1793; (*b*) S. Naeem, A. L. Thompson, L. Delaude and J. D. E. T. Wilton-Ely, *Chem.–Eur. J.*, 2010, **16**, 10971–10974; (*c*) S. Naeem, A. L. Thompson, A. J. P. White, L. Delaude and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2011, **40**, 3737–3747; (*d*) E. Y. Chia, S. Naeem, L. Delaude and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2011, **40**, 6645–6658.

23 M. Hans, Q. Willem, J. Wouters, A. Demonceau and L. Delaude, *Organometallics*, 2011, **30**, 6133–6142.

24 (*a*) O. Sereda, A. Blanrue and R. Wilhelm, *Chem. Commun.*, 2009, 1040–1042; (*b*) M. Hans, J. Wouters, A. Demonceau and L. Delaude, *Eur. J. Org. Chem.*, 2011, 7083–7091.

25 (*a*) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo and S. P. Nolan, *Organometallics*, 2003, **22**, 4322–4326; (*b*) L. Cavallo, A. Correa, C. Costabile and H. Jacobsen, *J. Organomet. Chem.*, 2005, **690**, 5407–5413; (*c*) H. Clavier and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 841–861.

26 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909–913.

27 F. H. Allen, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, in *International Tables for Crystallography*, ed. E. Prince, Springer, Berlin, 2006, vol. C, pp. 790–811.

28 (*a*) M. L. Ziegler, H. Weber, B. Nuber and O. Z. Serhadle, *Z. Naturforsch., B: Chem. Sci.*, 1987, **42b**, 1411–1418; (*b*) A. Nagasawa, I. Akiyama, S. Mashima and J. Nakayama, *Heteroat. Chem.*, 1995, **6**, 45–49; (*c*) T. Fujihara, T. Ohba, A. Nagasawa, J. Nakayama and K. Yoza, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2002, **58**, o558–o559; (*d*) S. R. Banerjee, A. Nagasawa and J. Zubieta, *Inorg. Chim. Acta*, 2002, **340**, 155–162.

29 (*a*) W. S. Sheldrick, A. Schönberg, E. Singer and P. Eckert, *Chem. Ber.*, 1980, **113**, 3605–3609; (*b*) L. L. Borer, J. V. Kong and D. E. Oram, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 1169–1170; (*c*) N. Kuhn, H. Bohnen and G. Z. Henkel, *Z. Naturforsch., B: Chem. Sci.*, 1994, **49b**, 1473–1480; (*d*) N. Kuhn, E. Niquet, M. Steimann and I. Z. Walker, *Z. Naturforsch., B: Chem. Sci.*, 1999, **54b**, 1181–1187; (*e*) M. Akkurt, S. Öztürk, H. Küçükbay, E. Orhan and O. Büyülgüngör, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, **60**, o219–o221; (*f*) J. Nakayama, T. Kitihara, Y. Sugihara, A. Sakamoto and A. Ishii, *J. Am. Chem. Soc.*, 2000, **122**, 9120–9126; (*g*) U. Siemeling, H. Memczak, C. Bruhn, F. Vogel, F. Träger, J. E. Baiod and T. Weidner, *Dalton Trans.*, 2012, **41**, 2986–2994.

30 (*a*) A. R. Dick, K. L. Hull and M. S. Sanford, *J. Am. Chem. Soc.*, 2004, **126**, 2300–2301; (*b*) L. V. Desai, K. L. Hull and M. S. Sanford, *J. Am. Chem. Soc.*, 2004, **126**, 9542–9543; (*c*) D. Kalyani, N. R. Deprez, L. V. Desai and M. S. Sanford, *J. Am. Chem. Soc.*, 2005, **127**, 7330–7331; (*d*) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147–1169.

31 L. Delaude, A. Demonceau and J. Wouters, *Eur. J. Inorg. Chem.*, 2009, 1882–1891.

32 A. Tudose, A. Demonceau and L. Delaude, *J. Organomet. Chem.*, 2006, **691**, 5356–5365.

33 J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge and M. M. Jones, *Inorg. Chem.*, 1970, **9**, 2374–2376.

34 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc.*, 1984, **106**, 158–163.

35 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **A64**, 112–122.

