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Insertion reactions of SO₂ into Pd–OR bonds: preparation of alkyl sulfito complexes of palladium(II) †

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Mononuclear palladium–hydroxo complexes of the type $[Pd(N-N)(C_6F_5)(OH)] [(N-N = 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (Me_2bipy), or <math>N, N, N', N'$ -tetramethylethylenediamine (tmeda) react with SO₂ (1 atm) at room temperature in alcohol (methanol, ethanol, propanol or isopropanol) to yield alkyl sulfito palladium complexes $[Pd(N-N)(C_6F_5)(SO_2OR)]$ (R = Me, Et, Pr or ⁱPr). Similar alkyl sulfito complexes $[Pd(N-N)(C_6F_5)(SO_2OR)]$ (N-N = bis(3,5-dimethylpyrazol-1-yl)methane); R = Me or Et) are obtained when $[Pd(N-N)(C_6F_5)Cl]$ is treated with KOH in the corresponding alcohol ROH and SO₂ is bubbled through the solution. The reaction of $[Pd(bipy)(C_6F_5)(SO_2OPr)]$ with SO₂ in tetrahydrofuran gives $[Pd(N-N)(C_6F_5)(SO_2OH)]$. The X-ray diffraction study of $[Pd(tmeda)(C_6F_5)(SO_2OPr)]$ has established the sulfur coordination of the propyl sulfito ligand.

Introduction

The reactions of CO (in alcohol, ROH) and CO₂ (in tetrahydrofuran) with $[(N-N)(C_6F_5)Pd(OH)]$ -type complexes have been recently studied,¹ the reaction products being the result of insertion of CO into the Pd–OR bond or of insertion of CO₂ into the Pd–OH bond to give $[(N-N)(C_6F_5)Pd(COOR)]$ or $[(N-N)(C_6F_5)Pd(CO_2OH)]$, respectively. By analogy with the observed formation of the methoxy carbonyl ligand, -C(O)OR, by nucleophilic attack of alkoxide on ligated CO and the hydrogen carbonate, -OC(O)OH, by nucleophilic attack of hydroxide on ligated CO₂, the presumed behavior of SO₂ toward $[(N-N)-(C_6F_5)Pd(OH)]$ should be the formation of hydrogen sulfito or alkyl sulfito complexes depending on the experimental conditions used.

Examples of transition-metal alkyl sulfito complexes are known for Mn,² Fe,² Co,³ Ru,^{4,5} Rh,⁶ Ir,⁷ Ni,³ Pd⁸⁻¹⁰ and Pt.⁹⁻¹³ Although no general synthetic routes to such compounds have been developed, the insertion of SO₂ into M–OR has been widely used. In the case of the group 10 metals, metal–sulfur bonding was established in [Ni(SO₂OEt)(np₃)]BF₄·0.5EtOH· $0.5H_2O^3$ (np₃ = tris(2-(diphenylphosphino)ethyl)amine) and [Pt(PPh₃)₂(SO₂OMe)₂]¹³ by X-ray crystallography, but no crystal structure has been reported for alkyl sulfite–palladium complexes [3D Search using the Cambridge Structural Database, July 2003 release].

We have now examined the reactions of the monomeric hydroxo complexes $[Pd(N-N)(OH)(C_6F_5)]$ in alcoholic solvents with SO₂ to yield complexes of the type $[Pd(N-N)(C_6F_5)-(SO_2OR)]$. We also report the first crystal structure of an alkyl sulfito–palladium complex. The synthetic method described herein may be of general use in the preparation of alkyl sulfite and hydrogen sulfite complexes of the Group 10 elements.

Results and discussion

Alkyl sulfito complexes [Pd(N-N)(C₆F₅)(SO₃R)]

When SO_2 is bubbled at room temperature through a solution of the monomeric hydroxo palladium complex [Pd(N–N)-

 $(C_6F_5)(OH)$] (N–N = bipy, Me₂bipy or tmeda) in alcohol (methanol, ethanol, propanol or isopropanol) for 10 min the corresponding alkyl sulfito complexes 1–9 are obtained (Scheme 1) in 68–90% yields. The structures were assigned on the basis of microanalytical, IR, and ¹H and ¹⁹F NMR data.



Scheme 1 Reagents and conditions: (i) SO₂, ROH, 10 min, room temp.

Complexes 1–9 are all air-stable solids and thermal analysis shows that they decompose above 190 °C in a dynamic N₂ atmosphere. The IR spectra show the characteristic absorptions of the C₆F₅ group¹⁴ at 1630, 1490, 1450, 1050, 950, and a single band at ca. 800 cm⁻¹ derived from the so-called X-sensitive mode¹⁵ in C_6F_5X (X = halogen) molecules, which is characteristic of the presence of only one C₆F₅ group in the coordination sphere of the palladium atom and behaves like a v(M-C)band.¹⁶ The strong absorptions in the IR spectra at ca. 1230 and 1095 cm⁻¹ (Experimental section) can be safely attributed to the alkyl sulfito group $SO_2(OR)$ and may be assigned³ to the $v_{as}(SO_2)$ and $v_s(SO_2)$ stretching vibrations, respectively, suggesting a sulfur-coordinated alkyl sulfite.7 The sulfur-coordination of alkyl sulfite to palladium has been confirmed by an X-ray diffraction study of complex 8 (vide infra). Metal-sulfur bonding was established in [Ni{SO₂(OC₂H₅)}(np₃)]BF₄·0.5C₂H₅OH· $0.5H_2O$ (np₃ = tris(2-diphenylphosphino)ethyl)amine) by X-ray crystallography,3 though an oxygen-coordinated methyl sulfito ligand in Ir(CO)[OS(O)OMe](SO₂)(PPh₃)₂ has been described.¹⁷ The characteristic resonances of the neutral ligands are observed in the ¹H NMR spectra.^{1,18-21} The signals corresponding to the alkyl group of the alkyl sulfite ligands are also observed (for example, at ca. 3.50 ppm due to the SO₃Me

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protons in complexes 1, 4 and 6). The ¹⁹F NMR spectra of complexes 1–9 reveal the presence of a freely rotating penta-fluorophenyl ring which gives the expected three resonances (in the ratio 2 : 1 : 2) for the *o*-, *p*- and *m*-fluorine atoms, respectively.

When SO₂ is bubbled through an alcoholic (methanol or ethanol) solution of $[Pd(N-N)(C_6F_5)(OH)]$ [N–N = bis(3,5-dimethylpyrazol-1-yl)methane], generated *in situ* by the addition of KOH to the complexes $[Pd(N-N)(C_6F_5)Cl]$, the corresponding bis(pyrazol-1-yl)methane complexes $[Pd(N-N)(C_6F_5)-(SO_3R)]$ [R = Me (10) or Et (11)] are obtained (Scheme 2).



Scheme 2 *Reagents and conditions*: (i) KOH, SO₂, ROH, 10 min, room temp.

The IR spectra of complexes 10 and 11 show two bands at ca. 1230 and 1100 cm^{-1} which are attributed to the alkyl sulfito group $SO_2(OR)$ and a single band located at 795 cm⁻¹ is indicative of the presence of only one C₆F₅ group in the coordination sphere of the palladium atom. Two sets of ¹H resonances are observed for the C₃HMe₂N₂ rings corresponding to one pyrazolate ligand trans to SO₃R and one pyrazolate ligand trans to C_6F_5 ; the lower field set is assigned to the pyrazolate ligand trans to C₆F₅. The proton resonances of the bridging methylene of the bis(pyrazol-1-yl)methane ligand in complexes 10 and 11 show that the boat-to-boat inversion usually observed in this type of complexes¹ is frozen at room temperature; the methylene protons are magnetically non-equivalent and give the NMR pattern corresponding to two diastereotopic protons: two doublets at δ 7.17 and 6.34 with ${}^{2}J_{H_{A}H_{B}} = 15$ Hz. The signals corresponding to the alkyl sulfite ligands are observed at δ 3.42 (SO₂OMe) and δ 3.85 and 0.97 (SO₂OEt), respectively. The ¹⁹F NMR spectra of complexes 10 and 11 at room temperature show hindered rotation of the C₆F₅ ring around the Pd-C bond and two separate signals are observed for the o- and m-fluorine atoms but only one for the p-fluorine atom.

The formation of complexes **1–11** is formally the insertion of SO₂ into the Pd–OR bond. By analogy with the carbonylation reactions of M–OMe complexes (M = group 10 metal), which are best described as inner-sphere migratory insertions involving precoordination of CO to the metal center,^{22,23} the mechanism shown in Scheme 3 may be proposed. Although no alkoxo complex has been isolated, it is formed in the alcoholic solution *via* the Brønsted acid–base reaction M–OH + ROH \rightleftharpoons M–OR +



H₂O. To a CDCl₃ (0.6 mL) solution of [(bipy)(C₆F₅)Pd(OH)] (30 mg) was added 1, 2, 4, 10 and 30 equiv. of methanol and the ¹⁹F NMR spectra of the solutions indicated that the equilibrium mixture of [(bipy)(C₆F₅)Pd(OH)] [δ -117.8 (2F_o), -158.7 (1F_p), -162.0 (2F_m)] and [(bipy)(C₆F₅)Pd(OMe)] [δ -118.9 (2F_o), -159.9 (1F_p), -162.3 (2F_m)] was present in every case with a methoxo complex : hydroxo complex ratio of 0.3, 0.4, 0.6, 0.75 and 1, respectively. The chemical shifts given above for both complexes refer to the solution to which 30 equiv. of MeOH were added; the figures are slightly different depending on the amount of MeOH added.

Hydrogen sulfito complex [Pd(bipy)(C₆F₅)(SO₂OH)]

The reaction of $[Pd(bipy)(C_6F_5)(OH)]$ with SO₂ in tetrahydrofuran gives the hydrogen sulfite complex **12** (Scheme 4), which can be viewed as the insertion product of SO₂ into the Pd–OH bond. Complexes containing the –SO₃H ligand are known but are less common than those with alkyl sulfito ligands. The related ruthenium complexes $[Ru(C_5Me_5)(CO)_2(SO_2OH)]$ and $[Ru(bipy)_2(py)(SO_2OH)]$ have been characterized by X-ray crystallography.^{24,25} On studying the insertion of SO₂ into the Pt–OH bonds of $[Pt(Ph_2PCH=CHPPh_2)(CH_2CN)(OH)]$ and $[Pt(Ph_2PCH=CHPPh_2)(CF_3)(OH)]$ the incipient formation of Pt–SO₂OH complexes was presumed but the experimental data did not support definite formulations.¹²



Scheme 4 Reagents and conditions: (i) SO₂, thf, 10 min, room temp.

The elemental analysis data are consistent with the proposed formula for **12**. The IR spectrum shows two absorptions at 1185 $(v_{as}(SO_2))$ and 1070 $(v_s(SO_2))$ cm⁻¹ as well as the characteristic single band at 790 cm⁻¹ corresponding to the Pd–C₆F₅ bond. Because of the insolubility of **12** in chloroform or acetone, the ¹H and ¹⁹F NMR spectra of **12** were recorded from (CD₃)₂SO solution and the resonance signals are not well resolved due to proton exchange on the SO₃H group. Unlike [Pd(bipy)(C₆F₅)-(CO₃H)],¹ the hydrogen sulfito complex does not react with the precursor [Pd(bipy)(C₆F₅)(OH)] to give the corresponding μ -sulfito complex [(bipy)(C₆F₅)Pd{OS(O)O}Pd(bipy)(C₆F₅)]. This different result may be taken as indirect evidence of the S-coordination of SO₃OH in complex **12**.

Crystal structure of 8

Colourless crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a benzene solution of $\mathbf{8}$. The crystal structure of complex $\mathbf{8}$ is shown in Fig. 1, together with some selected bond lengths and bond angles.

The coordination around Pd is distorted square-planar. The different Pd–N (Pd–N(1), 2.155(2) Å; Pd–N(2), 2.126(2) Å) distances are in agreement with the higher *trans* influence of the



Fig. 1 Crystal structure of complex 8. Selected bond lengths (Å): Pd–N(1) 2.155(2), Pd–N(2) 2.126(2), Pd–C(1) 2.017(2), Pd–S 2.2487(7), S–O(1) 1.451(2), S–O(2) 1.443(2), S–O(3) 1.619(2). Selected bond angles (°): N(1)–Pd–N(2) 83.78(8), C(1)–Pd–N(1) 173.77(8), N(2)–Pd–S 171.98(6), C(1)–Pd–S 91.82(7), O(1)–S–O(2) 115.60(14), O(1)–S–O(3) 105.48(11), O(2)–S–O(3) 101.70(11).

 C_6F_5 group compared to SO₃Pr. The Pd–S bond distance of 2.2487(7) Å is shorter than the sum of the covalent radii of palladium and sulfur (2.33 Å) suggesting a percentage of double bond character (in the aryl thiolate complex [Pd-(C₆F₅)(SC₆H₅)(*o*-Ph₂PC₆H₄CHN'Pr)] Pd–S is 2.357(2) Å).²⁶ The S–O bond distances of the terminal oxygen atoms are, as expected, significantly shorter than the S–OPr bond length (1.447(2) average vs. 1.619(2) Å). Also the O–S–O angles reflect the non-equivalence of the three oxygen atoms; such distortions can be accounted for by the larger bond order of the terminal S–O bond compared to that of S–OR in terms of electron pair repulsions. The Pd–C₆F₅ bond length (2.017(2) Å) is in the range found in the literature for pentafluorophenyl–palladium complexes.²¹ The chelate angle N(1)–Pd–N(2) (83.78(8)°) is similar to that found in [Pd(tmeda)(C₆F₅)(CO₂Me)].¹

Conclusion

S-Bound alkyl sulfite-palladium complexes are readily obtained when SO₂ is bubbled through an alcoholic solution of the mononuclear hydroxo complexes $[Pd(N-N)(C_6F_5)(OH)]$. The reaction products are the result of the insertion of SO₂ into the Pd-OR bond of alkoxy-palladium intermediates formed from the acid-base reaction between the hydroxo complex and the corresponding alcohol (Pd–OH + ROH = Pd–OR + H_2O). Although the presence of the Pd–OR complex is demonstrated by NMR spectroscopy, attempts made to isolate pure samples of the alkoxy complex were fruitless. This result is consistent with the previous one that the σ -ligand metathesis reaction Pt-OH + MeO-H = Pt-OMe + H-OH is reversible and nearly thermoneutral.27 Obviously, the subsequent reaction of added SO₂ with the alkoxy complex forces the equilibrium system in the direction of the Pd-OR complex. So alcoholic solutions of the hydroxo complex are convenient reagents for the preparation of alkyl sulfite-palladium complexes. The method parallels the recently reported syntheses of methoxy carbonylpalladium complexes by reaction of carbon monoxide with alcoholic solutions of hydroxo-palladium complexes. In the absence of alcohol the reaction of SO2 with the hydroxo complex leads to the insertion of SO₂ into the Pd-OH bond and the hydrogen sulfite complex (Pd-SO₂OH) is formed. When this result is compared with that obtained from the reaction of CO₂ with Pd-OH¹ some discrepancy is found. In latter case the hydrogen carbonate complex reacts with the starting hydroxo complex to finally give the carbonate-bridged binuclear complex $Pd\{OC(O)O\}Pd$ with the concomitant formation of water. The non-acidic behaviour of coordinated alkyl sulfite towards the hydroxo-palladium complex may be a consequence of the S-coordination of the SO₂OR ligand.

Experimental

Instrumental measurements

The C, H, N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min⁻¹ and the solid samples under nitrogen flow (100 mL min⁻¹). The NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using SiMe₄ and CFCl₃ as standards, respectively. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Solvents were dried by the usual methods.

Materials

The starting complexes $[(N-N)Pd(C_6F_5)(OH)]$ $(N-N = bipy, Me_2bipy and tmeda)$ and $[(N-N)Pd(C_6F_5)Cl]$ (N-N = bis(3,5-dimethylpyrazol-1-yl)methane) were prepared by procedures described elsewhere.¹

Preparation of complexes $[Pd(N-N)(C_6F_5)(SO_2OR)]$ (N-N = bipy, R = Me 1, Et 2 or Pr 3; N-N = Me_2bipy, R = Me 4 or Et 5)

Through an alcohol (methanol, ethanol, or propanol) solution (15 mL) of the hydroxo palladium complex [Pd(N-N)- $(C_{c}F_{5})(OH)$] (N–N = bipy or Me₂bipy) (0.134 mmol) at room temperature was passed SO₂ for 10 min. The solvent was partially evaporated under vacuum and a suspension was obtained from which a white solid was collected by filtration and airdried. 1: Yield: 90% (Found: C, 39.0; H, 2.0; N, 5.3; S, 6.3. C₁₇H₁₁N₂F₅O₃PdS requires C, 38.9; H, 2.1; N, 5.3; S, 6.1%). Mp: 229 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1250, $v_s(SO_2)$ 1105, ν(Pd-C₆F₅), 775. ¹H NMR (CDCl₃) δ 3.59 (s, 3 H, SO₂OCH₃). 2: Yield 77% (Found: C, 39.8; H, 2.3; N, 5.1; S, 6.0. C₁₈H₁₃N₂F₅O₃PdS requires C, 40.1; H, 2.4; N, 5.2; S, 6.0%). Mp: 227 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1230, $v_{s}(SO_{2})$ 1100, $v(Pd-C_{6}F_{5})$ 770. ¹H NMR (CDCl₃) δ 4.03 (q, 2 H, SO₂OCH₂CH₃, J 7.2 Hz), 1.13 (t, 3 H, SO₂OCH₂CH₃, J 7.2 Hz). 3: Yield 75% (Found: C, 41.2; H, 2.7; N, 5.0; S, 5.6. C₁₉H₁₅N₂F₅O₃PdS requires C, 41.3; H, 2.7; N, 5.1; S, 5.8%). Mp: 203 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1240, $v_s(SO_2)$ 1095, v(Pd-C₆F₅) 765. ¹H NMR (CDCl₃) δ 3.93 (t, 2 H, SO₂OCH₂CH₂CH₃, J 6.7 Hz), 1.49 (m, 2 H, SO₂OCH₂CH₂-CH₃), 1.13 (t, 3 H, SO₂OCH₂CH₂CH₃, J 7.3 Hz). 4: Yield 78% (Found: C, 41.2; H, 2.8; N, 5.0; S, 5.6. C₁₉H₁₅N₂F₅O₃PdS requires C, 41.3; H, 2.7; N, 5.1; S, 5.8%). Mp: 227 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1284, $v_s(SO_2)$ 1104, $v(Pd-C_6F_5)$ 796. ¹H NMR (CDCl₃) δ 3.51 (s, 3H, SO₂OCH₃). 5: Yield 70% (Found: C, 42.0; H, 3.1; N, 5.0; S, 5.6. C₂₀H₁₇N₂F₅O₃PdS requires C, 42.4; H, 3.0; N, 4.9; S, 5.7%). Mp: 215 °C (decomp.). IR (Nujol, cm⁻¹): v_{as}(SO₂) 1235, v_s(SO₂) 1095, v(Pd-C₆F₅) 795. ¹H NMR (CDCl₃) δ 4.03 (q, 2 H, SO₂OCH₂CH₃, J 6.8 Hz), 1.03 (t, 3 H, SO₂OCH₂CH₃, J 6.8 Hz).

Preparation of complexes $[Pd(N-N)(C_6F_5)(SO_2OR)]$ (N-N = tmeda, R = Me 6, Et 7, Pr 8, or ⁱPr 9)

Through an alcohol (methanol, ethanol, propanol or isopropanol) solution (15 mL) of the hydroxo palladium complex [Pd(tmeda)(C₆F₅)(OH)] (55 mg, 0.135 mmol) at room temperature was passed SO₂ for 10 min. After evaporation of the solvent under reduced pressure, the residue was treated with ether–hexane and a white solid was collected by filtration and air-dried. **6**: Yield 45 mg, 68% (Found: C, 31.9; H, 4.0; N, 6.0; S, 6.4. C₁₃H₁₉N₂F₅O₃PdS requires C, 32.2; H, 4.0; N, 5.8; S, 6.6%). Mp: 208 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1235, $v_s(SO_2)$ 1095, $v(Pd-C_6F_5)$ 770. ¹H NMR (CDCl₃) δ 3.42 (s, 3H, SO₂OCH₃). 7: Yield 73% (Found: C, 33.9; H, 4.3; N, 5.5; S, 6.3. C₁₄H₂₁N₂F₅O₃PdS requires C, 33.7; H, 4.2; N, 5.6; S, 6.4%).

Mp: 200 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1240, $v_s(SO_2)$ 1095, $v(Pd-C_6F_5)$ 770. ¹H NMR (CDCl₃) δ 3.90 (q, 2 H, SO₂OCH₂CH₃, J 7.0 Hz), 1.07 (t, 3 H, SO₂OCH₂CH₃, J 7.0 Hz). **8**: Yield 78% (Found: C, 34.9; H, 4.5; N, 5.4; S, 6.1. C₁₅H₂₃N₂F₅O₃PdS requires C, 35.1; H, 4.5; N, 5.5; S, 6.3%). Mp: 197 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1230, $v_s(SO_2)$ 1090, $v(Pd-C_6F_5)$ 775. ¹H NMR (CDCl₃) δ 3.72 (t, 2 H, SO₂OCH₂CH₂CH₃, J 6.7 Hz), 1.40 (m, 2 H, SO₂OCH₂CH₂CH₂-CH₃), 0.75 (t, 3 H, SO₂OCH₂CH₂CH₂CH₃, J 7.0 Hz). **9**: Yield 87% (Found: C, 34.9; H, 4.5; N, 5.5; S, 6.3%). Mp: 229 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1090, $v(Pd-C_6F_5)$ 770. ¹H NMR (CDCl₃) δ 4.64 (sept, 1H, SO₂OCH(CH₃)₂, J 6.3 Hz), 1.03 (d, 6H, SO₂OCH(CH₃)₂, J 6.3 Hz).

Preparation of complexes $[Pd(N-N)(C_6F_5)(SO_2OR)]$ (N-N = bis(3,5-dimethylpyrazol-1-yl)methane, $CH_2(C_3HMe_2N_2)_2$; R = Me 10, Et 11)

To a solution of [Pd(N-N)(C₆F₅)Cl] (100 mg, 0.19 mmol) in acetone (15 ml) was added AgClO₄ (40 mg, 0.19 mmol). The suspension was stirred at room temperature for 30 min protected from light. The white AgCl was then filtered off. The resulting solution was concentrated to dryness under vacuum. The residue was redissolved in the corresponding alcohol ROH (R = Me or Et) (10 ml) and KOH (aq) (11 mg, 0.19 mmol) was added. A SO₂ stream was then passed through the resulting mixture for 10 min. Then the solution was concentrated under vacuum. The addition of water caused the precipitation of a white solid which was collected by filtration, washed with water and air-dried. 10: Yield 76% (Found: C, 37.8; H, 3.4; N, 9.6; S, 5.4. C₁₈H₁₉N₄F₅O₃PdS requires C, 37.7; H, 3.3; N, 9.8; S, 5.6%). Mp: 211 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1228, $v_s(SO_2)$ 1106, ν(Pd-C₆F₅) 798. ¹H NMR (CDCl₃) δ 7.17 (d, 1H, CH, J_{ab} 14.9 Hz), 6.34 (d, 1H, CH, J_{ab} 14.9 Hz), 5.88 (s, 1H, H4'), 5.75 (s, 1 H, H4), 3.42 (s, 3H, SO₂OCH₃), 2.50 (s, 3H, Me3'), 2.31 (s, 6H, Me5 and Me5'), 1.72 (s, 3 H, Me3). ¹⁹F NMR $(CDCl_3) \delta - 119.8 \text{ (m, 1F}_{o}), -120.1 \text{ (m, 1F}_{o}), -159.8 \text{ (t, 1F}_{o})$ $J(F_mF_p)$ 20.3 Hz), -162.9 (m, 1F_m), -163.8 (m, 1F_m). 11: Yield 82% (Found: C, 38.6; H, 3.6; N, 9.8; S, 5.3. C₁₉H₂₁N₄F₅O₃PdS requires C, 38.9; H, 3.6; N, 9.6; S, 5.5%). Mp: 252 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1244, $v_s(SO_2)$ 1096, $v(Pd-C_6F_5)$ 794. ¹H NMR (CDCl₃) δ 7.17 (d, 1H, CH, J_{ab} 15.0 Hz), 6.34 (d, 1H, CH, J_{ab} 15.0 Hz), 5.88 (s, 1H, H4'), 5.74 (s, 1 H, H4), 3.85 (q, 2H, SO₂OCH₂CH₃, J 7.1 Hz), 2.51 (s, 3H, Me3'), 2.32 (s, 3H, Me5), 2.30 (s, 3H, Me5'), 1.72 (s, 3H, Me3), 0.97 (t, 3H, $SO_2OCH_2CH_3$, J7.1 Hz). ¹⁹F NMR (CDCl₃) δ -119.9 (m, 2F_o), -159.9 (t, $1F_p$, $J(F_mF_p)$ 20.3 Hz), -162.9 (m, $1F_m$), -164.1 (m, $1F_{m}$).

Preparation of the complex $[Pd(N-N)(C_6F_5)(SO_2OH)]$ (N-N = bipy 12)

Through a tetrahydrofuran solution (15 mL) of the hydroxo palladium complex [Pd(bipy)(C₆F₅)(OH)] (60 mg, 0.134 mmol) at room temperature was passed SO₂ for 10 min. The solvent was partially evaporated under vacuum and a suspension was obtained from which a white solid was collected by filtration and dried in the oven. Yield 90% (Found: C, 37.3; H, 2.0; N, 5.3; S, 6.3. C₁₆H₉N₂F₅O₃PdS requires C, 37.6; H, 1.8; N, 5.5; S, 6.3%). Mp: 236 °C (decomp.). IR (Nujol, cm⁻¹) $v_{as}(SO_2)$ 1185, $v_s(SO_2)$ 1070, $v(Pd-C_6F_5)$ 790

X-Ray structure determination

Suitable crystals of **8** were grown from benzene–hexane. The crystal was mounted onto the tip of a glass fiber, and the data collection was performed with a Enraf-Nonius CAD4 diffract-ometer. The scan mode was θ – 2θ . The structure was solved by heavy atom methods (SHELXS-86).²⁸ The structure was refined

by full matrix least squares Enraf-Nonius MolEN programs.²⁹ Hydrogen atoms were included using a riding model.

Crystal data. Formula: $C_{15}H_{23}F_5N_2O_3PdS$. $M_r = 512.8$, triclinic, space group $P\bar{1}$ (no. 2), a = 8.141(2), b = 8.6250(10), c = 15.837(2) Å, a = 96.830(10), $\beta = 98.26(2)$, $\gamma = 112.930(10)$, V = 994.7(3) Å³, Z = 2. T = 293 K, $\mu = 1.10$ mm⁻¹. Number of reflections measured: 5776. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.028$; *R* indices (all data): $R_1 = 0.034$.

CCDC reference number 227318.

See http://www.rsc.org/suppdata/dt/b3/b316697j/ for crystallographic data in CIF or other electronic format.

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