

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

Derek P. Gates, Peter S. White and Maurice Brookhart*

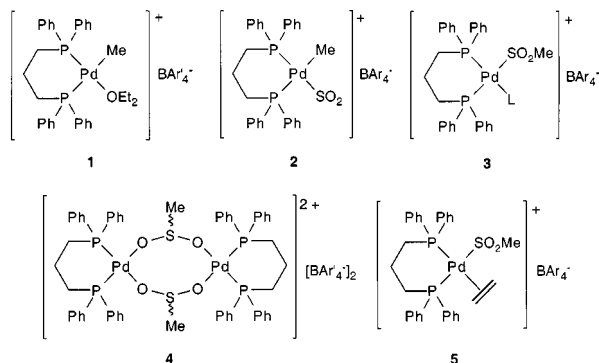
Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, USA. E-mail: brook@net.chem.unc.edu

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)(OEt₂)]BAR'₄ [Ar' = C₆H₃(CF₃)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 SO₂, 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 SO₂ using various palladium(II) complexes.⁴ In 1998, Sen and coworkers also reported that [(dppp)PdMe(NC-Me)]BF₄ was an effective catalyst for the copolymerisation of SO₂ with ethylene, propylene and cyclopentene.⁵ Here, we report our preliminary investigations of the insertion reactions of SO₂ into Pd(II)–methyl bonds and the attempted spectroscopic detection of the copolymerisation of ethylene and SO₂.

The cationic 1,3-bis(diphenylphosphino)propane (dppp) palladium(II) complex **1** can be prepared by the low temperature



reaction of (dppp)PdMe₂ **6** with H(OEt₂)₂[BAR'₄] [Ar' = C₆H₃(CF₃)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 CD₂Cl₂ with an excess of SO₂ (*ca.* 25 equiv.) at 193 K, the ¹H NMR spectrum shows the presence of free diethyl ether. Analysis of the reaction mixture by ³¹P 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 ¹H NMR spectrum exhibits three new singlets⁵ at δ 0.52 (78%), 0.42 (8%) and 0.25 (14%) which are assigned to –CH₃ groups, no signals were observed downfield at *ca.* 2–3 where resonances for an –S(O)₂CH₃ 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.[‡]

The molecular structure of the isolated product **4** is shown in Fig. 1, and confirms that insertion of SO₂ 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 ³¹P 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.

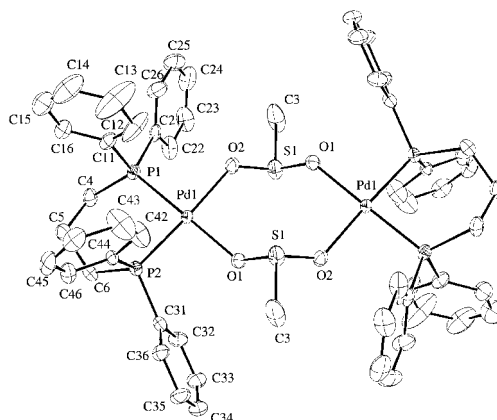
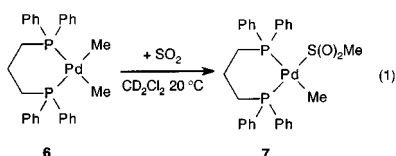


Fig. 1 Molecular structure of **4** (BAR'₄ anion omitted for clarity) with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.2354(20), Pd(1)–P(2) 2.2393(19), Pd(1)–O(1) 2.078(5), Pd(1)–O(2) 2.088(5), O(1)–S(1) 1.494(5), O(2)–S(1) 1.507(5), S(1)–C(3) 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 CD₂Cl₂ solution. As the temperature is raised from 193 K the three singlet ³¹P 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 here⁹ 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 SO₂ in an attempt to spectroscopically observe the insertion of SO₂ and ethylene in an alternating fashion. Thus, treatment of a solution of **1** in CD₂Cl₂ with a mixture of ethylene (10 equiv.) and SO₂ (10 equiv.) results in quantitative displacement of ether with ethylene at 193 K forming [(dppp)Pd(Me)(η²-C₂H₄)]BAR'₄¹⁰ which was characterised by ³¹P [δ = 17.5 (d, *J* 56 Hz), –1.5 (d, *J* 56 Hz)] and ¹H NMR spectroscopy [δ 5.18 (bound C₂H₄), 0.34 (dd, Pd–CH₃, *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 SO₂ into the Pd–Me bond of the methyl ethylene complex observed to form **5**. This suggests that formation of **4** from [(dppp)Pd(Me)(η²-C₂H₄)]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 L₂PtMe₂ complexes which readily insert SO₂ *via* a five coordinate intermediate.⁸ We have also carried out the analogous reaction of Pd complex **6** with SO₂ to form **7** presumably also *via* a five coordinate intermediate [eqn. (1)].[†]



In an attempt to obtain conclusive evidence for a migratory insertion mechanism, a low-temperature NMR experiment was carried out using CDCl₂F as solvent. Thus, SO₂ (10 equiv.) was added to a solution of ether complex **1** in CDCl₂F at 153 K. Upon warming to 173 K several new products could be detected in addition to **1**. The ³¹P 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–CH₃ group of a (dppp)Pd(CH₃)⁺ moiety and, since this species is not observed in the absence of SO₂, we assign this resonance to complex **2**, [(dppp)Pd(CH₃)(SO₂)]⁺. The ³¹P 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 [³¹P 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 SO₂ or Et₂O. 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 SO₂Me 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 CH₂Cl₂ purged with SO₂ 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 ¹³C NMR data are identical with those reported for the hex-1-ene/SO₂ 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 SO₂ 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 coworkers⁵ 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 CDCl₂F and to S. Shultz for useful discussions.

Notes and references

[†] *Preparation of 4*: under an atmosphere of argon, SO₂(g) (150 mL, 6 mmol) was slowly purged through a cloudy white stirred suspension of **1** (102 mg, 0.07 mmol) in CH₂Cl₂ (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 CH₂Cl₂ 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 (CD₂Cl₂, 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, C₆H₅), 2.49 (br, 2H, PCH₂), 2.34 (br, 2H, PCH₂), 2.07 (m, 2H, CH₂), 0.52 (s, CH₃), minor isomers: δ 0.42 (s, CH₃) (8%), 0.25 (s, CH₃) (14%); ³¹P (CD₂Cl₂, 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 (CD₂Cl₂, 293 K) δ 7.6–7.2 (m, 20H, C₆H₅), 2.4 (m, 4H, PCH₂), 2.21 (s, 3H, SO₂CH₃), 2.1 (m, 2H, CH₂), 0.52 (pseudo t, *J*_{PH} 6 Hz, 3H, CH₃); ³¹P NMR (CD₂Cl₂, 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 CH₂Cl₂ (45 mL) was purged with SO₂ 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 (CDCl₃) δ 4.1–3.6 [br, 2H, SO₂CH₂], 3.3 [br, 1H, CH(Bu)SO₂], 2.5–1.7 (br, α-CH₂), 1.7–1.3 (br, 4H, CH₂CH₂), 0.9 (t, 3H, CH₃); 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 C₆₅H₄₄BCl₄F₂₄O₂P₂PdS **4**: *M* = 1666.04, triclinic, space group *P*1̄, *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) Å³, *T* = 173 K, *Z* = 2, μ(Mo-Kα) = 0.59 mm^{–1}, 2θ ≤ 56°, 42774 reflections measured, 17105 unique (*R*_{int} = 0.031), 10812 observed [*I*_{net} > 2.5σ(*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.

- See, for example: A. Sen, *Adv. Polym. Sci.*, 1986, **73/74**, 125; E. Drent, J. A. M. van Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235; M. Brookhart, F. C. Rix, J. M. DeSimone, J. C. Barborak, *J. Am. Chem. Soc.*, 1992, **114**, 5894; F. C. Rix, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, 1996, **118**, 4746.
- For general reviews, see: G. J. Kubas, *Acc. Chem. Res.*, 1994, **27**, 183; A. Wojcicki, *Adv. Organomet. Chem.*, 1974, **12**, 31; W. Kitching and C. W. Fong, *Organomet. Chem. Rev. A*, 1970, **5**, 281.
- The reaction of SO₂ with ethylene in the presence of catalytic amounts of PdCl₂ has been reported to produce EtS(O)₂CH₂CH=CHCH₃. See: H. S. Klein, *Chem. Commun.*, 1968, 377.
- E. Drent, *US Pat.* 4 808 697, 1989.
- L. M. Wojcinski, M. T. Boyer and A. Sen, *Inorg. Chim. Acta*, 1998, **270**, 8.
- M. Brookhart, B. Grant and A. F. Volpe, *Organometallics*, 1992, **11**, 3920.
- J. Ledford, C. S. Shultz and M. Brookhart, unpublished work.
- M. S. Morton, R. J. Lachicotte, D. A. Vicic and W. D. Jones, *Organometallics*, 1999, **18**, 227.
- Quantitative analysis of the spectra were not performed but the barrier to isomer interconversions must lie in the range 14–15 kcal mol^{–1} based on ³¹P NMR linewidths at 263 K.
- J. Ledford and M. Brookhart, unpublished work.
- Hex-1-ene was chosen as comonomer because the ethylene/SO₂ copolymers are poorly soluble and difficult to characterise.
- K. J. Ivin, M. Navratil and N. A. Walker, *J. Polym. Sci. Part A-1*, 1972, **10**, 701.
- Polysulfones are generally prepared by radical initiated copolymerisation of SO₂ with olefins. Temperatures as low as –100 °C can be used. C. P. Tsonis, in *Polymeric Materials Encyclopedia*, ed. J. C. Salamone, CRC Press, New York, 1996, vol. 9, p. 6866.

Communication a905993h