Catalytic transformations of sulfur dioxide into organic sulfur compounds

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The applications of catalytic transformations of SO_2 into sulfur-containing organic compounds, reported in the literature, are briefly reviewed. The authors' studies in this field of chemistry, *viz.*, the hydrosulfination of alkenes, the synthesis of γ-oxo sulfones *via* hydrosulfination, and the synthesis of aromatic sulfinic acids from diazonium salts, are summarized. Current results on the synthesis of the new sulfinato complex $[Pd(SO_2Ph)(Cl)dppp]$ and its hydrogenation to $PhSO_2H$ are presented, and a mechanism for the catalytic synthesis of sulfinic acids is proposed. The structure of $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}(SO_4)^{2-}\cdot 4SO_2$ salt is studied by X-ray diffraction analysis.

Key words: sulfur dioxide, catalysis, hydrosulfination, sulfinic acids, γ-oxo sulfones, sulfinate complexes, structure of di[1,3-bis(diphenylphosphino)propane]di-μ-chlorodipalladium sulfate.

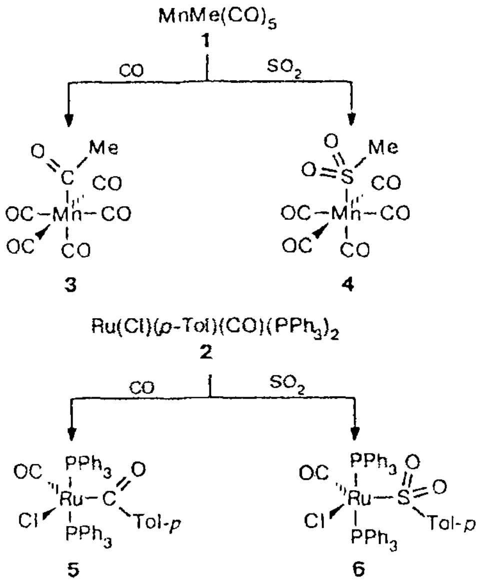
Despite its importance as an intermediate in the mass production of sulfuric acid, sulfur dioxide has received little attention in other catalytic applications. Noteworthy examples of transformations of SO_2 into sulfur containing organic compounds are scarce.

This is somewhat surprising when one considers the overall importance of a similar molecule, namely carbon monoxide, which is of immense industrial interest, *e.g.*, in hydroformylation reactions or in the synthesis of acetic acid. Moreover, CO is widely used as a raw material in numerous carbonylation reactions in organic chemistry.

A comparison of the coordination chemistry of CO and SO_2 reveals various similarities, and sulfur dioxide in the η^1-coplanar binding mode, *e.g.*, in $[Mn(Cp)(Me)(CO)_2SO_2]$, behaves more like CO in its overall bonding effects than any other ligand studied.[1] One of the most important CO transformations mediated by transition metals is the insertion of CO into a metal carbon bond. This reaction is also known for a variety of SO_2 complexes (see reviews[2a,b]).

Selected examples of the similarities between the insertion reactions of CO and SO_2 are given in Scheme 1. The reactions of CO with **1**[3] or **2**[4] result in the formation of the acyl complexes **3** or **5**, respectively. The insertion of SO_2 yields the corresponding S-sulfinato complexes **4**[5] or **6**[6].

Scheme 1



Acyl complexes have turned out to be important substrates or intermediates in the synthesis of a variety of compounds[7] as illustrated in Scheme 2.

Unexpectedly, the use of sulfinato complexes in the metal-mediated syntheses of organic compounds seems to have been hitherto neglected. Before our group started

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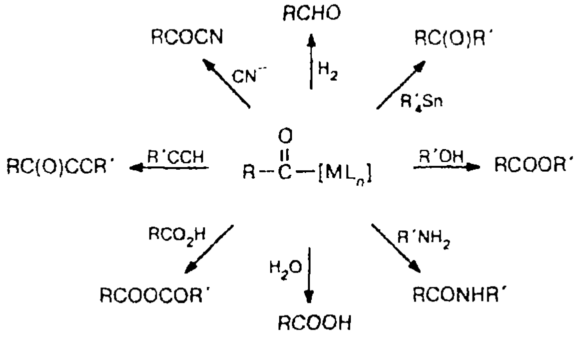
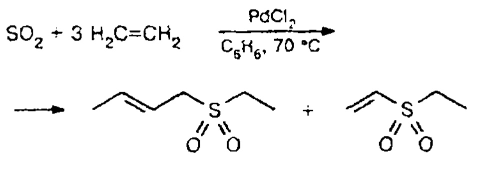
Scheme 2



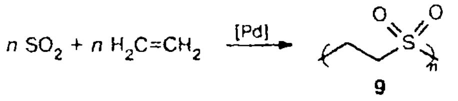
investigations in the field of SO_2 chemistry, there were only three examples of catalytic applications reported in the literature.

The first one, published in 1968,[8] was the reaction of ethylene with SO_2 in the presence of $PdCl_2$ leading to a mixture of ethyl *trans*-but-2-enyl sulfone **7** (80 wt.%) and ethyl vinyl sulfone **8** (15 wt.%) (Eq. (1)). A maximum turnover number of six is achieved; the reaction is terminated by the precipitation of palladium black. The reaction does not take place in the total absence of moisture, indicative of the involvement of a palladium hydride species.



7 8 (1)

Under different reaction conditions, one can obtain ethylene—sulfur dioxide copolymers **9** from the same substrates (Eq. (2)). This reaction was patented in 1989.[9] In general, no catalyst is necessary for the synthesis of polysulfones, as this reaction can also be carried out *via* a radical pathway. However, when palladium catalyst[9] is employed, perfectly alternating copolymers are obtained. In the case of the radically produced copolymers the maximum degree of alternation is 90%.



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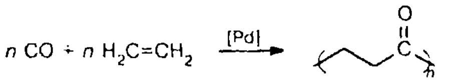
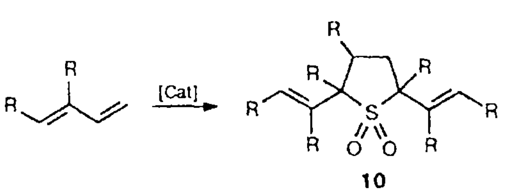


(3)

It is of interest to note that both the copolymerization of ethylene with CO (Eq. (3))[10] and the copolymerization of ethylene with SO_2 proceed with identical catalysts. However, the activities in the case of SO_2 are an order of magnitude lower than those for CO.

The third application in the field of catalytic SO_2 transformations is the synthesis of 2,5-dialkenylsulfolane derivatives **10** from conjugated dienes (Eq. (4)).[11]



10 (4)

R = H, Me

A $Pd(acac)_2$—PPh_3—$AlEt_3$ system is employed as catalyst. To achieve yields of more than 25%, a twentyfold excess of PPh_3 is necessary, thus increasing the yield up to 75%. This is traced back to the formation of $Ph_3P{=}O$ and $Ph_3P{=}S$ from PPh_3 and SO_2 according to Eq. (5).

$$3\,PPh_3 + SO_2 \xrightarrow{[Pd]} 2\,Ph_3P{=}O + Ph_3P{=}S \qquad (5)$$

The paucity of examples of catalytic applications for SO_2, in spite of the analogies between SO_2 and CO, prompted us to enter into this interesting field of chemistry. Our first investigations dealt with the copolymerization of alkenes with SO_2.[12a] We were able to confirm Drent's findings.[9] Moreover, we compared for the first time by ^{13}C-MAS-NMR study a polyethylenesulfone produced *via* a radical pathway (PES-H_2) with a copolymer formed by Pd-catalysis (PES-Pd). The MAS-NMR spectrum of PES-H_2 is given in Fig. 1. The main resonance at 46.5 ppm is identified as methylene carbon atoms in $\text{-}(CH_2CH_2SO_2)_n\text{-}$. The other resonance at 21 ppm is assigned to the C(2) and C(3) methylene carbons in the $\text{-}(CH_2CH_2CH_2CH_2SO_2)\text{-}$ unit. In contrast to this, the MAS-NMR spectrum of PES-Pd (Fig. 2) also exhibts resonance at 46.5 ppm, but the resonance of the tetramethylene unit at 21 ppm is much lower. The relative intensities of the different carbon types are summarized in Table 1.

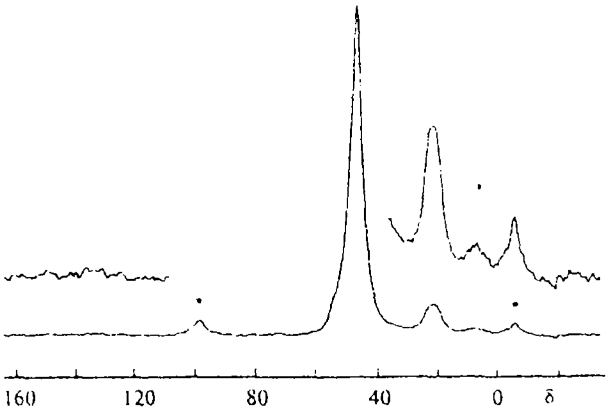


Fig. 1. ^{13}C CP/MAS NMR spectrum of polysulfone, produced *via* a radical pathway (PES-H_2). By asterisk (*) "side" signals are marked. The spectrum contains low-intensity signals at ~10 ppm (terminal CH_3 groups) and ~130 ppm (C_{olef}).

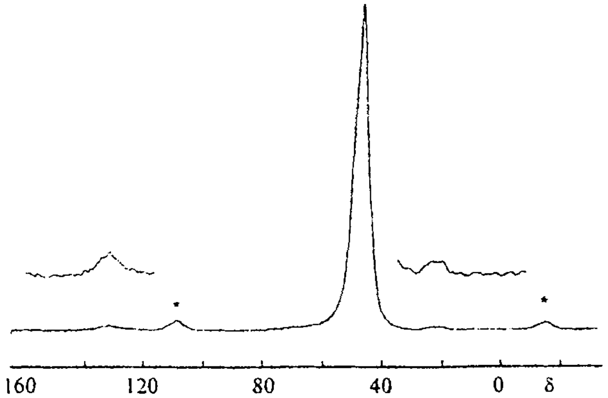


Fig. 2. ^{13}C CP/MAS NMR spectrum of polysulfone, produced with the use of Pd-catalyst (PES-Pd). By asterisk (*) "side" signals are marked. The spectrum contains low-intensity signal at ~130 ppm (C_{olef}).

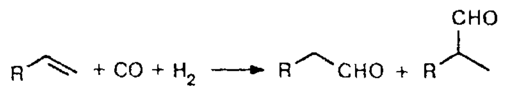
Table 1. Relative intensities of signals (I_{rel}) in ^{13}C MAS NMR spectra of polyethylenesulfones (PES)

Atom	δ	I_{rel} (%)	
		PES-H_2	PES-Pd
C_{Me}	6.7	1.2	0.1
C—$\underline{C}$—$\underline{C}$—C	21.0	9.6	1.0
C—SO_2—C	46	87.3	96.6
C_{olef}	132	1.9	2.3

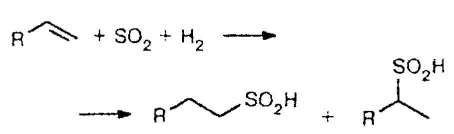
Note. Molecular weight (estimated) is 7.200 (PES-H_2) and >85.000 (PES-Pd); fragments C_2 : C_4 ratios is 18 (PES-H_2) and 190 (PES-Pd).

As can be seen in Table 1, a significant difference is the number of tetramethylene units present: <1% in the PES-Pd as compared to >10% in the radically formed PES-H_2. Hence, one can describe PES-Pd as a perfectly alternating copolymer.

When the reaction of SO_2 with alkenes and H_2 is carried out above the ceiling temperature T_c of a copolymer, monomeric products, sulfinic acids **11**, or, depending on the reaction conditions, their disproportionation products are obtained. Thus, this particular reaction constitutes the SO_2 analogy of the hydroformylation reaction (Eq. (6)) and is consequently called *hydrosulfination* (Eq. (7)).[12]



(6)



n-**11** *iso*-**11**

(7)

The active catalysts are cationic Pd^{II} or Pt^{II} complexes of the type $[M(MeCN)(P^\wedge P)](BF_4)_2$ with P^P representing a chelating diphosphine ligand. The palladium catalysts are prepared *in situ* from $[PdCl_2(P^\wedge P)]$ by addition of $AgBF_4$ in MeCN.[12c] The platinum catalysts are obtained *in situ* from $[PtCl_2(COD)]$ by stirring with an equimolar amount of the diphosphine in CH_2Cl_2.[13] The abstraction of the chloride is performed in the same manner as for the Pd compounds.

The palladium catalysts turned out to be much more active (even at lower temperatures) than the corresponding platinum ones. For example, $[M(MeCN)(P^\wedge P)](BF_4)_2$ complex has activity of 6050 g (mol Cat)$^{-1}$ h^{-1} at 80 °C for M = Pd. For M = Pt, the activity is 1600 g mol^{-1} h^{-1} at 120 °C. On the other hand, an inherent advantage of the platinum systems is to be seen in a higher *n* : *iso*-selectivity, especially with the dippp ligand: an *n* : *iso* ratio of 72 : 1 (equivalent to more than 98% of the linear product) can be achieved, whereas the maximum *n* : *iso* ratio obtainable with palladium lies at 12 : 1.

A decrease in activity is observed with a longer alkyl substituent. Thus, the relative activities of propene, 1-butene, and 1-hexene are 2.8 : 2.1 : 1.0. So far, ethylene itself cannot be hydrosulfinated due to the high ceiling temperature of the corresponding co-polymer.

Under the standard reaction conditions, the alkanesulfinic acids are not stable but disproportionate into *S*-alkyl alkanethiosulfonates **12**, alkanesulfonic acids **13**, and water (Eq. (8)).

$$3\,RSO_2H \longrightarrow \underset{\mathbf{12}}{RSSO_2R} + \underset{\mathbf{13}}{RSO_3H} + H_2O \qquad (8)$$

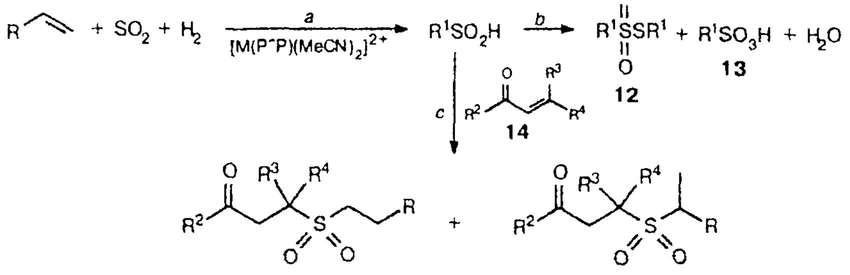
However, by addition of polar solvents like MeOH or H_2O in small amounts, the disproportionation is suppressed and the isolation of free alkanesulfinic acids becomes practicable. Depending on the reaction conditions, methyl alkanesufinates can be obtained as well. A general correlation between the main products and the reaction conditions can be derived from Table 2.

Another possible route to make use of the intermediate sulfinic acids as synthetic building blocks is to trap them *in situ*. We have recently introduced a simple method (Scheme 3) for an *in situ* Michael addition to form γ-oxo sulfones **15**.[13] In the presence of α,β-unsaturated carbonyl compounds **14**, the sulfinic acids add

Table 2. Required reaction conditions to obtain a certain product in hydrosulfination

Product	Temperature	Time	Concentration of alcohol
Sulfinate	High	Long	High
S-Thiosulfinate	High	Minor influence	—
Sulfinic acid	Low	Short	6—10 vol.%

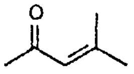
Scheme 3

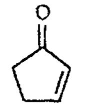


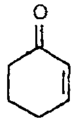
Note: *a* is hydrosulfination, *b* is disproportionation, and *c* is Michael addition.

smoothly to the activated double bond of the Michael acceptor. This reaction proceeds with high selectivity with no disproportionation products found.

In comparison to hydrosulfination without trapping reagent, the catalytic activities are lower. Among the acceptors employed, the best results are obtained with compounds **14a—c** that achieve turnover numbers of about 200 in 3—4 h.

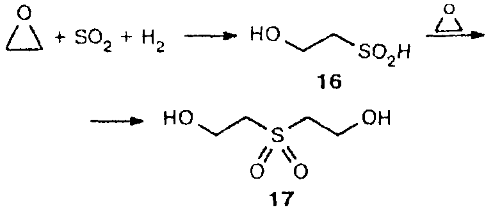

14a


14b


14c

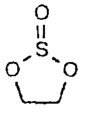
Unfortunately, this method seems to be restricted to aldehydes and ketones. When we tried to apply α,β-unsaturated nitriles, imines, or nitro compounds, the desired Michael adducts were not formed. This may be due to the interaction of either the catalyst or sulfur dioxide with these substrates at their nitrogen atoms.

Besides alkenes, oxiranes have been reported to undergo hydroformylation as well.[14] For this reason, we included ethylene oxide as substrate in the hydrosulfination reaction, expecting to obtain β-hydroxy sulfinic acids **16** or β,β′-dihydroxy sulfones **17**, respectively (Eq. (9)).



(9)

Instead, a 1 : 1 mixture of cyclic ethylene sulfite **18** and polyethylene sulfite **19** was formed. The products **18** and **19** are obtained with a number of different catalysts and even in the absence of hydrogen.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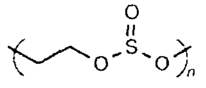
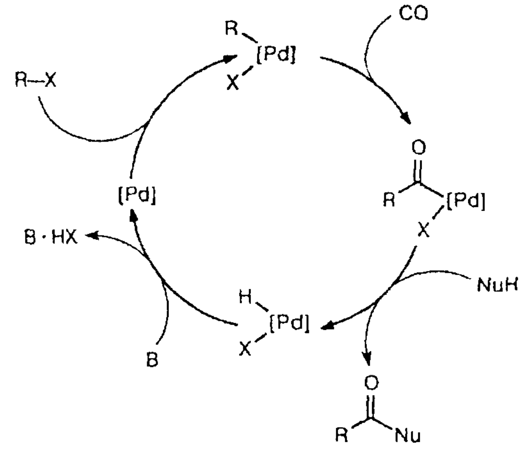

19

Apart from the successful synthesis of aliphatic sulfinic acids, the question arose as to whether aromatic sulfinic acids are also accessible *via* a catalytic pathway from SO_2. Here again, we were guided by the analogy with palladium-catalyzed carbonylation reactions.

To perform the transformations shown in Scheme 2 in a catalytic manner, it is necessary to regenerate the initial palladium complex. This can be done, for instance, by means of a base, as illustrated in Scheme 4.

Scheme 4

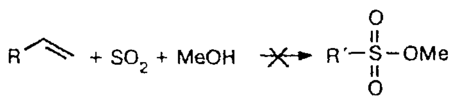


B is base; NuH = ROH, H_2O, RNH_2, RCOOH

To perform a similar reaction with SO_2 one has to take into account that SO_2 is a much stronger acid than CO and therefore the bases, which are essential for the catalyst regeneration, might react with SO_2. So, the strongest applicable bases are salts M_nSO_3 because they are conjugated bases of sulfurous acid, of which in turn SO_2 is its anhydride.

We used $Pd(PPh_3)_4$ as Pd complex, either in isolated form or *in situ* in the presence of dppe or dppp, iodobenzene or iodomethane as RX species, and Na_2SO_3 as base. Methanol was employed as nucleophile, either neat or added to a benzene solution. Varying the temperature between 20 °C and 120 °C and the reaction time between 2 hours and 7 days, the expected sulfonates RSO_2OMe could not be detected by NMR nor by GC-MS. Instead, only traces of sulfites $(MeO)_2S{=}O$ were identified in the GC-MS.

It should be mentioned that attempts to perform a reaction analogous to the hydroesterification of alkenes failed as well (Eq. (10)).

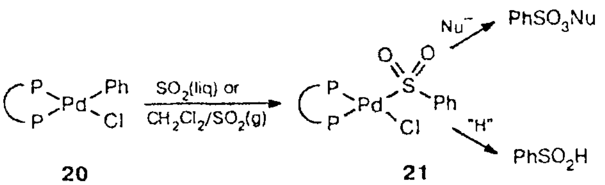


(10)

We then tried not to attack the intermediate sulfinato complex by nucleophiles, but to eliminate the sulfonyl halide directly. This would constitute the back reaction of the desulfonylation of aromatic sulfonyl halides reported by Blum and Scharf.[15] However, these attempts were not successful either. With chlorobenzene and a large excess of sulfur dioxide, using $[RhCl(PPh_3)_3]$ and $[Pd(PPh_3)_4]$, no $PhSO_2Cl$ was formed (conditions: T = 20—150 °C, t = 20—70 h).

To find out whether the postulated intermediary sulfinato complex is of interest from the preparative standpoint we synthesized $[Pd(SO_2Ph)Cl(dppp)]$ (**21**) and investigated its capabilities in the syntheses of sulfonates and sulfinic acids (Scheme 5).

Scheme 5



20 **21**

The insertion of SO_2 into the palladium—phenyl bond of **20** has not been reported so far. We have now achieved formation of **21** by dissolving **20** in liquid sulfur dioxide.

The yellow powder remaining after evaporation of SO_2 shows two absorptions in the IR spectrum at 1190 and 1044 cm^{-1}, which are in accordance with the symmetric and asymmetric stretching modes of a S-bonded sulfinate complex.[16]

Attempts to obtain the NMR spectra of the yellow powder failed, because the compound was either insoluble or decomposed in the solvents used. A possible pathway for decomposition is the extrusion of sulfur dioxide. To overcome this problem, we suspended the substrate complex **20** in CD_2Cl_2 and bubbled gaseous SO_2 through this solution. The color changed to yellow immediately. We then succeeded in the NMR spectroscopic examination of this solution, saturated with SO_2.

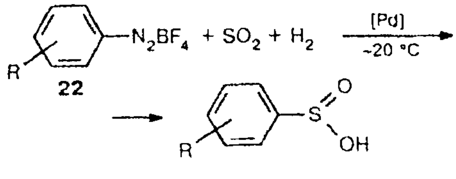
The ^{31}P NMR spectrum shows two doublets at 14.6 and 5.6 ppm (J = 55 Hz), respectively. This is a low-field shift of 3.9 ppm for the P_{trans} to the chloride and a low-field shift of 12.7 ppm for the P_{cis} to Cl compared with the complex **20**.[17] A small, broadened singlet signal at 12.3 ppm is presumably indicative of the start of decomposition of the complex **21**.

The signals in the ^1H NMR spectra are broadened, perhaps due to some influence of SO_2 on relaxation processes. Thus, a clear peak assignment is not possible, but it is evident that the signals of the aromatic protons of the phenyl ring attached to the palladium atom in **20** in the region between 6 and 7 ppm have disappeared. The ^{13}C NMR spectrum reveals a significant high-field shift of 8 ppm of the C_{ipso} of the phenyl substituent.

It is worth mentioning that the crystals formed in a solution of **21** in liquid sulfur dioxide on standing turned out to be $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}[SO_4]^{2-} \cdot 4SO_2$. The structure of this unexpected compound is discussed below.

Confirming our previous results, benzene sulfonates were not accessible from **21** even in stoichiometric amounts and using MeOH and Bu^{t}OH in a temperature range between 20 °C and 140 °C. The use of cationic complexes, which in general exhibit a higher reactivity than the corresponding neutral ones,[18] was similarly unsuccessful. Nevertheless, we could isolate benzenesulfinic acid (50% yield, not optimized) when complex **21** was treated with hydrogen at room temperature for 4 h. This interesting result, which, to our knowledge, is the first example of a synthetic organic conversion of a transition metal sulfinate complex, motivated us to search for a catalytic version.

Indeed, we could show that aromatic sulfinic acids can be synthesized in a new palladium-catalyzed pathway from diazonium tetrafluoroborates **22** (Eq (11)).[19] Interestingly, this reaction is a further example of an outstanding analogy between reactions involving carbon monoxide and sulfur dioxide, since a comparable reaction with CO has been reported[20] (Eq. (12)).



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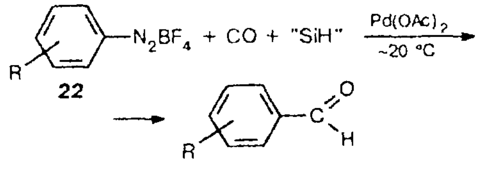


(12)

In contrast to known procedure[20] we initially used palladium on activated charcoal as catalyst. This catalyst was also used for the first heterogeneous Heck olefination of diazonium salts.[21] We have also been able to carry out

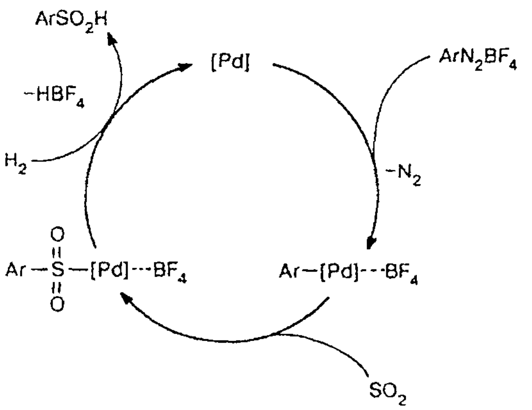
Table 3. Synthesis of sulfinic acids from diazonium salts using $Pd(OAc)_2$ as catalyst

Substrate	Yield	Conversion	Selectivity
		(%)	
PhN_2BF_4	81—97	100	81—97
p-$ClC_6H_4N_2BF_4$	78—80	100	78—80
p-$TolN_2BF_4$	0—37	0—57	0—100

Note. Conditions: 2.6 mmol ArN_2BF_4, substrate : catalyst = 55 : 1, solvent: 40 mL Et_2O + 1 mL MeOH, room temperature, p_{SO_2} = 2 bar, p_{H_2} = 30 bar, t = 4 h.

the reaction with palladium(II) acetate, as in carbonylation.[20] Yet, in contrast to the Pd/C catalyzed reactions, the results varied widely, as can be seen from Table 3. We attribute this to the use of a Pd^{II} species, which undergo reduction to Pd^0 by hydrogen. This may result in an induction period, which makes the reaction difficult to reproduce. Taking into account the stoichiometric reaction involving complex **21**, we postulate the following catalytic cycle (Scheme 6).

Scheme 6



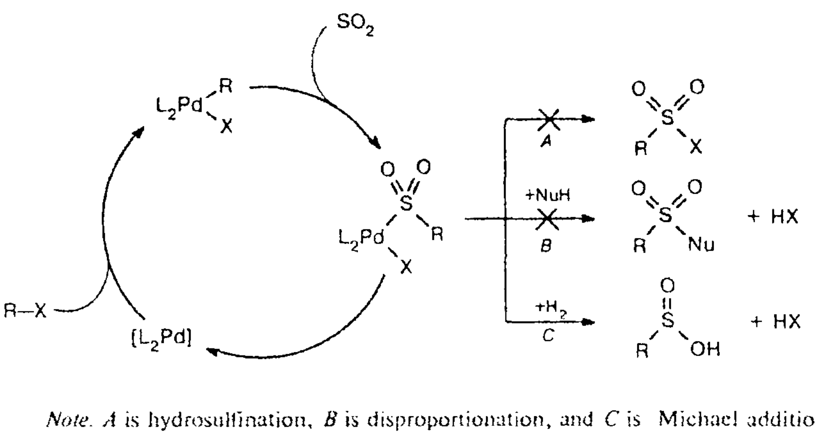
The character of BF_4^- as a weakly coordinating anion is probably the key to success, because in this way no base is necessary to trap the HX species, as mentioned above.

Our new results concerning the use of sulfinate complexes as intermediates in organic synthesis mediated by transition metals are summarized in Scheme 7.

A catalytic synthesis of sulfonyl chlorides could not be accomplished (path *A*). The synthesis of sulfonates (path *B*), which would parallel the alkoxycarbonylation of organic halides, is not feasible in a catalytic or stoichiometric pathway. Apart from this, successful palladium-catalyzed synthesis of aromatic sulfinic acids from diazonium salts is possible (path *C*). Furthermore, stoichiometric reaction of the palladium sulfinate complex **21** with hydrogen leads to the formation of benzenesulfinic acid.

The main results of the X-ray crystal structure analysis (see Experimental for further details) of $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}[SO_4]^{2-} \cdot 4SO_2$ formed in a solution of **21** in liquid sulfur dioxide are summarized in Fig. 3, which shows the molecular structure of the $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}$ dication, and in Tables 4 and 5, which give selected geometric parameters and the atomic coordinates of all the non-hydrogen atoms, respectively. The crystal structure comprises a solid solution of $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}[SO_4]^{2-}$ in SO_2. In the elementary unit there are two independent $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}$ cations, which differ only in the torsional arrangement of two phenyl groups (maximum torsional difference 32°), and the dications together with their $[SO_4]^{2-}$ counterions are surrounded by eight SO_2 molecules, consistent with the composition $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}[SO_4]^{2-} \cdot 4SO_2$. The coordination around each Pd atom is square planar, with Cl(1), Cl(2), and the two bonded P atoms situated in the coordination plane (±0.04 Å). The $P_2PdCl_2PdP_2$ moiety is, however, not planar, but folded along the Cl(1)...Cl(2) axis such that the mean planes through the coordination planes of the two metals make an angle of 140(1)° with one another. This is in contrast to the

Scheme 7



Note. A is hydrosulfination, *B* is disproportionation, and *C* is Michael addition.

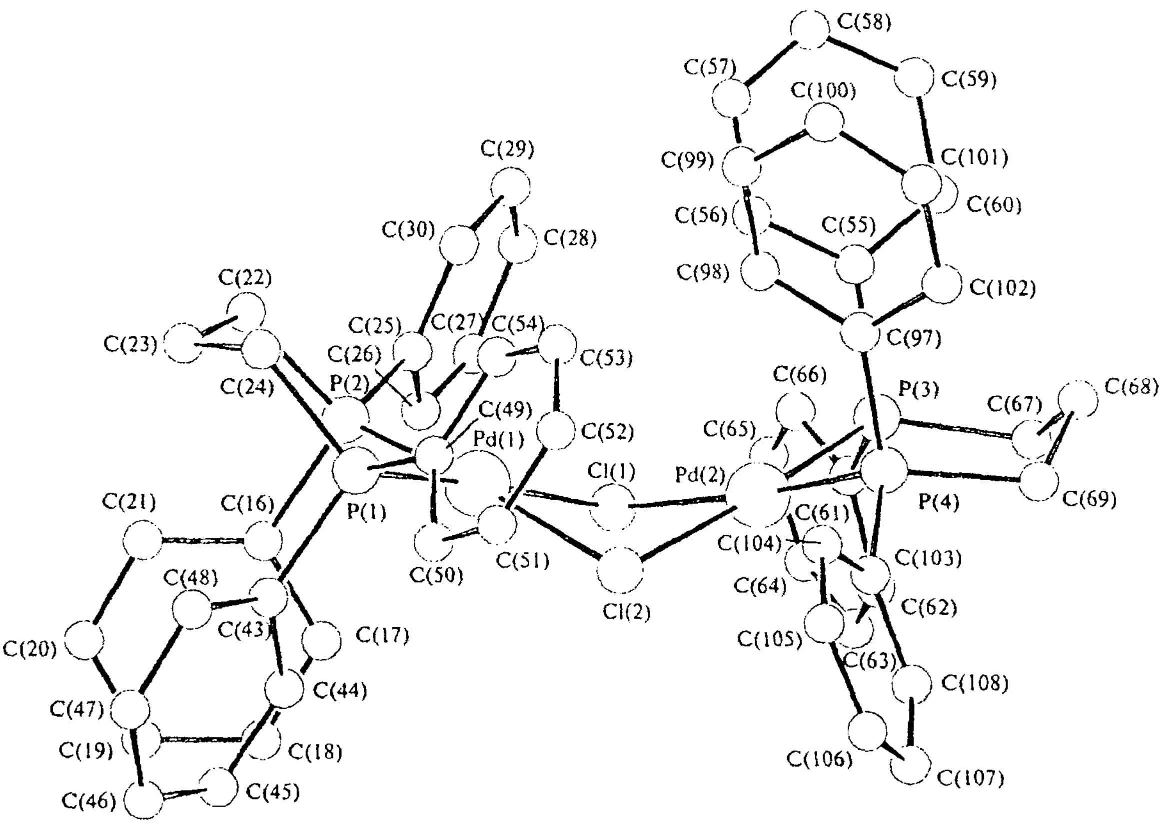


Fig. 3. Structure of dication $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}$ in the molecule $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}[SO_4]^{2-} \cdot 4SO_2$.

crystal structures of other diphosphine palladium chloride dimers reported in the literature,[22] which, except for a cationic palladium(II) complex containing the bulky diphenyl(4,4,6,6-tetramethyl-1,3-dioxan-2-ylmethyl)phosphine ligand,[23] where the comparable angle is 168°, all have a planar central Pd_2Cl_2 unit.

Experimental

The general procedure for the hydrosulfination has been reported in Ref. 12. The synthesis of γ-oxo sulfones *via* hydrosulfination has been published previously[13]. The reaction of diazonium salts with SO_2 and H_2 catalyzed by Pd/C has been submitted to "*Journal of Organic Chemistry*". The procedure is the same when $Pd(OAc)_2$ is used. All preparations were carried out under an argon atmosphere using the usual Schlenk technique.

Table 4. Selected interatomic distances (*r*), bond angles (ω), and interplanar angle (φ) in $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}$ dication

Distance	*r*/Å	Angle	ω/deg
Pd(1)...Pd(2)	3.339(1)	Cl(1)—Pd(1)—Cl(2)	84.44(5)
Pd(1)—Cl(1)	2.400(1)	Cl(1)—Pd(2)—Cl(2)	85.13(5)
Pd(1)—Cl(2)	2.414(2)	P(1)—Pd(1)—P(2)	90.92(6)
Pd(1)—P(1)	2.252(2)	P(3)—Pd(2)—P(4)	92.02(6)
Pd(1)—P(2)	2.256(2)		
Pd(2)—Cl(1)	2.394(2)	Interplanar angle	φ/deg
Pd(2)—Cl(2)	2.388(2)		
Pd(2)—P(3)	2.241(2)	Pd(1)Cl(1)Cl(2)P(1)P(2)/	
Pd(2)—P(4)	2.247(2)	Pd(2)Cl(1)Cl(2)P(3)P(4)	140(1)

IR spectra were recorded on a Nicolet FT-IR 510P spectometer. NMR spectra were obtained on a Bruker DPX 300 (^{1}H at 300 MHz, ^{31} C at 75 MHz, ^{31}P 121 MHz) and ^{13}C CP/MAS NMR spectra on a Bruker MSL 300 instruments in CD_2Cl_2. X-ray diffraction data were collected in a Siemens D5000 diffractometer with Cu-Kα radiation.

Benzene-*S*-sulfinato[1,3-bis(diphenylphosphino)propane]-chloropalladium(II) $[Pd(PhSO_2)(Cl)(dppp)]$ (21). *A.* In a glass autoclave equipped with a magnetic stirring bar Pd(Cl)(Ph)(dppp) complex (**20**) prepared according to Ref. 17 was placed and while stirring, SO_2 was condensed into the autoclave at −60 °C. The homogeneous bright yellow solution that formed rapidly was stirred for a further hour. The solution was then allowed to warm to room temperature with the pressure rising to ~4 bar. After releasing the pressure and drying in vacuum, a yellow powder was obtained. IR (KBr), $\nu(SO_2)/cm^{-1}$: 1190, 1044.

B. To perform NMR studies of the complex **21**, 200 mg of **20** was placed in a 15 mL Schlenk tube, equipped with a magnetic stirring bar, and CD_2Cl_2 (2 mL) was added. With stirring, gaseous SO_2 was bubbled through this suspension, resulting immediately in a yellow solution. After a few minutes, the stream of SO_2 was stopped. Stirring was continued for 30 minutes in the open Schlenk tube under a stream of argon, thus avoiding an excess SO_2. The solution was transferred into a NMR tube with a screw cap by means of a double-ended

Table 5. Atomic coordinates and equivalent isotropic thermal parameters (U_{eq})^a in the $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}[SO_4]^{2-} \cdot 4SO_2$ structure

Atom	x	y	z	U_{eq}/Å^2
Pd(1)	0.0292(1)	−0.4411(1)	0.4415(1)	0.015(1)
Pd(2)	0.0548(1)	−0.4140(1)	0.3535(1)	0.017(1)
Pd(3)	−0.0290(1)	−0.9099(1)	0.5586(1)	0.017(1)
Pd(4)	−0.0550(1)	−0.9351(1)	0.6475(1)	0.020(1)
Cl(1)	0.0460(1)	−0.3450(1)	0.4060(1)	0.019(1)
Cl(2)	0.1074(1)	−0.4937(1)	0.4005(1)	0.021(1)
Cl(3)	−0.0472(1)	−1.0047(1)	0.5950(1)	0.021(1)
Cl(4)	−0.1048(1)	−0.8552(1)	0.5997(1)	0.021(1)
P(1)	0.0205(1)	−0.5341(1)	0.4736(1)	0.019(1)
P(2)	−0.0330(1)	−0.3851(1)	0.4815(1)	0.018(1)
P(3)	−0.0018(1)	−0.3360(1)	0.3129(1)	0.018(1)
P(4)	0.0525(1)	−0.4860(1)	0.3064(1)	0.027(1)
P(5)	−0.0190(1)	−0.8180(1)	0.5257(1)	0.019(1)
P(6)	0.0316(1)	−0.9674(1)	0.5187(1)	0.020(1)
P(7)	−0.0013(1)	−1.0128(1)	0.6895(1)	0.024(1)
P(8)	−0.0439(1)	−0.8620(1)	0.6947(1)	0.025(1)
C(1)	−0.0479(4)	−0.9955(3)	0.4797(2)	0.022(1)
C(2)	−0.1207(5)	−1.0204(3)	0.4879(2)	0.026(1)
C(3)	−0.1848(5)	−1.0392(4)	0.4587(2)	0.031(1)
C(4)	−0.1778(5)	−1.0314(4)	0.4209(3)	0.032(1)
C(5)	−0.1057(5)	−1.0076(4)	0.4130(2)	0.028(1)
C(6)	−0.0401(5)	−0.9901(3)	0.4421(2)	0.026(1)
C(7)	0.1114(5)	−0.9271(4)	0.4989(2)	0.027(1)
C(8)	0.0889(5)	−0.8608(3)	0.4797(2)	0.025(1)
C(9)	0.0748(5)	−0.8079(3)	0.5068(2)	0.027(1)
C(10)	0.0812(4)	−1.0394(3)	0.5419(2)	0.024(1)
C(11)	0.0477(5)	−1.1015(4)	0.5367(2)	0.031(1)
C(12)	0.0882(6)	−1.1546(4)	0.5552(3)	0.037(2)
C(13)	0.1639(6)	−1.1464(4)	0.5796(3)	0.034(2)
C(14)	0.1970(6)	−1.0847(4)	0.5857(3)	0.039(2)
C(15)	0.1587(5)	−1.0308(4)	0.5676(2)	0.030(1)
C(16)	0.0458(4)	−0.3571(3)	0.5207(2)	0.019(1)
C(17)	0.1191(4)	−0.3309(3)	0.5130(2)	0.024(1)
C(18)	0.1842(5)	−0.3139(4)	0.5426(2)	0.029(1)
C(19)	0.1747(5)	−0.3228(4)	0.5802(2)	0.030(1)
C(20)	0.1031(5)	−0.3471(4)	0.5875(3)	0.032(1)
C(21)	0.0370(5)	−0.3642(3)	0.5585(2)	0.026(1)
C(22)	−0.1130(5)	−0.4273(3)	0.5004(2)	0.025(1)
C(23)	−0.0886(5)	−0.4931(3)	0.5192(2)	0.026(1)
C(24)	−0.0726(4)	−0.5460(3)	0.4919(2)	0.021(1)
C(25)	−0.0847(4)	−0.3135(3)	0.4578(2)	0.022(1)
C(26)	−0.0486(5)	−0.2510(4)	0.4646(2)	0.029(1)
C(27)	−0.0907(5)	−0.1978(4)	0.4457(2)	0.031(1)
C(28)	−0.1643(6)	−0.2049(4)	0.4212(3)	0.035(2)
C(29)	−0.1996(6)	−0.2675(4)	0.4143(3)	0.034(2)
C(30)	−0.1569(5)	−0.3212(4)	0.4328(2)	0.027(1)
C(31)	−0.1061(5)	−0.8101(3)	0.4864(2)	0.026(1)
C(32)	−0.1684(5)	−0.8563(4)	0.4805(2)	0.028(1)
C(33)	−0.2364(7)	−0.8476(4)	0.4507(3)	0.040(2)
C(34)	−0.2442(8)	−0.7906(6)	0.4291(4)	0.053(2)
C(35)	−0.1810(8)	−0.7439(6)	0.4351(4)	0.055(3)
C(36)	−0.1111(6)	−0.7546(5)	0.4624(3)	0.040(2)
C(37)	−0.0204(5)	−0.7474(3)	0.5558(2)	0.025(1)
C(38)	0.0464(6)	−0.7354(4)	0.5847(3)	0.035(2)
C(39)	0.0451(7)	−0.6818(5)	0.6083(3)	0.048(2)
C(40)	−0.0187(7)	−0.6404(5)	0.6036(3)	0.048(2)
C(41)	−0.0882(7)	−0.6513(5)	0.5737(3)	0.044(2)
C(42)	−0.0883(6)	−0.7060(4)	0.5503(3)	0.035(2)
C(43)	0.1061(4)	−0.5427(3)	0.5130(2)	0.024(1)
C(44)	0.1685(4)	−0.4947(3)	0.5196(2)	0.024(1)
C(45)	0.2358(6)	−0.5024(4)	0.5497(3)	0.035(2)
C(46)	0.2448(6)	−0.5600(5)	0.5706(3)	0.040(2)
C(47)	0.1842(6)	−0.6097(5)	0.5633(3)	0.040(2)
C(48)	0.1159(6)	−0.6002(4)	0.5349(3)	0.036(2)
C(49)	0.0230(5)	−0.6038(3)	0.4428(2)	0.025(1)
C(50)	0.0895(5)	−0.6465(4)	0.4484(2)	0.029(1)
C(51)	0.0876(6)	−0.7002(4)	0.4230(3)	0.039(2)
C(52)	0.0236(7)	−0.7091(5)	0.3945(3)	0.043(2)
C(53)	−0.0411(6)	−0.6664(4)	0.3888(3)	0.039(2)
C(54)	−0.0429(5)	−0.6128(4)	0.4125(2)	0.032(1)
C(55)	−0.1126(4)	−0.3353(3)	0.3058(2)	0.019(1)
C(56)	−0.1509(4)	−0.3638(3)	0.3327(2)	0.023(1)
C(57)	−0.2369(5)	−0.3600(4)	0.3287(2)	0.028(1)
C(58)	−0.2839(5)	−0.3269(4)	0.2985(2)	0.031(1)
C(59)	−0.2462(5)	−0.2974(4)	0.2716(2)	0.029(1)
C(60)	−0.1616(5)	−0.3013(3)	0.2752(2)	0.027(1)
C(61)	0.0300(4)	−0.2567(3)	0.3322(2)	0.021(1)
C(62)	0.1100(6)	−0.2344(5)	0.3355(3)	0.040(2)
C(63)	0.1319(7)	−0.1712(5)	0.3503(3)	0.048(2)
C(64)	0.0755(8)	−0.1332(6)	0.3614(4)	0.057(3)
C(65)	−0.0004(8)	−0.1556(6)	0.3614(4)	0.051(2)
C(66)	−0.0246(6)	−0.2159(4)	0.3460(3)	0.036(2)
C(67)	0.0243(4)	−0.3356(3)	0.2666(2)	0.024(1)
C(68)	0.0049(5)	−0.4001(4)	0.2443(2)	0.028(1)
C(69)	0.0671(5)	−0.4537(4)	0.2613(2)	0.032(1)
C(70)	−0.1132(4)	−0.7931(3)	0.6831(2)	0.021(1)
C(71)	−0.0838(5)	−0.7300(4)	0.6771(2)	0.029(1)
C(72)	−0.1395(5)	−0.6778(4)	0.6701(2)	0.034(2)
C(73)	−0.2226(5)	−0.6890(4)	0.6704(2)	0.030(1)
C(74)	−0.2521(5)	−0.7513(4)	0.6756(2)	0.032(1)
C(75)	−0.1971(5)	−0.8026(4)	0.6817(2)	0.030(1)
C(76)	0.0595(5)	−0.8277(4)	0.7027(2)	0.031(1)
C(77)	0.1000(5)	−0.8080(4)	0.7391(2)	0.031(1)
C(78)	0.1763(6)	−0.7766(4)	0.7435(3)	0.040(2)
C(79)	0.2109(7)	−0.7650(5)	0.7134(3)	0.051(2)
C(80)	0.1718(9)	−0.7868(7)	0.6782(4)	0.065(3)
C(81)	0.0953(7)	−0.8180(5)	0.6731(3)	0.049(2)
C(82)	−0.0631(6)	−0.8900(4)	0.7404(3)	0.038(2)
C(83)	−0.0117(6)	−0.9478(4)	0.7576(3)	0.039(2)
C(84)	−0.0323(6)	−1.0119(4)	0.7349(3)	0.036(2)
C(85)	0.1096(4)	−1.0113(3)	0.6982(2)	0.023(1)
C(86)	0.1586(5)	−1.0385(3)	0.7301(2)	0.028(1)
C(87)	0.2432(6)	−1.0418(4)	0.7344(3)	0.039(2)
C(88)	0.2797(5)	−1.0187(4)	0.7053(2)	0.032(1)
C(89)	0.2316(6)	−0.9899(4)	0.6739(3)	0.035(2)
C(90)	0.1481(5)	−0.9856(4)	0.6698(2)	0.032(1)
C(91)	−0.0319(5)	−1.0934(4)	0.6703(2)	0.028(1)
C(92)	−0.1132(7)	−1.1145(5)	0.6670(3)	0.047(2)
C(93)	−0.1363(8)	−1.1750(6)	0.6514(4)	0.056(3)
C(94)	−0.0776(8)	−1.2150(6)	0.6386(4)	0.058(3)
C(95)	0.0029(9)	−1.1935(7)	0.6415(4)	0.065(3)
C(96)	0.0230(7)	−1.1316(5)	0.6569(3)	0.047(2)
C(97)	−0.0432(5)	−0.5296(4)	0.2981(2)	0.032(1)
C(98)	−0.0928(6)	−0.5270(4)	0.3249(3)	0.038(2)
C(99)	−0.1651(9)	−0.5633(7)	0.3192(4)	0.062(3)
C(100)	−0.1880(8)	−0.6013(6)	0.2860(4)	0.058(3)
C(101)	−0.1379(7)	−0.6038(6)	0.2607(4)	0.053(2)
C(102)	−0.0672(7)	−0.5686(5)	0.2660(3)	0.047(2)
C(103)	0.1333(5)	−0.5461(4)	0.3170(2)	0.034(1)
C(104)	0.1156(7)	−0.6109(5)	0.3256(3)	0.043(2)

(to be continued)

Table 5 (*continued*)

Atom	*x*	*y*	*z*	U_{eq}/Å^2
C(105)	0.1772(7)	−0.6584(5)	0.3304(3)	0.047(2)
C(106)	0.2550(7)	−0.6404(6)	0.3269(3)	0.052(2)
C(107)	0.2778(8)	−0.5763(5)	0.3211(3)	0.052(2)
C(108)	0.2130(7)	−0.5292(5)	0.3154(3)	0.046(2)
S(1a)^b	0.2503(2)	−0.8445(1)	0.5979(1)	0.015(1)
S(1b)^b	0.2700(5)	−0.8660(4)	0.5923(2)	0.063(2)
S(2a)^b	0.0980(7)	−0.6398(5)	0.2239(3)	0.083(3)
S(2b)^b	0.1220(5)	−0.6285(3)	0.2298(2)	0.051(1)
S(3a)^b	−0.2500(2)	−0.4921(1)	−0.0987(1)	0.021(1)
S(3b)^b	−0.2889(3)	−0.5231(2)	−0.0940(2)	0.041(1)
S(4a)^b	−0.0257(4)	−0.4528(3)	−0.3431(2)	0.035(1)
S(4b)^b	−0.0415(5)	−0.4637(4)	−0.3498(2)	0.054(2)
S(5)	0.1781(2)	0.1183(1)	−0.0228(1)	0.051(1)
S(6)	−0.1783(2)	−0.7621(2)	0.0240(1)	0.054(1)
S(7a)^c	0.0219(6)	0.0823(4)	0.3429(2)	0.031(1)
S(7b)^c	0.0348(6)	0.0998(5)	0.3451(3)	0.047(2)
S(7c)^c	−0.0063(4)	0.0852(3)	0.3346(2)	0.027(1)
S(8)	0.1762(3)	−0.4917(2)	0.1458(1)	0.073(1)
S(9a)^b	−0.1762(5)	0.1668(4)	0.3399(3)	0.068(2)
S(9b)^b	−0.1795(5)	0.1599(3)	0.3587(2)	0.060(1)
S(10a)^c	−0.0208(8)	0.2124(6)	0.2577(4)	0.059(3)
S(10b)^c	−0.0318(7)	0.2110(5)	0.2666(3)	0.051(2)
S(10c)^c	−0.196(1)	0.1012(8)	0.2579(5)	0.098(4)
O(11)^d	0.2995(6)	−0.8469(4)	0.6368(3)	0.031(2)
O(12)^d	0.325(2)	−0.840(2)	0.631(1)	0.18(1)
O(13)^d	0.188(1)	−0.8775(8)	0.5888(5)	0.065(4)
O(14)^d	0.1693(7)	−0.8749(5)	0.5962(3)	0.032(2)
O(15)^d	0.2466(6)	−0.7816(4)	0.5808(3)	0.036(2)
O(16)^d	0.2982(7)	−0.8905(5)	0.5741(3)	0.042(2)
O(21)	0.1963(9)	−0.6098(7)	0.2310(4)	0.105(4)
O(22)	0.094(1)	−0.6990(8)	0.2144(5)	0.130(5)
O(31)^d	−0.3174(8)	−0.5907(6)	−0.0897(4)	0.059(3)
O(32)^d	−0.1775(6)	−0.5246(4)	−0.0944(3)	0.035(2)
O(33)^d	−0.3049(8)	−0.5355(6)	−0.0757(4)	0.055(3)
O(34)^d	−0.2430(7)	−0.4287(5)	−0.0809(3)	0.047(2)
O(35)^d	−0.2967(8)	−0.4880(6)	−0.1381(4)	0.046(3)
O(36)^d	−0.3211(9)	−0.4993(6)	−0.1340(4)	0.052(3)
O(41)^c	−0.068(1)	−0.4371(8)	−0.3866(5)	0.026(3)
O(42)^c	−0.042(1)	−0.453(1)	−0.3821(6)	0.038(4)
O(43)^c	−0.0473(8)	−0.5170(6)	−0.3308(4)	0.016(2)
O(44)^c	0.058(1)	−0.4405(8)	−0.3319(5)	0.030(3)
O(45)^c	−0.065(1)	−0.3975(8)	−0.3240(5)	0.023(3)
O(46)^c	−0.082(1)	−0.4128(9)	−0.3246(5)	0.025(3)
O(51)^b	0.125(1)	0.162(1)	−0.0422(6)	0.062(5)
O(52)^b	0.150(1)	0.182(1)	−0.0370(6)	0.062(5)
O(53)^b	0.257(1)	0.132(1)	−0.0018(6)	0.052(4)
O(54)^b	0.250(2)	0.111(1)	0.0012(7)	0.070(6)
O(61)^b	−0.257(2)	−0.787(1)	0.0029(9)	0.089(8)
O(62)^b	−0.255(1)	−0.7644(9)	−0.0020(5)	0.044(3)
O(63)^b	−0.189(1)	−0.7940(9)	0.0477(5)	0.063(4)
O(64)^b	−0.1354(8)	−0.8180(6)	0.0405(4)	0.034(2)
O(71)^e	−0.090(1)	0.0861(9)	0.3252(6)	0.015(3)
O(72)^e	0.033(1)	0.115(1)	0.3063(7)	0.021(4)
O(73)^e	−0.051(2)	0.058(1)	0.3339(8)	0.031(5)
O(74)^d	0.0844(7)	0.0590(5)	0.3211(3)	0.032(2)
O(75)^e	0.020(1)	0.015(1)	0.3422(7)	0.020(4)
O(76)^e	0.059(1)	0.081(1)	0.3831(7)	0.017(4)
O(77)^e	0.026(1)	0.1180(8)	0.3737(5)	0.010(3)
O(78)^e	0.022(1)	0.159(1)	0.3294(7)	0.020(4)
O(81)^b	0.1716(8)	−0.4307(6)	0.1652(4)	0.037(3)
O(82)^b	0.175(1)	−0.487(1)	0.1819(6)	0.072(5)
O(83)^b	0.248(1)	−0.5253(9)	0.1696(6)	0.057(4)
O(84)^b	0.239(1)	−0.5369(9)	0.1533(6)	0.055(4)
O(91)^b	−0.257(2)	0.126(1)	0.3451(9)	0.099(8)
O(92)^b	−0.247(2)	0.134(1)	0.3170(8)	0.097(7)
O(93)^b	−0.176(1)	0.2304(9)	0.3316(6)	0.050(4)
O(94)^b	−0.173(1)	0.223(1)	0.3449(6)	0.061(5)
O(101)	−0.102(2)	0.202(1)	0.2566(7)	0.173(8)
O(102)	−0.017(2)	0.252(1)	0.2798(7)	0.184(9)

[a] $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$ or U_{iso}. [b] Occupancy 0.5. [c] Occupancy 0.3333. [d] Occupancy 0.6667. [e] Occupancy 0.2.

needle. ^{31}P NMR, δ: 14.6 (d, P_{trans}—Cl, J = 55 Hz); 5.6 (d, P_{cis}—Cl, J = 55 Hz); a small signal at 12.3 ppm (br.s) is presumably assigned to $[Pd(\mu\text{-}Cl)(dppp)]_2$. ^{1}H NMR, δ: 1.8—1.9 (br.m, 2 H); 2.2—2.3 (br.m, 4 H); 7.2—7.3 (br.m, 3 H); 7.4—7.6 (br.m, 14 H); 7.7 (br.m, 4 H); 7.8—7.9 (br.m, 4 H). ^{13}C NMR, δ: 18.6 (s, $CH_2\underline{C}H_2CH_2$); 24.7 (dd, $\underline{C}H_2CH_2CH_2$, ^1J = 26 Hz, ^2J = 7 Hz); 28.6 (dd, $CH_2CH_2\underline{C}H_2$, ^1J = 33 Hz, ^2J = 11 Hz); 127.2—134.5 (C_{ar}); 152.5 (dd, $\underline{C}SO_2$, ^1J = 25 Hz, ^2J < 2 Hz).

Reaction of complex 21 with H_2 (the procedure has not been optimized). To 10 mL Et_2O and 0.7 mL MeOH placed in a Hastelloy autoclave cooled to −40 °C a solution of 2.8 mmol of **21** in SO_2(liq) (prepared as described above) was transferred by means of a double-ended needle. The autoclave was then pressurized with H_2 (30 bar). After stirring for 4 h at room temperature, the pressure was released and the resulting solution after filtration was treated as described in Ref. 13, yielding 50% of benzenesulfinic acid.

Attempts at preparation of benzenesulfonyl chloride from chlorobenzene. To $Pd(PPh_3)_4$ or $RhCl(PPh_3)_3$ placed in a glass or a Hastelloy autoclave equipped with a magnetic stirring bar PhCl was added and the autoclave was pressurized with SO_2. The mixture was stirred by a magnetic stirrer. After depressurizing, PhCl was distilled off and the residue was examined by ^{1}H and ^{13}C NMR. In no case was the desired $PhSO_2Cl$ detected. The parameters were varied in the following ranges: n([M]) = 0.09—0.26 mmol, n(PhCl) = 61—296 mmol, $n(SO_2)$ = 43—1200 mmol, T = 20—150 °C, t = 20—70 h.

X-ray diffraction study of $\{[Pd(\mu\text{-}Cl)(dppp)]_2\}^{2+}[SO_4]^{2-} \times \times 4SO_2$. A yellow-green crystal of $[C_{54}H_{52}Cl_2P_4Pd_2]^{2+}[SO_4]^{2-} \times \times 4SO_2$ (M = 1460.8), 0.81×0.77×0.60 mm, monoclinic; at 100 K, a = 16.5908(4) Å, b = 20.5201(4) Å, c = 36.1138(8) Å, β = 101.882(1)°, V = 12031.3(5) Å^3, d_{calc} = 1.61 g cm^{-3}, space group Cc [No. 9], Z = 8, μ = 10.25 cm^{-1}, F(000) = 5904 e, was investigated on a Siemens SMART diffractometer (ω-scan mode (CCD), $[(\sin\theta)/\lambda]_{max}$ = 0.76 Å^{-1}, no absorption correction, 66137 measured reflections (±h, ±k, ±l), 34155 independent reflections (R_{av} = 0.033), 31757 observed reflections with $I \geq 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97)[24] and refined by full-matrix least squares[25] against F^2 for all data with Chebyshev weights, R = 0.070 (obs. data), wR = 0.173 for 837 refined parameters, Pd, Cl, and P anisotropic, remaining atoms isotropic, $[SO_4]^{2-}$ anions and SO_2 molecules disordered, H atoms riding, residual electron density 2.39 eÅ^{-3}.

Atomic coordinates, atomic displacement parameters, and details of the crystal structure analysis have been deposited at