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Bridge cleavage reactions of cyclopalladated nitrosamines with thioamides and related compounds

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ABSTRACT

The palladacycle $[Pd(\mu\text{-}O_2CMe)\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}]_2$ readily undergoes bridge cleavage reactions with a variety of compounds containing donor functionalities including thioamides, 8-hydroxyquinoline, thioureas, selenoureas, acetylacetone derivatives, dithiocarbamates, xanthates, as well as bidentate N-donors to afford either the monomeric, neutral Pd(II) complexes $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}\{L\text{-}L\}]$ or the monocationic complexes $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}(N\text{-}N)]PF_6$ in high yields. A series of 15 different complexes was prepared and fully characterised spectroscopically and, in some cases, by X-ray diffraction. It was also found that the dithiocarbamato complex undergoes a disproportionation reaction in solution to give the bis(cyclometallated) complex $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}_2]$ as well as the bis(dithiocarbamato) complex $[Pd\{\kappa^2S\text{-}S_2CNEt_2\}_2]$.

1. Introduction

The process of C–H bond activation of aromatic or aliphatic compounds containing donor atoms such as N, O and P by palladium species giving cyclic organo-palladium complexes is known as cyclopalladation. This reaction has been known for more than 30 years and there are numerous examples of cyclopalladated complexes derived from a large variety of aromatic and aliphatic compounds [1]. From a synthetic point of view, cyclopalladated complexes are important in the synthesis of heterocycles and other organic molecules [2,3]. Recent renewed interest in cyclopalladated complexes has arisen from their extremely high catalytic activity in a variety of important C–C coupling reactions including Heck reactions, Stille coupling and Suzuki coupling [4–7]. Generally, the acetate- or chloro-bridged cyclopalladated dimers have been prepared, characterised and tested for their catalytic activity. However, apart from bridge cleavage reactions of chloro-bridged dimers with various phosphines to generate more soluble species, very little other chemistry has been carried out so far with either acetato- or chloro-bridged cyclopalladated dimers. To the best of our knowledge, there are only two papers that describe the preparation and characterisation of cyclopalladated derivatives containing co-ligands other than halide, acetate or phosphines. These include complexes of the type [Pd(C–E)(S–S)], where C–E is a cyclometallated ligand and S–S a dithiolato ligand [8] and also the cationic complexes $[Pd(C\text{–}N)(N\text{–}N)]^+$, where C–N is the cyclometallated ligand and N–N a bidentate donor ligand [9]. In order to increase the known structural diversity and variation, which is important for future development and fine-tuning of palladacyclic catalysis precursors, we carried out a systematic synthetic study of the reactivity of a nitrosamine derived palladacycle with various organic molecules containing donor functionalities. The results of this study are reported herein.

2. Results and discussion

The dimeric palladium complex $[Pd(\mu\text{-}O_2CMe)\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}]_2$ readily undergoes bridge cleavage reactions with a variety of compounds containing donor functionalities including thioamides, 8-hydroxyquinoline, thioureas, selenoureas, acetylacetone derivatives, dithiocarbamates and xanthates to afford the monomeric, neutral Pd(II) complexes $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}\{L\text{-}L\}]$ (**1**–**10**) (L-L = bifunctional donor ligand) in high yields as yellow solids (Scheme 1).

Similarly, the bidentate N-donors 1,10-phenanthroline (phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), 4,4′-di(*tert*-butyl)-2,2′-dipyridyl ($^tBu_2$bipy), di(2-pyridyl)ketone as well as TMEDA also cleave the acetato-bridges to give the monocationic complexes $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}(N\text{-}N)]PF_6$ (**11**–**15**) (N-N = bidentate N-donor ligand) as yellow solids in high yields (Scheme 2).

Complexes **1**–**15** were fully characterised by spectroscopic methods including NMR spectroscopy and electrospray mass

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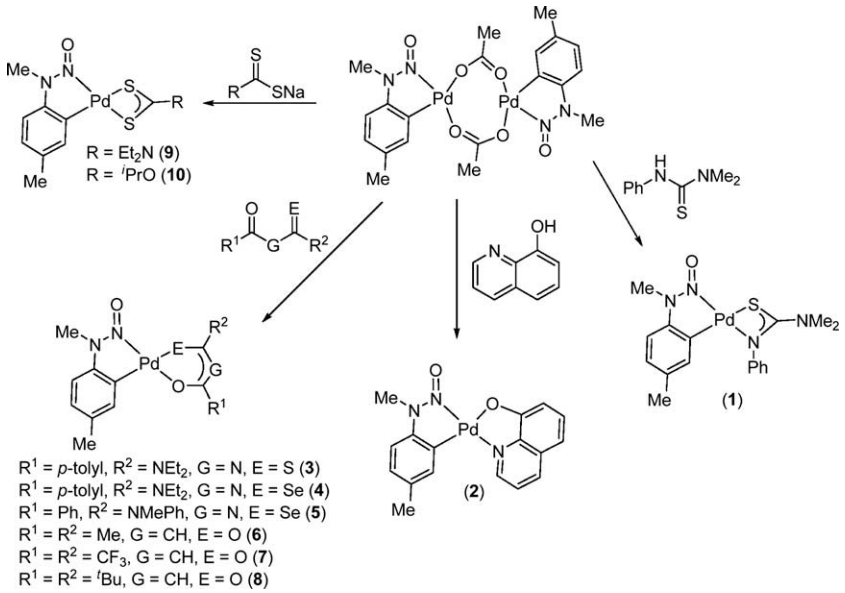
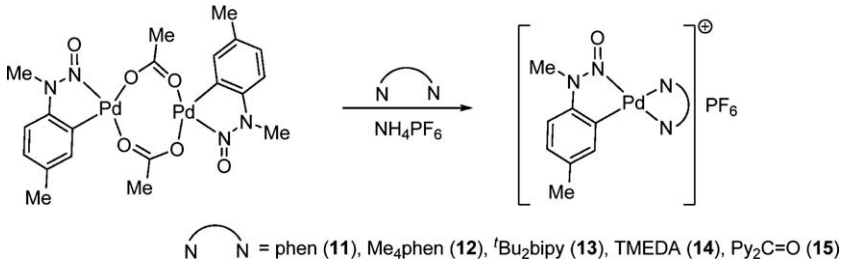


Scheme 1.



Scheme 2.

spectrometry. In addition, the solid-state structures of complexes **3** and **5** were determined by X-ray diffraction. The common feature of the donor ligand precursors in complexes **1**–**8** is the presence of an acidic proton which usually requires a base for deprotonation prior to chelation to the metal. In this case, no additional base is required since the acetate ions from the cyclopalladated dimer are able to deprotonate the donor ligand precursors. The ^{1}H NMR spectra of compounds **1**–**15** are fully consistent with the proposed structures, showing, in addition to the donor ligand signals, three doublets for the cyclometallated ring and two singlet resonances due the two Me groups. The doublet due to the proton *ortho* to Pd (H^3) experiences an upfield shift to *ca.* 6.8 ppm; similar to that observed in the starting dimer [10]. In the case of complexes **1** and **2**, the stereochemistry about the palladium i.e. whether the N atom of the donor ligand is *cis* or *trans* to C is difficult to determine spectroscopically. However, based on the *trans* effect, one would expect O and S to be *trans* to C in complexes **1** and **2**, respectively. Unfortunately we were unable to obtain X-ray quality crystals for these complexes to unambiguously confirm this assignment. We were however able to determine the solid-state structures of complexes **3** and **5** by X-ray diffraction. Molecular structures of the two complexes are shown in Figs. 1 and 2, respectively; important geometric parameters are collected in Table 1.

Given that the two complexes are structurally very similar, we shall discuss their structures together. In both compounds the palladium shows square planar coordination geometry, the angles C–Pd–O and N–Pd–S(Se) range from *ca.* 172° to 175°. The thio- or selenourea derivatives coordinate to the palladium as monoanionic, chelate ligands *via* oxygen and sulfur/selenium forming a six-membered ring. In both complexes, the oxygen atom of the thio- or selenourea ligand is *trans* to the carbon atom of the

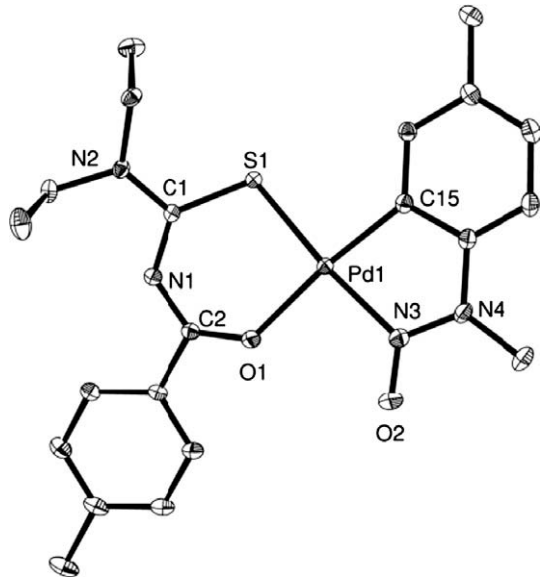


Fig. 1. Molecular structure of complex **3**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity.

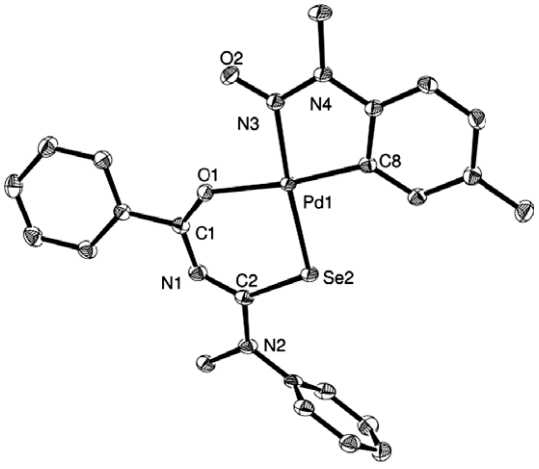


Fig. 2. Molecular structure of complex **5**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) of complexes **3** and **5**.

	3	5
Pd(1)–N(3)	2.0410(9)	2.0342(15)
Pd(1)–O(1)	2.0715(7)	2.0573(13)
Pd(1)–S(1)/Se(2)	2.2612(2)	2.3470(4)
Pd(1)–C(15)/C(8)	1.9770(9)	1.9756(17)
C(1)/C(2)–N(1)	1.3411(12)	1.333(2)
C(1)–S(1)/C(2)–Se(2)	1.7464(9)	1.9014(17)
C(2)/C(1)–O(1)	1.2637(11)	1.255(2)
C(2)/C(1)–N(1)	1.3295(12)	1.335(2)
C(14)–C(15) / C(3)–C(8)	1.4112(13)	1.403(2)
C(14)/C(3)–N(4)	1.4175(13)	1.419(2)
C(21)/C(10)–N(4)	1.4594(13)	1.449(2)
N(3)–O(2)	1.2334(12)	1.2288(19)
N(3)–N(4)	1.3306(12)	1.328(2)
O(1)–Pd(1)–C(15)/C(8)	173.87(3)	172.71(6)
N(3)–Pd(1)–S(1)/Se(2)	174.06(3)	175.00(4)
N(3)–Pd(1)–O(1)	93.00(3)	91.44(6)
C(15)/C(8)–Pd(1)–S(1)/Se(2)	93.09(3)	94.11(5)
O(1)–Pd(1)–S(1)/Se(2)	92.94(2)	93.18(4)
N(3)–Pd(1)–C(15)/C(8)	80.97(4)	81.27(6)

cyclometallated ring. Coordination about Pd is completed by the cyclometallated nitrosamine, which is bound to the metal through the carbon atom of the aromatic ring *ortho* to the nitrosamine substituent as well as the nitrogen atom of the nitroso group giving a five-membered chelate ring. In both complexes the five-membered ring from the cyclometallated ligand is almost planar, the maximum deviation from the least-squares plane is 0.01 Å in case of the Se-complex and 0.03 Å for the S-complex. The six-membered ring of the coordinated thio- and selenourea derivatives adopts a flattened twist-boat conformation. The Pd–Se distance in complex **5** [2.3470(4) Å] is similar to those observed in the bis(chelate) complex [Pd{κ^2*O,Se*-$C_6H_5C(Se)NC(O)N^nBu_2$}$_2$] [Pd–Se = 2.3411(3), 2.3489(3) Å] [11]. As expected, the Pd–S bond length in complex **3** [2.2612(2) Å] is slightly shorter than the Pd–Se bond distance of complex **5**. The bond lengths of the thiourea moiety in complex **3** are similar to those in the bis(chelate) complexes [Pd{κ^2*O,S*-$C_6H_5C(S)NC(O)NEt_2$}$_2$] [12] and [Pd{κ^2*O,S*-3,5-$(CF_3)_2C_6H_3C(S)NC(O)NEt_2$}$_2$] [13]. Compared to the free thiourea and selenourea ligands, and in line with earlier observations [13], all C–N bonds are shortened, while the carbon–chalcogen bonds are elongated. The lengthening of the C=S and C=Se bond is more pronounced [from 1.669(8) Å to 1.7464(9) Å and from 1.834(12) Å to 1.9014(17) Å] than that of the C=O bonds, which increase by only 0.046(8) Å [14]. The Pd–C and Pd–N bond lengths [Pd–C = 1.9756(17) **5** 1.9770(9) **3** Å, Pd–N = 2.0342(15) **5** 2.0410(9) **3** Å] in both complexes **3** and **5** are shorter than those observed in the Ph_3P complex [PdCl{κ^2*C,N*-$C_6H_4N(Me)NO$}(PPh_3)] [Pd–C = 2.031(15) Å, Pd–N = 2.088(12) Å] [15]. These shorter bond lengths can be reconciled through the structural *trans* effect. The Ph_3P ligand in the latter complex will have a stronger *trans* effect on the Pd–N bond distance than on the Pd–chalcogen distances in complexes **3** and **5**. The same holds for the comparison between the chloride and oxygen *trans* to carbon. The spectral data for complexes **6**–**10** are fully consistent with the proposed structures shown in Scheme 1. Curiously, crystals grown from a CH_2Cl_2 solution layered with Et_2O of the dithiocarbamato complex **9** contained two types of morphologically distinct crystals. X-diffraction studies on both types showed that one set was the bis(cyclometallated) complex [Pd{κ^2*C,N*-4-$MeC_6H_3N(Me)NO$}$_2$] (**9***) shown in Fig. 3, and the other set was the known bis(dithiocarbamato)palladium(II) complex [Pd{κ^2*S*-S_2CNEt_2}$_2$], the crystal structure of which was first reported by Beurskens [16].

While the molecular structure of **9*** is overall very similar to that of [Pd{κ^2*C,N*-$C_6H_4N(Me)NO$}$_2$], reported by Pregosin in 1990 [10] it is crystallographically not isostructural. The complex crystallises in the less frequent orthorhombic space group *Fdd*2, with the palladium occupying a special position with twofold symmetry, enforcing a molecular C_2 symmetry. In comparison, the complex of Pregosin crystallises in the ubiquitous space group $P2_12_12_1$, which is devoid of special positions. The palladium is coordinated by two cyclometallated nitrosamine ligands in distorted square planar geometry; the metallated carbon atom being *trans* to the nitrosamine nitrogen. While each five-membered ring is almost planar (the maximum distance to the least-squares plane is 0.058 Å), the two rings are twisted with the respect to each other by 20.1°. The two benzo rings show an even larger dihedral angle of 32.9°. The corresponding angles in the Pregosin complex are 16.2° and 28.2°, respectively. According to Pregosin's earlier observation this distortion between the two bidentate ligands increases the intra-molecular distance between the two *ortho*-hydrogen atoms. Assuming normalised C–H bond lengths (1.083 Å), this distance equals 1.91 Å and is slightly shorter than the sum of the van-

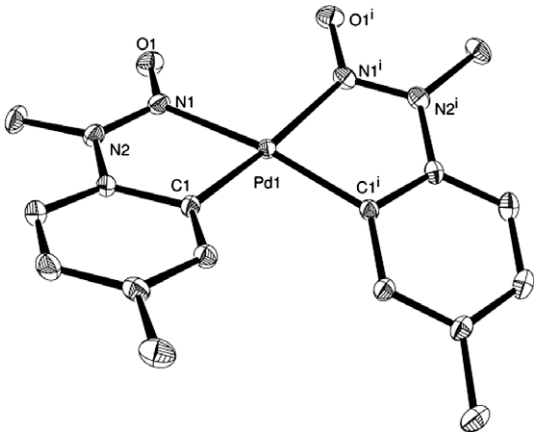


Fig. 3. Molecular structure of the bis(cyclometallated) complex **9***. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. (IO6370) Selected bond lengths (in Å) and angles (in °) are: Pd(1)–C(1) 1.9941(17), Pd(1)–N(1) 2.0956(14), C(1)–C(2) 1.412(2), C(2)–N(2) 1.4226(15), N(2)–C(8) 1.4589(16), N(1)–N(2) 1.3209(19), N(1)–O(1) 1.2422(18); C(1)–Pd(1)–N(1) 80.27(3),C(1)^i–Pd(1)–N(1) 168.36(3), C(1)^i–Pd(1)–C(1) 100.42(9), N(1)^i–Pd(1)–N(1) 101.43(8), C(2)–C(1)–Pd(1) 112.85(12), C(1)–C(2)–N(2) 117.03(15), C(2)–N(2)–N(1) 115.25(14), N(2)–N(1)–Pd(1) 113.73(10). Symmetry transformation used to generate equivalent atoms: i = $-x$, $-y+1$, z.

der-Waals radii [17]. On the other hand, the two neighbouring nitrosamine oxygen atoms, which are 3.2721(18) Å apart will contribute negligibly to the steric repulsion. This analysis is supported further if a hypothetical planar complex **9*** is considered [18]. While the O···O distance is changing only marginally (minimum distance 3.16 Å), there is a major contraction of the H···H distance. In a nearly planar molecule the hydrogen atoms would be as close as 1.42 Å.

This result of the facile formation a bis(cyclometallated) species is somewhat surprising, given that such complexes are usually prepared from the reaction of organolithium- or Grignard reagents with $[PdCl_2(SMe_2)_2]$. Interestingly, Pregosin also reported the formation of the bis(cyclometallated) compound $[Pd\{\kappa^2C,N\text{-}C_6H_4N(Me)NO\}_2]$ when trying to crystallise products obtained from the reaction of $[Pd(\mu\text{-}Cl)\{\kappa^2C,N\text{-}C_6H_4N(Me)NO\}]_2$ with various organotin reagents [10]. They state, that in their system "the bis(cyclometallated) complex is only formed when a coordination site at Pd becomes available and when the second coordination site is occupied by a carbon ligand arising from methylation, allylation or carbonylation." In our case, it is of course possible to generate a vacant coordination site at palladium by dissociation of one of the sulfur atoms of the dithiocarbamate. This species could then undergo a sequence of reactions similar to those suggested by Pregosin to give the bis(cyclometallated) complex as well as the bis(dithiocarbamato) complex as final products. Overall, the reaction can be seen as a disproportionation reaction in which two molecules of **9** generate one molecule of the bis(cyclometallated) complex **9*** and one molecule of the bis(dithiocarbamato) complex (Scheme 3). In our case, we could confirm the presence of both these species in the reaction mixture by X-ray diffraction. ES-MS data of a fresh solution of the original bulk sample indicates the presence of only complex **9**, suggesting that the disproportionation is a slow process in solution. At this point in time however, we have not made any further attempts to study this reaction in more detail.

The cationic complexes **11**–**15** (Scheme 2) were readily characterised by NMR spectroscopy and, in particular, by electrospray mass spectrometry. The ^1H NMR spectra of complexes **11**–**15** show the three resonances for the cyclometallated aromatic ring and the signals for the Me groups in addition to the resonances due to the bidentate N-donor ligands. Loss of symmetry of the N–N ligands upon coordination to the palladium is evident from the two sets of slightly different resonances observed in the ^1H NMR spectra of these compounds. Electrospray mass spectra of complexes **11**–**15** all show intense molecular ion peaks as well as a weaker signal corresponding to loss of NO; the observed isotope patterns are in excellent agreement with those calculated for the given formulae.

In conclusion, we present here the preparation and structures of rare examples of orthometallated palladium(II) complexes derived from bridge cleavage reactions of an acetato-bridged palladacycle with various organic compounds containing two donor functionalities including S–N, O–S, O–Se, O–N, S–S, O–O and N–N. Detailed studies of the catalytic activity of these new compounds are presently being carried out and will be reported separately in due course.

3. Experimental

3.1. General

^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a 400 MHz Bruker ARX spectrometer. Chemical shifts are quoted relative to external $SiMe_4$ (^1H), Freon (^{19}F) and 85% H_3PO_4 (^{31}P). Electrospray mass spectra were measured on a Bruker MicroTOF spectrometer in positive ion mode. Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. All reactions were carried out under aerobic conditions unless stated otherwise. The palladacycle $[Pd(\mu\text{-}O_2CMe)\{4\text{-}MeC_6H_3N(Me)NO\}]_2$ as well as the acylselenoureas $4\text{-}MeC_6H_4C(O)NHC(Se)NEt_2$ and $C_6H_5C(O)NHC(Se)NPhMe$ were prepared by modified literature procedures [10,19]. All other chemicals and solvents (HPLC grade) were sourced commercially and used as received.

3.2. $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}\{\kappa^2S,N\text{-}PhNC(S)NMe_2\}]$ (**1**)

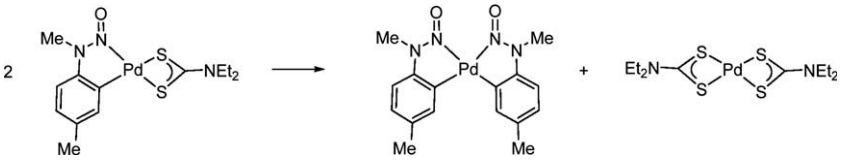
A suspension of $[Pd(\mu\text{-}O_2CMe)\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}]_2$ (0.050 g, 0.079 mmol) and $PhNHC(S)NMe_2$ (0.029 g, 0.161 mmol) in MeOH (15 mL) was refluxed for *ca.* 10 min. The initially orange solution turned yellow and on cooling to room temperature a yellow precipitate formed. The solid was isolated by filtration and was washed with a small amount of MeOH, Et_2O and was subsequently dried in air. 0.048 g (69%) of a yellow solid was obtained. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.29 (t, J = 8.1 Hz, 2H, *m*-NPh), 6.92–7.07 (m, 5H, NPh, H^4,H^6), 6.77 (d, J = 8.1 Hz, 1H, H^3), 3.42 (s, 3H, NMe), 2.88 (s, 3H, NMe_2), 2.31 (s, 3H, Me). ES-MS (*m*/*z*): 457.0288 $[M+Na]^+$, 435.0457 $[M+H]^+$, 427.0310 $[M-NO+Na]^+$. Anal. Calc. for $C_{15}H_{20}N_4OPdS$ (434.85): C, 46.95; H, 4.64; N, 12.88. Found: C, 47.04; H, 4.99; N, 12.75%.

3.3. $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}\{\kappa^2N,O\text{-quinolinolate}\}]$ (**2**)

This was prepared as above from $[Pd(\mu\text{-}O_2CMe)\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}]_2$ (0.050 g, 0.079 mmol) and 8-hydroxyquinoline (0.023 g, 0.158 mmol). 0.049 g (77%) of a yellow solid was obtained. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.09 (dd, J = 4.5/1.5 Hz, 1H, $H^{2\prime}$), 8.25 (dd, J = 8.6/1.5 Hz, 1H, $H^{4\prime}$), 7.78 (d, J = 1.0 Hz, 1H, H^6), 7.50 (ddd, J = 8.6/4.5/1.5 Hz, 1H, $H^{3\prime}$), 7.44 (t, J = 7.6 Hz, 1H, $H^{6\prime}$), 7.21 (dd, J = 7.6/1.0 Hz, 1H, $H^{5\prime}$), 7.05 (dd, J = 7.6/1.0 Hz, 1H, $H^{7\prime}$), 7.01 (dd, J = 8.1/1.0 Hz, 1H, H^4), 6.84 (d, J = 8.1 Hz, 1H, H^3), 3.59 (s, 3H, NMe), 2.45 (s, 3H, MeAr). ES-MS (*m*/*z*): 422.0102 $[M+Na]^+$, 392.0122 $[M-NO+Na]^+$. Anal. Calc. for $C_{17}H_{15}N_3O_2Pd$ (399.74): C, 51.08; H, 3.78; N, 10.51. Found: C, 51.25; H, 3.74; N, 10.69%.

3.4. $[Pd\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}\{\kappa^2S,O\text{-}4\text{-}MeC_6H_4C(O)NC(S)NEt_2\}]$ (**3**)

This was prepared as above from $[Pd(\mu\text{-}O_2CMe)\{\kappa^2C,N\text{-}4\text{-}MeC_6H_3N(Me)NO\}]_2$ (0.050 g, 0.079 mmol) and $4\text{-}MeC_6H_4C(O)NHC(S)NEt_2$ (0.040 g, 0.159 mmol). 0.060 g (75%) of a yellow solid was obtained. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.18 (d,



Scheme 3.

J = 8.1 Hz, 2H, H^a), 7.26 (br. s, 1H, H^6), 7.21 (d, J = 8.1 Hz, 2H, H^b), 6.99 (dd, J = 8.1/1.0 Hz, 1H, H^4), 6.85 (d, J = 8.1 Hz, 1H, H^3), 4.02 (q, J = 7.1 Hz, 2H, NCH_2), 3.88 (q, J = 7.1 Hz, 2H, NCH_2), 3.60 (s, 3H, NMe), 2.40 (s, 3H, MeAr), 2.36 (s, 3H, MeAr), 1.43 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.27 (t, J = 7.1 Hz, 3H, CH_2CH_3). ES-MS (m/z): 527.0708 $[M+Na]^+$, 497.0730 $[M-NO+Na]^+$. Anal. Calc. for $C_{21}H_{26}N_4O_2PdS$ (504.94): C, 46.95; H, 5.19; N, 11.10. Found: C, 46.94; H, 5.39; N, 11.05%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

3.5. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}{κ²Se,O-4-MeC$_6$H$_4$C(O)NC(Se)NEt$_2$)}] (**4**)

This was prepared as above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and 4-MeC_6H_4-C(O)NHC(Se)NEt_2 (0.047 g, 0.158 mmol). 0.065 g (74%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.17 (d, J = 8.1 Hz, 2H, H^a), 7.20 (d, J = 8.1 Hz, 2H, H^b), 7.15 (br. s, 1H, H^6), 6.90 (dd, J = 8.1/1.0 Hz, 1H, H^4), 6.84 (d, J = 8.1 Hz, 1H, H^3), 4.03 (q, J = 7.1 Hz, 2H, NCH_2), 3.87 (q, J = 7.1 Hz, 2H, NCH_2), 3.60 (s, 3H, NMe), 2.39 (s, 3H, MeAr), 2.33 (s, 3H, MeAr), 1.44 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.27 (t, J = 7.1 Hz, 3H, CH_2CH_3). ES-MS (m/z): 575.0153 $[M+Na]^+$, 553.0343 $[M+H]^+$, 545.0175 $[M-NO+Na]^+$. Anal. Calc. for $C_{21}H_{26}N_4O_2PdSe$ (551.84): C, 45.71; H, 4.75; N, 10.15. Found: C, 45.94; H, 4.74; N, 10.09%.

3.6. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}{κ²Se,O-C$_6$H$_5$C(O)NC(Se)NMePh)}] (**5**)

This was prepared as above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and $C_6H_5C(O)NHC(Se)NMePh$ (0.050 g, 0.159 mmol). 0.091 g (80%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.40 (m, 2H, Ph), 7.29–7.55 (m, 8H, Ph), 6.93 (m, 1H, H^6), 6.78–6.84 (m, 2H, H^3, H^4), 3.72 (s, 3H, NMe), 3.59 (s, 3H, NMe), 2.23 (s, 3H, MeAr). ES-MS (m/z): 594.9840 $[M+Na]^+$, 573.0005 $[M+H]^+$, 564.9858 $[M-NO+Na]^+$. Anal. Calc. for $C_{23}H_{22}N_4O_2PdSe$ (571.83): C, 48.31; H, 3.88; N, 9.80. Found: C, 48.45; H, 3.59; N, 10.01%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

3.7. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}{κ²O,O-MeC(O)CHC(O)Me}] (**6**)

This was prepared as above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and acetylacetone (20 μL). 0.040 g (71%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, J = 1.0 Hz, 1H, H^6), 7.02 (dd, J = 8.1/1.0 Hz, 1H, H^4), 6.79 (d, J = 8.1 Hz, 1H, H^3), 5.42 (s, 1H, CH), 3.52 (s, 3H, NMe), 2.40 (s, 3H, MeAr), 2.12 (s, 3H, MeC=O), 2.11 (s, 3H, MeC=O). ES-MS (m/z): 377.0087 $[M+Na]^+$, 347.0111 $[M-NO+Na]^+$. Anal. Calc. for $C_{13}H_{16}N_2O_3Pd$ (354.70): C, 44.02; H, 4.55; N, 7.90. Found: C, 43.87; H, 4.38; N, 8.16%.

3.8. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}{κ²O,O-CF$_3$C(O)CHC(O)CF$_3$}] (**7**)

This was prepared as above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and hfacac (23 μL). 0.063 g (86%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.25 (d, J = 1.5 Hz, 1H, H^6), 7.06 (dd, J = 8.1/1.5 Hz, 1H, H^4), 6.79 (d, J = 8.1 Hz, 1H, H^3), 6.12 (s, 1H, CH), 3.55 (s, 3H, NMe), 2.30 (s, 3H, MeAr). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = −75.13, −75.77. Anal. Calc. for $C_{13}H_{16}F_6N_2O_3Pd$ (462.64): C, 33.75; H, 2.18; N, 6.06. Found: C, 33.94; H, 2.02; N, 5.82%.

3.9. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}{κ²O,O-^{t}BuC(O)CHC(O)^{t}Bu}] (**8**)

This was prepared as above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and ^{t}Bu$_2$acac (34 μL). 0.049 g (70%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.52 (br. s, 1H, H^6), 7.01 (dd, J = 8.1/1.0 Hz, 1H, H^4), 6.78 (d, J = 8.1 Hz, 1H, H^3), 5.75 (s, 1H, CH), 3.51 (s, 3H, NMe), 2.40 (s, 3H, MeAr), 1.26 (s, 9H, ^{t}Bu), 1.23 (s, 9H, ^{t}Bu). ES-MS (m/z): 461.1031 $[M+Na]^+$, 431.1047 $[M-NO+Na]^+$. Anal. Calc. for $C_{19}H_{28}N_2O_3Pd$ (438.66): C, 52.00; H, 6.43; N, 6.38. Found: C, 51.70; H, 6.67; N, 6.03%.

3.10. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}(κ²S,S-Et$_2$NCS$_2$)] (**9**)

This was prepared as above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and Et_2NCS_2Na (0.036 g, 0.159 mmol). 0.047 g (72%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.01 (br. s, 1H, H^4), 6.99 (s, 1H, H^6), 6.83 (d, J = 8.1 Hz, 1H, H^3), 3.80–3.88 (m, 4H, NCH_2), 3.52 (s, 3H, NMe), 2.33 (s, 3H, MeAr), 1.35 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.30 (t, J = 7.1 Hz, 3H, CH_2CH_3). ES-MS (m/z): 425.9897 $[M+Na]^+$, 395,9926 $[M-NO+Na]^+$. Anal. Calc. for $C_{13}H_{19}N_3OPdS_2$ (403.86): C, 38.66; H, 4.74; N, 10.40. Found: C, 38.65; H, 4.69; N, 10.53%. Slow diffusion of Et_2O into a CH_2Cl_2 solution of the compound gave two types of crystals, which turned out to be complex **9*** and [Pd{κ²S-S_2CNEt_2}$_2$].

3.11. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}(κ²S,S-^{i}PrOCS$_2$)] (**10**)

This was prepared as described above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and ^{i}PrOCS$_2$K (0.028 g, 0.161 mmol). 0.050 g (81%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.04 (br. d, J = 8.1 Hz, 1H, H^4), 6.97 (br. s, 1H, H^6), 6.86 (d, J = 8.1 Hz, 1H, H^3), 5.65 (sept, J = 6.1 Hz, 1H, MeC*H*), 3.54 (s, 3H, NMe), 2.34 (s, 3H, MeAr), 1.49 (d, J = 6.1 Hz, 6H, *Me*CH). ES-MS (m/z): 412.9586 $[M+Na]^+$, 382.9604 $[M-NO+Na]^+$. Anal. Calc. for $C_{12}H_{16}N_2O_2PdS_2$ (390.82): C, 36.88; H, 4.13; N, 7.17. Found: C, 36.99; H, 4.36; N, 7.29%.

3.12. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}{phen}]PF$_6$ (**11**)

A mixture of [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and 1,10-phenanthroline (0.032 g, 0.161 mmol) in MeOH (15 mL) was refluxed for *ca.* 10 min. The initially orange solution turned yellow. Upon addition of 0.028 g (0.172 mmol) NH_4PF_6 to the cold solution a bright yellow precipitate formed. The solid was isolated by filtration and was washed with H_2O, MeOH and Et_2O and was subsequently dried in air. 0.080 g (87%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, dmso-d_6, 25 °C): δ = 8.78 (dd, J = 5.0/1.0 Hz, 2H, $H^{2\prime}$, $H^{9\prime}$), 8.59 (dd, J = 8.0/1.0 Hz, 2H, $H^{4\prime}$, $H^{7\prime}$), 8.08 (s, 2H, $H^{5\prime}$, $H^{6\prime}$), 8.05 (dd, J = 8.0/5.0 Hz, 2H, $H^{3\prime}$, $H^{8\prime}$), 6.86–6.97 (m, 2H, H^3, H^4), 6.72 (s, 1H, H^6), 3.29 (s, 3H, NMe), 2.25 (s, 3H, MeAr). ES-MS (m/z): 435.0425 $[M]^+$, 405.0439 $[M-NO]^+$. Anal. Calc. for $C_{20}H_{17}F_6N_4OPPd$ (580.76): C, 41.36; H, 2.95; N, 9.65. Found: C, 41.71; H, 3.16; N, 9.94%.

3.13. [Pd{κ²C,N-4-MeC$_6$H$_3$N(Me)NO}{Me$_4$phen}]PF$_6$ (**12**)

This was prepared as described above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and 3,4,7,8-tetramethyl-1,10-phenanthroline (0.038 g, 0.160 mmol). 0.092 g (91%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 8.84 (br. s, 2H, $H^{2\prime}$, $H^{9\prime}$), 8.25 (br. s, 2H, $H^{5\prime}$, $H^{6\prime}$), 7.16–7.27 (m, 3H, H^3, H^4, H^6), 3.57 (s, 3H, NMe), 2.83 (s, 6H,

Me phen), 2.67 (s, 6H, Me phen), 2.48 (s, 3H, MeAr). ES-MS (*m/z*): 491.1073 $[M]^+$, 461.1095 $[M-NO]^+$. Anal. Calc. for $C_{24}H_{25}F_6N_4OPPd$ (636.87): C, 45.26; H, 3.96; N, 8.80. Found: C, 44.97; H, 3.63; N, 8.34%.

3.14. [Pd{κ²C,N-4-MeC₆H₃N(Me)NO}{ᵗBu₂bipy}]PF₆ (**13**)

This was prepared as described above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and $^tBu_2$bipy (0.043 g, 0.160 mmol). 0.096 g (91%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, dmso-d_6, 25 °C): δ = 8.87 (d, J = 5.6 Hz, 2H, $H^{3'}$), 8.62 (s, 2H, $H^{6'}$), 7.85 (d, J = 6.1 Hz, 2H, $H^{4'}$), 7.22 (d, J = 8.1 Hz, 1H, H^3), 7.11 (m, 2H, H^4, H^6), 3.62 (s, 3H, NMe), 2.36 (s, 3H, MeAr), 1.46 (s, 18H, ^{t}Bu). ES-MS (*m/z*): 523.1695 $[M]^+$, 493.1687 $[M-NO]^+$. Anal. Calc. for $C_{26}H_{33}F_6N_4OPPd$ (668.95): C, 46.68; H, 4.97; N, 8.38. Found: C, 46.22; H, 5.17; N, 8.09%.

3.15. [Pd{κ²C,N-4-MeC₆H₃N(Me)NO}{TMEDA}]PF₆ (**14**)

This was prepared as described above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and TMEDA (24 μL). 0.054 g (66%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 7.40 (br. s, 1H, H^6), 7.25 (d, J = 8.1 Hz, 1H, H^3), 7.19 (dd, J = 8.1/1.0 Hz, 1H, H^4), 3.75 (s, 3H, NMe), 3.17 (br. s, 2H, NCH_2CH_2N), 3.12 (s, 6H, NMe_2), 2.97 (br. s, 2H, NCH_2CH_2N), 2.85 (s, 6H, NMe_2), 2.42 (s, 3H, MeAr). ES-MS (*m/z*): 371.1062 $[M]^+$, 341.1085 $[M-NO]^+$. Anal. Calc. for $C_{14}H_{25}F_6N_4OPPd$ (516.76): C, 32.54; H, 4.88; N, 10.84. Found: C, 32.39; H, 5.26; N, 11.02%.

3.16. [Pd{κ²C,N-4-MeC₆H₃N(Me)NO}{Py₂C=O}]PF₆ (**15**)

This was prepared as described above from [Pd(μ-O_2CMe){κ²C,N-4-$MeC_6H_3N(Me)NO$}]$_2$ (0.050 g, 0.079 mmol) and Py_2C=O (0.029, 0.160 mmol). 0.046 g (50%) of an orange solid was obtained. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 9.18 (dd, J = 4.6/1.0 Hz, 1H, $H^{6'}$), 8.90 (dd, J = 4.6/1.0 Hz, 1H, $H^{6'}$), 8.33 (dt, J = 7.6/1.5 Hz, 1H, $H^{4'}$), 8.16–8.23 (m, 2H, $H^{4'}$, $H^{3'}$), 8.05–8.13 (m, 2H, $H^{5'}$, $H^{3'}$), 7.79 (ddd, J = 7.6/4.6/1.0 Hz, 1H, $H^{5'}$), 7.56 (br. s, 1H, H^6), 7.17 (d, J = 8.1 Hz, 1H, H^3), 7.05 (dd, J = 8.1/1.0 Hz, 1H, H^4), 3.75 (s, 3H, NMe), 2.19 (s, 3H, MeAr). ES-MS (*m/z*): 439.0579 $[M]^+$, 409.0581 $[M-NO]^+$.Anal. Calc. for $C_{19}H_{17}F_6N_4O_2PPd$ (584.75): C, 39.03; H, 2.93; N, 9.58. Found: C, 39.21; H, 3.24; N, 9.76%.

3.17. X-ray crystallography

Diffraction data for complexes **5** and **9*** were collected using a Bruker AXS Apex2 System, while the data for **3** were obtained using a Nonius KappaCCD system. The diffractometers utilised Mo Kα radiation (λ = 0.71073 Å) originating from a FR591 rotating anode equipped with a graphite monochromator (KappaCCD) or in case of the Apex2 a graded multilayer optic (Incoatec). An Oxford CryoStream 700 series liquid nitrogen cooling device operated at 100 K was employed for low temperature data collection. Diffracted intensities were obtained using Denzo-SMN [20] (KappaCCD) and Saint Ver. 7.34A integrated into the APEX2 software suite, followed by scaling and absorption correction with SADABS. Structure solution for all compounds was accomplished using SHELXS-97 [21] employing direct methods. Full matrix least-squares against F^2 as implemented in SHELXL-97 [22] was used for structure refinement. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All relevant crystal data and refinement details were compiled in Table 2. According to the refined value of the Flack parameter for **9*** equalling 0.5 within one standard uncertainty, the crystal under investigation was a racemic twin [23].

4. Supplementary material

CCDC 718455, 718456 and 718457 contains the supplementary crystallographic data for **3**, **5** and **9***. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2
Crystal data and refinement details of complexes **3**, **5** and **9***.

	3	**5**	**9***
Empirical formula	$C_{21}H_{26}N_4O_2PdS$	$C_{23}H_{22}N_4O_2PdSe$	$C_{16}H_{18}N_4O_2Pd$
Colour	Yellow-orange	Yellow-orange	Orange
M_r (g mol^{-1})	504.92	571.81	404.74
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pna*2$_1$, (no. 33)	*P*2$_1$/c, (no. 14)	*Fdd*2, (no. 43)
a (Å)	11.8375(1)	15.974(3)	21.016(3)
b (Å)	22.9660(2)	13.226(3)	10.6385(12)
c (Å)	8.0096(1)	10.261(2)	13.7369(15)
β (°)		93.938(4)	
V (Å^3)	2177.49(4)	2162.7(7)	3071.2(6)
Z	4	4	8
$D_{calc.}$ (g cm^{-3})	1.540	1.756	1.751
μ (mm^{-1})	0.972	2.569	1.224
Crystal size (mm^3)	0.41 × 0.34 × 0.25	0.08 × 0.07 × 0.04	0.08 × 0.05 × 0.04
θ range for data collection (°)	3.17–37.56	1.28–30.63	2.61–36.40
Reflection collected	65 702	53 638	27 700
Independent reflections	11 377	6636	3642
Reflection with $I > 2\sigma(I)$	11 240	5771	3587
Absorption correction		Empirical	Empirical
Maximum/minimum transitions	0.81/0.67	0.75/0.42	1.00/0.79
Parameters	267	283	107
S	1.036	1.105	1.089
R_1	0.019	0.022	0.014
wR_2	0.049	0.066	0.039
Absorbed structure parameters	−0.012(9)		0.483(18)
Largest difference peak/hole (e Å^{-3})	0.5/−0.9	0.7/−0.3	0.8/−0.5

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