ChemComm

The insertion of sulfur dioxide into palladium–methyl bonds: the synthesis and X-ray crystal structure of an unusual [(dppp)PdOS(Me)O]$_2$[BAr′$_4$]$_2$ dimer

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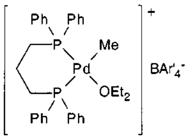
Received (in Bloomington, IN, USA) 26th July 1999, Accepted 22nd October 1999

The migratory insertion of sulfur dioxide into the palladium(II)–methyl bond of [(dppp)Pd(Me)(OEt$_2$)]BAr′$_4$ [Ar′ = $C_6H_3(CF_3)_2$-3,5] to yield a unique dimeric eight-membered palladacycle was followed by NMR spectroscopy, and the product characterised by X-ray crystallography.

Palladium(II) complexes possessing bidentate ligands are known to efficiently catalyse the copolymerisation of olefins with carbon monoxide to form polyketones.[1] Sulfur dioxide is an attractive monomer for catalytic copolymerisations with olefins since SO_2, like CO, is known to undergo facile insertion reactions into a variety of transition metal–alkyl bonds.[2,3] Indeed, Drent recently patented alternating copolymerisation of ethylene with SO_2 using various palladium(II) complexes.[4] In 1998, Sen and coworkers also reported that [(dppp)PdMe(NCMe)]BF_4 was an effective catalyst for the copolymerisation of SO_2 with ethylene, propylene and cyclopentene.[5] Here, we report our preliminary investigations of the insertion reactions of SO_2 into Pd(II)–methyl bonds and the attempted spectroscopic detection of the copolymerisation of ethylene and SO_2.

The cationic 1,3-bis(diphenylphosphino)propane (dppp) palladium(II) complex **1** can be prepared by the low temperature reaction of (dppp)PdMe$_2$ **6** with H(OEt$_2$)$_2$[BAr′$_4$] [Ar′ = $C_6H_3(CF_3)_2$-3,5].[6] We have previously studied the reactions of carbon monoxide with **1** at −70 °C, and have found that insertion proceeds *via* initial displacement of diethyl ether with CO followed by migratory insertion into the Pd–Me bond.[7] Immediately after treating a solution of **1** in CD_2Cl_2 with an excess of SO_2 (*ca.* 25 equiv.) at 193 K, the ^{1}H NMR spectrum shows the presence of free diethyl ether. Analysis of the reaction mixture by ^{31}P NMR spectroscopy (193 K) shows the formation of a major product (*ca.* 80%) which exhibits a singlet at δ 15.7 indicating equivalence of the phosphorus nuclei. In addition, two minor products (*ca.* 20%) with singlet resonances at δ 15.4 and 14.5 are also observed. The expected products, **2** and **3**, both of which would possess inequivalent phosphorus atoms, are not observed under these conditions. In addition, the ^{1}H NMR spectrum exhibits three new singlets[5] at δ 0.52 (78%), 0.42 (8%) and 0.25 (14%) which are assigned to $-CH_3$ groups, no signals were observed downfield at *ca.* 2–3 where resonances for an $-S(O)_2CH_3$ group would be expected.[8] A preparative scale reaction† was carried out in an attempt to isolate single crystals. Indeed, pale yellow crystals suitable for X-ray diffraction were isolated after recrystallisation of the crude product from dichloromethane–hexanes at −30 °C.‡



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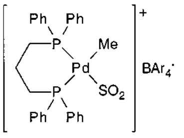

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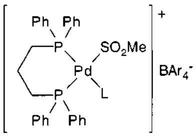

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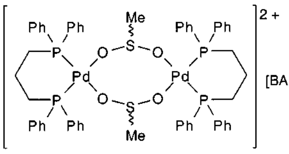

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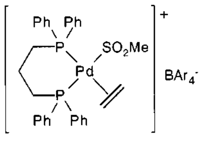

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The molecular structure of the isolated product **4** is shown in Fig. 1, and confirms that insertion of SO_2 into the Pd–Me bond had taken place, however dimerisation resulted in the formation of an eight-membered cyclic compound in which the phosphorus atoms are equivalent, consistent with the ^{31}P NMR observations. In particular, the eight-membered ring consists of a plane of palladium and oxygen atoms, with the sulfur atoms located above and below the plane. The six-membered rings formed by the dppp ligand are in the chair conformation.

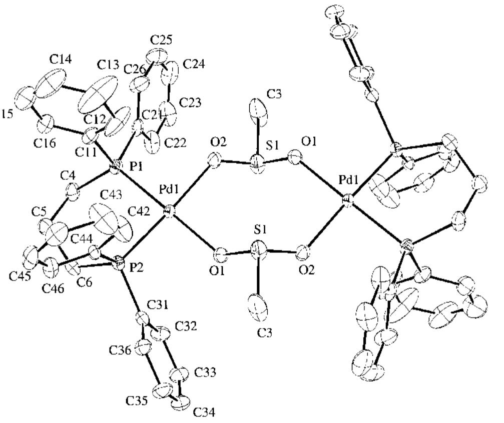
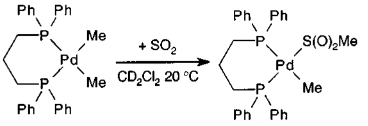


Fig. 1 Molecular structure of **4** (BAr′$_4$ anion omitted for clarity) with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.2354(20), Pd(1)–P(2) 2.2393(19), Pd(1)–O(1) 2.078(5), Pd(1)–O(2) 2.088(5), O(1)–S(1) 1.494(5), O(2)–S(1) 1.507(5), S(1)–C(3) 1.786(10); P(1)–Pd(1)–P(2) 90.12(7), P(1)–Pd(1)–O(2) 89.00(15), P(2)–Pd(1)–O(1) 90.47(15), O(1)–Pd(1)–O(2) 90.92(19), O(1)–S(1)–O(2) 109.5(3), O(1)–S(1)–C(3) 98.4(5), Pd(1)–O(1)–S(1) 128.0(3).

A variable temperature NMR experiment was carried out on **4** in CD_2Cl_2 solution. As the temperature is raised from 193 K the three singlet ^{31}P resonances (δ 15.7, 15.4, 14.5) begin to broaden at *ca.* 260 K and coalesce to a singlet above *ca.* 300 K. This process is reversible. Similarly, the three methyl signals also coalesce to a singlet but at a somewhat lower temperature (*ca.* 280 K) owing to the smaller spread in resonance frequencies. Since the inversion barrier at tetrahedral sulfur in **4** is expected to be high, the most likely source of the isomerism observed here[9] comes from ring inversion of the chair conformation of the dppp ligand.

We have also studied the behaviour of **1** towards mixtures of ethylene and SO_2 in an attempt to spectroscopically observe the insertion of SO_2 and ethylene in an alternating fashion. Thus, treatment of a solution of **1** in CD_2Cl_2 with a mixture of ethylene (10 equiv.) and SO_2 (10 equiv.) results in quantitative displacement of ether with ethylene at 193 K forming [(dppp)Pd(Me)(η^2-C_2H_4)]BAr′$_4$[10] which was characterised by ^{31}P [δ = 17.5 (d, *J* 56 Hz), −1.5 (d, *J* 56 Hz)] and ^{1}H NMR spectroscopy [δ 5.18 (bound C_2H_4), 0.34 (dd, Pd–CH_3, *J* 7, 4 Hz)]. Upon warming the reaction mixture to 223 K for *ca.* 30

min complex **4** was formed in nearly quantitative yield. No evidence for insertion of ethylene into the Pd–Me bond was detected, nor was any direct insertion of SO_2 into the Pd–Me bond of the methyl ethylene complex observed to form **5**. This suggests that formation of **4** from $[(dppp)Pd(Me)(\eta^2\text{-}C_2H_4)]BAr'_4$ (or **1**) involves displacement of ethylene (or diethyl ether for **1**) to yield **2** which then undergoes a rapid migratory insertion reaction to form **3** which then dimerises yielding **4**. This is in contrast to observations by Jones for analogous L_2PtMe_2 complexes which readily insert SO_2 *via* a five coordinate intermediate.[8] We have also carried out the analogous reaction of Pd complex **6** with SO_2 to form **7** presumably also *via* a five coordinate intermediate [eqn. (1)].†



6 **7**

(1)

In an attempt to obtain conclusive evidence for a migratory insertion mechanism, a low-temperature NMR experiment was carried out using $CDCl_2F$ as solvent. Thus, SO_2 (10 equiv.) was added to a solution of ether complex **1** in $CDCl_2F$ at 153 K. Upon warming to 173 K several new products could be detected in addition to **1**. The ^{31}P NMR spectrum exhibited resonances assigned to **4**, and also two sets of doublets at δ 22.0 and −5.5 (J_{PP} 50 Hz) and δ 18.8 and 17.4 (J_{PP} 20 Hz). In the ^1H NMR spectrum, in addition to **4**, two new products were observed which exhibited a methyl singlet at δ 1.6 and a methyl doublet of doublets at δ 0.0 (J_{HP} 7, 4 Hz). The signal at δ 0.0 is clearly due to a $Pd–CH_3$ group of a $(dppp)Pd(CH_3)^+$ moiety and, since this species is not observed in the absence of SO_2, we assign this resonance to complex **2**, $[(dppp)Pd(CH_3)(SO_2)]^+$. The ^{31}P resonances at δ 22.1 (d, J 50 Hz) and δ −5.6 (d, J 50 Hz) can be assigned to **2**. The low field methyl resonance at δ 1.6 [^{31}P resonances δ 18.8 (d, J 20 Hz), δ 17.4 (d, J 20 Hz)] is assigned to monomer **3**, a precursor to dimer **4**, formed *via* a migratory insertion reaction of **2**. The ligand (L) occupying the fourth coordination site in **3** is likely to be either SO_2 or Et_2O. As the reaction mixture was warmed in 5 °C increments, the signals for **2**, **3** and **4** increased in intensity and those for **1** decreased. At 213 K, only isomers of **4** could be detected. We speculate that in **3** the SO_2Me is bound through oxygen, rather than sulfur, based on the molecular structure of the final product **4**.

A copolymerisation was attempted using hex-1-ene (10% v/v) in CH_2Cl_2 purged with SO_2 in the presence of a catalytic quantity of **1** (14 mg).[11]† After *ca.* 14 h, the reaction was quenched with methanol. Solvent removal *in vacuo*, yielded a small amount of a polymeric material (23 mg). The polymer was precipitated with methanol and was characterised by gel permeation chromatography (M_n = 61 000: PDI = 5.8), and the ^1H and ^{13}C NMR data are identical with those reported for the hex-1-ene/SO_2 alternating copolymer prepared using a free-radical initiator.[12] Comparing the amount of **1** used as initiator (9×10^{-6} mol), the amount of hex-1-ene consumed (1.6×10^{-4} mol) and the estimated M_n of the polymer produced (61000) suggests that if chain growth occurred at Pd only a very small fraction of the Pd centers were active (< 5%). Results from repeated polymerisations proved quite erratic with varying amounts of polymer produced both in the presence and absence of **1**. Reactions conducted in the presence of the radical scavenger galvinoxyl failed to produce polymer.[13] These results, coupled with the failure to spectroscopically observe ethylene insertion in these systems and the ready formation of the stable dimer **4**, suggest that the copolymerisation of hex-1-ene and SO_2 under conditions reported above does not occur by a coordination–insertion process initiated by **1**. A radical chain growth mechanism appears very likely, although we cannot rule out copolymerization in the presence of **1** which is initiated by traces of a palladium complex of unknown structure present in **1** and which can be deactivated by galvinoxyl. The copolymerizations reported by Sen and coworkers[5] were carried out at higher pressures (600 psi), so it is uncertain how these results relate to those experiments.

We thank NSF for support of this work. D. P. G gratefully acknowledges NSERC of Canada for a Postdoctoral Fellowship. Thanks to S. Svejda for providing a sample of $CDCl_2F$ and to S. Shultz for useful discussions.

Notes and references

† *Preparation* of **4**: under an atmosphere of argon, $SO_2(g)$ (150 mL, 6 mmol) was slowly purged through a cloudy white stirred suspension of **1** (102 mg, 0.07 mmol) in CH_2Cl_2 (7 mL) at −78 °C. After stirring for 10 min a clear yellow solution was observed and the solvent was removed *in vacuo* yielding a yellow solid. The crude product was recrystallized by dissolution in 3 mL of CH_2Cl_2 at −78 °C and layering pentanes (1.5 mL) over the solution. Overnight at −30 °C light yellow crystals formed. Yield 28 mg (30%). ^1H NMR (CD_2Cl_2, 193 K); major isomer (78%): δ 7.72 (s, 8H, BAr'_4: *o*-H), 7.53 (s, 4H, BAr'_4: *p*-H), 7.5–7.2 (m, 20H, C_6H_5), 2.49 (br, 2H, PCH_2), 2.34 (br, 2H, PCH_2), 2.07 (m, 2H, CH_2), 0.52 (s, CH_3), minor isomers: δ 0.42 (s, CH_3) (8%), 0.25 (s, CH_3) (14%); ^{31}P (CD_2Cl_2, 193 K) δ 15.7 (major isomer, *ca.* 80%), 15.4, 14.5 (minor isomers, *ca.* 20%). Anal. Calc.: C, 49.32; H, 2.83. Found: C, 49.37; H, 2.81%.

$(dppp)Pd(Me)S(O)_2Me$ **7**: ^1H NMR (CD_2Cl_2, 293 K) δ 7.6–7.2 (m, 20H, C_6H_5), 2.4 (m, 4H, PCH_2), 2.21 (s, 3H, SO_2CH_3), 2.1 (m, 2H, CH_2), 0.52 (pseudo t, J_{PH} 6 Hz, 3H, CH_3); ^{31}P NMR (CD_2Cl_2, 293 K); δ 18.9 (J_{PP} 48 Hz), 3.1 (J_{PP} 48 Hz).

Polymerisation studies: a 10% solution of freshly distilled hex-1-ene (5 mL) in CH_2Cl_2 (45 mL) was purged with SO_2 for 7 min at room temperature. A solution of **1** (14 mg, 9 μmol) was added at −78 °C, and the reaction was stirred at room temperature for 14 h. Methanol (*ca.* 10 mL) was added to quench the reaction, the solution concentrated *in vacuo*, and methanol added to precipitate the polymer. Yield 23 mg. ^1H NMR ($CDCl_3$) δ 4.1–3.6 [br, 2H, SO_2CH_2], 3.3 [br, 1H, $CH(Bu)SO_2$], 2.5–1.7 (br, $\alpha\text{-}CH_2$), 1.7–1.3 (br, 4H, CH_2CH_2), 0.9 (t, 3H, CH_3); GPC (THF, *vs.* PS standards): M_n = 61000, PDI 5.8. Identical conditions were applied for the reactions in the absence of **1** or in the presence of galvinoxyl (10 mg).

‡ *Crystal data* for $C_{65}H_{44}BCl_4F_{24}O_2P_2PdS$ **4**: M = 1666.04, triclinic, space group $P\bar{1}$, a = 13.0395(6), b = 17.1606(8), c = 17.9784(8) Å, α = 72.309(1), β = 78.658(1), γ = 68.341(1)°, V = 3545.8(3) Å^3, T = 173 K, Z = 2, μ(Mo-Kα) = 0.59 mm^{-1}, $2\theta \leqslant 56°$, 42774 reflections measured, 17105 unique (R_{int} = 0.031), 10812 observed [$I_{net} > 2.5\sigma(I_{net})$]. R_f = 0.079 (observed data), R_w = 0.104 (unique data). The data were collected using a Bruker SMART diffractometer using the ω scan mode, and solved using direct methods and refined by full matrix least squares on F_o. CCDC 129/236.

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Communication a905993h