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SULPHUR DIOXIDE INSERTION REACTIONS WITH DICYCLOPENTADIENYLTITANIUM AND -ZIRCONIUM ALKYL AND ARYL COMPOUNDS

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SUMMARY

Sulphur dioxide was found to react in the expected manner with alkyl- and aryldicyclopentadienyltitanium compounds to yield the red monomeric *O*-sulphinates $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$, $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl$, and $(\pi\text{-}C_5H_5)_2Ti(O_2SC_6H_5)_2$. With dicyclopentadienylzirconium compounds, the sulphur dioxide inserts into the zirconium–alkyl bond and also into the zirconium–cyclopentadienyl bond in certain cases, even though the cyclopentadienyl group is π-bonded to zirconium. The preparations of the *O*-sulphinates $[\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)Cl]_n$, $[\pi\text{-}C_5H_5(C_5H_5SO_2)ZrO]_n$ and $[\pi\text{-}C_5H_5(C_5H_5SO_2)ZrSO_3]_n$ are reported.

INTRODUCTION

While alkyl and aryl derivatives of Zr and especially Ti have been known for some time, the reactivity of these compounds towards sulphur dioxide has never been studied. In this paper the reactions of SO_2 with several dicyclopentadienyl compounds of Ti^{IV} and Zr^{IV} are reported.

RESULTS AND DISCUSSION

(*a*). *Titanium compounds*

The reaction of solid $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ and SO_2 at solid CO_2/EtOH temtemperatures is too vigorous and results in a large amount of decomposition of the dimethyl compound. To moderate the reaction, the alkyltitanium was dissolved in light petroleum or in CH_2Cl_2 and gaseous SO_2 condensed into the solution.

When light petroleum is used as solvent, the product precipitates as a dark red oil which slowly solidifies on standing. On the basis of elemental analysis, molecular weight in chloroform, and NMR spectrum, the product was considered to be dicyclopentadienyltitanium bis(methanesulphinate) formed according to eqn. (1).

$$(\pi\text{-}C_5H_5)_2Ti(CH_3)_2+2\,SO_2 \xrightarrow[\text{solvent}]{-78°} (\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2 \qquad (1)$$

With dichloromethane as solvent, the product, which is very soluble in this solvent, may be obtained as an orange-red solid after removing the dichloromethane

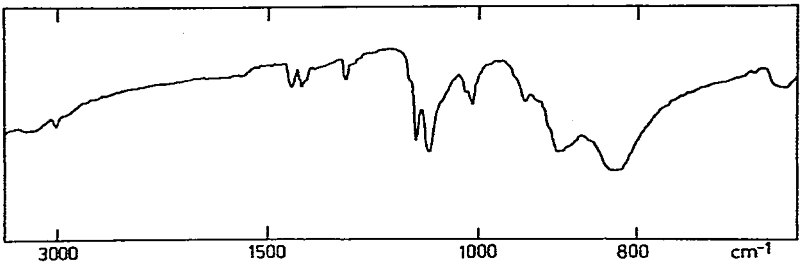

Fig. 1. IR spectrum of $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$ (KCl disc).

under reduced pressure. The IR spectrum of this compound (and in fact all other compounds investigated) in the SO_2 absorption region is similar in either KCl mull, chloroform or nujol. The peaks which can be assigned to the sulphinate moiety are found at 1115, 1090 and 885 cm^{-1}, indicating that the methanesulphinate groups are *O*-bonded to titanium[1] (Fig. 1). This of course is not unexpected in view of the high affinity which Ti shows for oxygen. The relatively large separation in the energy of the S–O stretching vibrations suggests that the sulphinate may not be symmetrically bound through both oxygens to the metal.

Reaction of $(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$ with SO_2 is much less vigorous and hence can be carried out by condensation of the SO_2 on to solid $(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$ cooled in a solid CO_2/ethanol bath. The product, which was shown to be dicyclopentadienylmonochlorotitanium methanesulphinate was isolated after evaporation of SO_2 as a red oil which solidified slowly on standing. Again, as in the dimethyl case above, if the reaction is carried out in CH_2Cl_2 the product is obtained as an orange-red solid.

The bands in the IR spectrum at 1090, 1070 and 872 cm^{-1} could be assigned to the S–O stretching vibrations. On this basis the compound was considered to be an *O*-sulphinate. The NMR spectrum in $CDCl_3$ of the compound prepared in CH_2Cl_2 was interesting in that the C_5H_5 and the methyl peaks were both split, the bands being at δ 6.62 and 6.55 ppm for the C_5H_5 and at δ 2.43 and 2.48 ppm for the methyl. The intensities of the C_5H_5 and CH_3 bands at lower field were approximately 50% of those of the higher field bands and this intensity ratio was consistent from preparation to preparation in SO_2 or in CH_2Cl_2. The ratio of the integrated intensities of the two sets of bands was C_5H_5/CH_3 9.6/3, which together with elemental analyses and a monomeric molecular weight in chloroform, is in good agreement with the suggested formula $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl$. In view of these results it seems likely that two isomers are present, possibly and *O,O'*-sulphinate as well as an *O*-sulphinate.

An equilibrium of the type:

$$2\,(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl \rightleftarrows (\pi\text{-}C_5H_5)_2TiCl_2 + (\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$$

can be discounted since only two C_5H_5 absorptions were found.

SO_2 will also insert into $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ to form the red bis(benzenesulphinato) compound. Insertion will not occur in dichloromethane as solvent at solid CO_2/EtOH temperatures, but only on allowing the solution to warm up to room temperature. The compound is monomeric in chloroform. The NMR spectrum in C_6D_6 has a sharp C_5H_5 singlet at δ 6.11 ppm (intensity 10) and two complex multiplets due to the phenyl groups, one centred at δ 7.78 ppm (intensity 4) and the other at

δ 7.10 ppm (intensity 6) which can be ascribed to the *ortho* and *meta*+*para* hydrogens respectively of the phenyl groups. The IR spectrum of the compound has two bands in the S–O asym. stretching region at 1092 and 1060 cm^{-1}, and a broad shoulder centred at approximately 880 cm^{-1} on the high energy side of the strong π-C_5H_5 band at 815 cm^{-1}.

(*b*). *Zirconium compounds*

At the time of this investigation there were no known organometallic sulphinato compounds of zirconium. Recently Lindner *et al.*[2] prepared $(\pi\text{-}C_5H_5)_2Zr(O_2SCH_3)_2$ by the reaction of CH_3SO_2Na with $(\pi\text{-}C_5H_5)_2ZrCl_2$ in THF. They suggest, on the basis of the S–O absorptions in the IR that it is an *O,O'*-sulphinato complex. When the reaction was carried out in boiling ethanol for 12 h, the cyclopentadienyls were displaced from the zirconium giving $Zr(O_2SCH_3)_4$. This of course is not surprising as the cyclopentadienyl groups on zirconium are relatively labile. Their lability is highly dependent on the nature of the other groups attached to the zirconium. The more electron donating the group, the higher the ionicity of the π-C_5H_5–Zr bond and hence the higher the lability of the cyclopentadienyls. Thus, $(\pi\text{-}C_5H_5)_2ZrCl_2$ is stable to moisture and may be refluxed with methanol for some hours without appreciable decomposition. However after 1 h in boiling ethanol $(\pi\text{-}C_5H_5)_2Zr(OCOCH_3)_2$* is converted quantitatively to $(EtO)_2Zr(OCOCH_3)_2$. Similarly, $(\pi\text{-}C_5H_5)_2Zr(O\text{-}i\text{-}Pr)_2$ will dissolve in cold isopropanol to give $Zr(O\text{-}i\text{-}Pr)_4$[3].

The difference in behaviour of $(C_5H_5)_2ZrH_2$ with acetic acid to form $\pi\text{-}C_5H_5\text{-}Zr(OCOCH_3)_3$, and with trifluoroacetic acid to give $(\pi\text{-}C_5H_5)_2Zr(OCOCF_3)_2$ can also be rationalised on the basis of the higher basicity of the acetato group over the trifluoroacetato group[3].

Thus, we believe that the ethanol plays an important part in the reaction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with CH_3SO_2Na. The reaction:

$$(\pi\text{-}C_5H_5)_2ZrCl_2+4\ CH_3SO_2Na \xrightarrow[12\ h]{\text{Reflux in EtOH,}} Zr(O_2SCH_3)_4+2\ NaCl+2\ NaC_5H_5$$

is probably more correctly considered as being a series of reactions, namely:

$$(\pi\text{-}C_5H_5)_2ZrCl_2+2\ CH_3SO_2Na \rightarrow (\pi\text{-}C_5H_5)_2Zr(O_2SCH_3)_2+2\ NaCl$$
$$(\pi\text{-}C_5H_5)_2Zr(O_2SCH_3)_2+2\ C_2H_5OH \rightarrow (C_2H_5O)_2Zr(O_2SCH_3)_2+2\ C_5H_6$$
$$(C_2H_5O)_2Zr(O_2SCH_3)_2+2\ (CH_3SO_2)Na \rightarrow Zr(O_2SCH_3)_4+2\ C_2H_5ONa$$

The majority of the C_5H_6 generally escapes from the reaction mixture as the monomer has a boiling point of only 42°. Certainly, C_5H_5Na is not stable in ethanol.

In this study we attempted to insert SO_2 into Zr–C bonds rather than using the ligand exchange reactions such as Lindner *et al.* used. Further, if the ionicity of the C_5H_5–Zr band is increased on forming the sulphinato compound, as postulated above, it may well be possible to insert a further SO_2 group between the zirconium and the π-C_5H_5 groups, a process which appears not to have been observed before.

When $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$ was treated with SO_2, the expected product (π-

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* Prepared by refluxing $(\pi\text{-}C_5H_5)_2ZrCl_2$ with excess $NaOCOCH_3$ in benzene and then recrystallizing it from a benzene/light petroleum solution; NMR, π-C_5H_5, δ 6.32 ppm; CH_3, δ 2.03 ppm in $CDCl_3$.

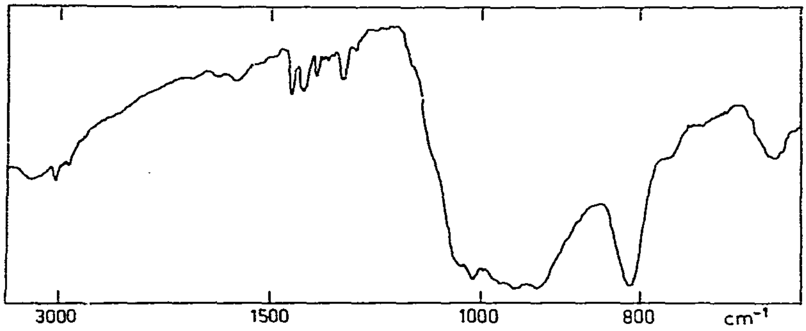

Fig. 2. IR spectrum of π-$C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)Cl$ (KCl disc).

$C_5H_5)_2Zr(O_2SCH_3)Cl$ was not obtained. Instead, a pale yellow product analysing for $(\pi$-$C_5H_5)_2Zr(CH_3)Cl \cdot 2\,SO_2$, and which we believe is π-$C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)Cl$ was obtained. Both sulphinato groups appear to be oxygen-bonded as the S–O stretching absorptions are all strong, the maxima occurring at 1041, 980 (sh), 955 and 925 cm^{-1}. No other strong absorption which may be associated with an S–O moiety were observed in the IR spectrum (Fig. 2).*

It would appear that the reaction involves firstly the insertion of an SO_2 group between the metal and the methyl group to form $(\pi$-$C_5H_5)_2Zr(O_2SCH_3)Cl$. Now, the ionicity of the C_5H_5–Zr bond is increased sufficiently to allow the SO_2 to react across it, the electrophilic sulphur reacting with the C_5H_5 and the oxygens with the zirconium. This reaction of course, parallels the reaction pathway of the ionic C_5H_5–Zr bond with, for example, ethanol or acetic acid.

TABLE 1

NMR POSITIONS OF THE C_5H_5 PROTONS IN SOME ZIRCONIUM COMPOUNDS

	δ (ppm) in $CDCl_3$	δ (ppm) in C_6D_6
$(\pi$-$C_5H_5)_2ZrCl_2$	6.52	5.83
$(\pi$-$C_5H_5)_2Zr(OC_6H_5)_2$	6.35	5.88
$(\pi$-$C_5H_5)_2Zr(OCH_3)Cl$	6.35	
$(\pi$-$C_5H_5)_2Zr(O$-i-$Pr)Cl$	6.33	6.00
$(\pi$-$C_5H_5)_2Zr(OC_2H_5)Cl$	6.32	5.90
$[(\pi$-$C_5H_5)_2ZrCl]_2O$	6.28	5.89
$(\pi$-$C_5H_5)_2Zr(CH_3)Cl$	6.27	5.73
$(\pi$-$C_5H_5)_2Zr(O$-i-$Pr)_2$	6.17	5.95

Since $(\pi$-$C_5H_5)_2ZrCl_2$ is reasonably stable to ethanol and water, and only reacts with acetic acid under refluxing conditions[4] when the side products are removed from the reaction medium, it was considered unlikely that the cyclopentadienyl groups in $(\pi$-$C_5H_5)_2ZrCl_2$ were sufficiently reactive to insert SO_2. This was

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* The possibility of SO_2 addition to the cyclopentadienyl ring was considered and discarded, largely on the basis of the IR spectral evidence. Any type of addition would, we believe, cause IR absorption different to that observed.

in fact found to be the case, as the $(\pi\text{-}C_5H_5)_2ZrCl_2$ could be recovered unchanged from liquid SO_2 at room temperature after periods exceeding 10 days.

The position of the cyclopentadienyl peak in the spectrum of $(\pi\text{-}C_5H_5)_2TiX_2$ type compounds has been used as a guide to the ionicity of the metal–C_5H_5 bond[5]. This can also be applied to cyclopentadienyl zirconium compounds. However, it should be pointed out that the NMR spectra in perdeutero benzene (and presumably other aromatic solvents) cannot be used as a guide to the ionicity of the Zr–C_5H_5 bond. C_6D_6 (see Table 1) has a drastic effect on the position of the C_5H_5 bands, moving them upfield. The bridged oxide $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ has the C_5H_5 absorption at δ 6.24 ppm while $(\pi\text{-}C_5H_5)_2ZrCl_2$ absorbs at δ 6.41 ppm in the same solvent, *viz.* dichloromethane. Accordingly this bridged oxide was treated with SO_2.

When SO_2 was bubbled through a methylene dichloride solution of $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ an insoluble white precipitate analyzing for $(C_5H_5)_2ZrO_3S$ was formed, together with the soluble $(\pi\text{-}C_5H_5)_2ZrCl_2$. The sulphur-containing compound had a strong band at 708 cm^{-1} in the IR which can be assigned to a Zr–O–Zr stretching vibration. This band occurs at 750–775 cm^{-1} in the bridged oxide. On treatment of this compound with acid, no sulphur dioxide is evolved, so that the compound is not a sulphite, but in fact an oxygen-bridged zirconium compound. The bands in the IR that are associated with the SO_2 stretching vibrations occur at 1157 cm^{-1} and at 918 and 902 cm^{-1} (see Fig. 3). The large separation between the bands would suggest that the SO_2 group is present in the complex as an unsymmetrically bonded *O*-sulphinate which is possibly bridging to another zirconium atom through the sulphur. This possibility was suggested by Chatt and Mingos[6] to explain IR absorption at 1200 and 950 cm^{-1} in certain platinum compounds. We believe therefore that the SO_2 has inserted between the Zr and what was initially a π-bonded-C_5H_5.

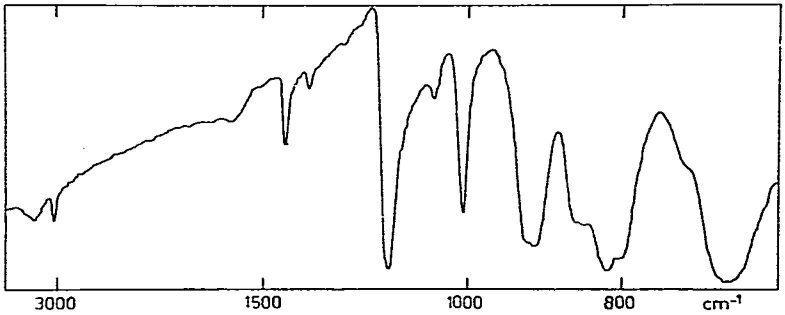

Fig. 3. IR spectrum of $[\pi\text{-}C_5H_5(C_5H_5SO_2)ZrO]_n$ (KCl disc).

The reaction for the formation of this bridged oxide sulphinato complex may be written as:

$$n\,[(\pi\text{-}C_5H_5)_2ZrCl]_2O + n\,SO_2 \rightarrow [(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrO]_n + n(\pi\text{-}C_5H_5)_2ZrCl_2$$

This sulphinato complex will react further with SO_2 at room temperature over a period of several days, forming a compound which analyzes for $(C_5H_5)_2ZrO\cdot 2\,SO_2$. This compound, insoluble in liquid SO_2, does not have an IR band which can be associated with the Zr–O–Zr moiety. Furthermore, on treatment with acid, it is decomposed liberating SO_2. The IR spectrum now shows one very broad and intense

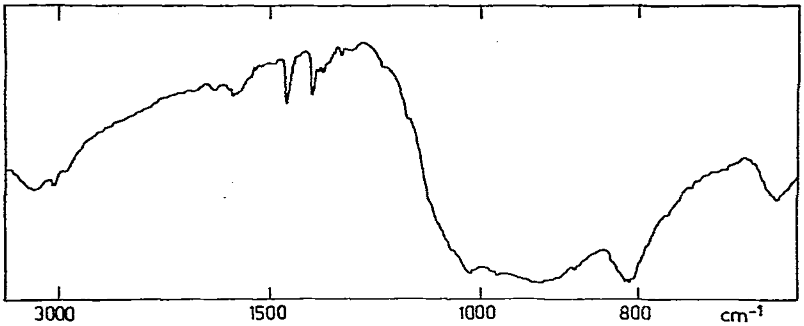

Fig. 4. IR spectrum of [π-C_5H_5($C_5H_5SO_2$)$ZrSO_3$]$_n$ (KCl disc).

band between 1100 and 850 cm^{-1} which may be assigned to S–O stretches (Fig. 4). We therefore consider the compound to be a sulphite and the sulphinato group to be bidentate through the oxygens. Thus the reaction of the sulphinato oxide compound with SO_2 can be written as:

$$[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrO]_n + n\ SO_2 \rightarrow \frac{n}{m}[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrSO_3]_m$$

It was not possible to insert an SO_2 molecule between the second π-C_5H_5 group and the metal even by allowing the reactants to stand at room temperature for up to 10 days.

We are continuing our investigations of SO_2 insertions including into Ti–OR and Zr–OR bonds.

EXPERIMENTAL

NMR

The NMR spectra were measured on either the Varian HA 100 or T60 instruments using tetramethylsilane as internal calibrant in all solvents except benzene in which hexamethyldisiloxane was used.

Solvents

C_6D_6 was distilled from $LiAlH_4$ under argon; $CDCl_3$ was distilled from P_2O_5 under argon as was the CH_2Cl_2 after first washing it with Na_2CO_3 and water and drying with $CaCl_2$.

General

All reactions were carried out under Ar or N_2; (π-C_5H_5)$_2ZrCl_2$ was obtained from Arapahoe Chemicals, Inc.; [(π-C_5H_5)$_2ZrCl$]$_2O$ was prepared by the previously published method[7]. The SO_2 was obtained from BDH. Reactions with SO_2 at room temp. were carried out in a tube containing a magnetic stirring bar and sealed with a threaded glass valve with Teflon stem. Analyses were carried out by the Australian Microanalytical Service.

Preparations

(π-C_5H_5)$_2Ti(CH_3)_2$. This was prepared by the method of Clauss and Bestian[8] with minor modifications. The methyllithium solution was added over less than 5 min

to $(\pi\text{-}C_5H_5)_2TiCl_2$ (11.5 g) suspended in ether (70 ml) and cooled in ice. The NMR spectrum of the product in C_6D_6 showed peaks at δ 5.65 (C_5H_5) and 0.02 ppm (CH_3).

$(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$. Sulphur dioxide was bubbled into a solution of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ (2 g) in CH_2Cl_2 cooled in a solid CO_2/EtOH bath. The colour deepened to red but no precipitate was formed even at $-78°$. Removal of SO_2 and solvent gave the bis(methanesulphinate) as an orange-red solid. (Found: C, 40.3; H, 4.8; S, 19.4; Ti, 14.2; mol.wt. ebulliometric in $CHCl_3$, 322. $C_{12}H_{16}O_4S_2Ti$ calcd.: C, 42.89; H, 4.80; S, 19.07; Ti, 14.24%; mol.wt., 336.3.) NMR, $\pi\text{-}C_5H_5$, δ 6.57 ppm; CH_3, δ 2.48 ppm in $CDCl_3$.

$(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl$. Excess SO_2 was condensed into a solution of $(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$ (2 g, prepared by the method of Clauss and Bestian[8]) in CH_2Cl_2 (30 ml) cooled to $-78°$. The reaction mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure to give an orange-red solid. (Found: C, 45.0; H, 4.6; S, 10.8; Ti, 16.3; mol.wt. ebulliometric in $CHCl_3$, 296. $C_{11}H_{13}ClO_2STi$ calcd.: C, 45.14; H, 4.48; S, 10.96; Ti, 16.37%; mol. wt., 292.6)

$(\pi\text{-}C_5H_5)_2Ti(O_2SC_6H_5)_2$. Liquid SO_2 was condensed on to $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ [prepared by the method of Summers, Uloth and Holmes[9], NMR (C_6D_6), δ 5.68 (singlet, C_5H_5) and 6.92 ppm (multiplet, C_6H_6)] cooled in solid CO_2/EtOH, and the SO_2 was then allowed to distil off leaving the bis(benzenesulphinate) as a dark red oil which slowly solidified. (Found: C, 56.8; H, 4.4; S, 13.7; Ti, 10.7; mol.wt. ebulliometric in $CHCl_3$, 498. $C_{22}H_{20}O_4S_2Ti$ calcd.: C, 57.37; H, 4.38; S, 13.93; T, 10.40%; mol.wt., 460.4.)

In CH_2Cl_2 sulphur dioxide will not insert into $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ at $-78°$ but reacts readily at room temperature giving the bis(benzenesulphinate). Care must be taken not to heat the sulphinate above 50°, at which temperature it melts to a red oil.

$(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$. This compound was originally prepared by J. R. Surtees[10] of these laboratories but the following improved method is due to Adcock and Wailes. To a slurry of $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ in CH_2Cl_2 (80 ml) was added $Al_2(CH_3)_6$ (5.5 ml). The oxide rapidly dissolved to give a pale yellow solution which was stirred for a further 30 min before diethyl ether (30 ml) was added. Solvent was pumped off to low bulk and light petroleum (100 ml. b.p. 30–40°) was added with stirring to precipitate $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$ as pale yellow crystals (8 g, 75% yield) which were collected by filtration in an inert atmosphere, washed several times with light petroleum and dried by pumping under vacuum at 40°. NMR (C_6D_6), δ 5.73 (C_5H_5, intensity 10) and 0.32 ppm (CH_3, intensity 2.99). The compound is very soluble in aromatic solvents and is highly sensitive to moisture forming the bridged oxide again with elimination of methane.

$(\pi\text{-}C_5H_5)(C_5H_5SO_2)Zr(O_2SCH_3)Cl$. $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$ (2 g) was dissolved in 15 ml of SO_2 in a Schlenk flask cooled in solid CO_2/EtOH. The cooling bath was removed and SO_2 allowed to evaporate over a period of several hours before removing the last traces by pumping. The product was a white solid. (Found: C, 32.7; H, 3.2; Cl. 9.0; S, 15.7; Zr, 23.4. $C_{11}H_{13}ClO_4S_2Zr$ calcd.: C, 33.08; H, 3.26; Cl, 8.87; S, 16.03; Zr, 22.81%.)

$[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrO]_n$. $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (8.5 g) was dissolved in CH_2Cl_2 (130 ml) and a steady stream of SO_2 was passed through the solution. After about 1–2 min the solution suddenly became cloudy. Passage of SO_2 was continued for a further 15 min during which the solution became slightly warm and precipitation continued. The supernatant liquid was decanted from the dense white precipitate, which was then washed with several 50 ml aliquots of CH_2Cl_2. After drying by pumping, 4.0 g of product (83% yield) was obtained. The compound is air-stable. (Found: C, 39.8; H, 3.4; S, 10.4; Zr, 30.4. $C_{10}H_{10}O_3SZr$ calcd.: C, 39.84; H, 3.34; S, 10.64; Zr, 30.23%.)

[(π-C_5H_5)($C_5H_5SO_2$)$ZrSO_3$]$_n$. [(π-C_5H_5)($C_5H_5SO_2$)ZrO]$_n$ (2 g) was sealed in a tube containing 20 ml of liquid SO_2 and the mixture was stirred at room temperature for 4 to 10 days. A gel formed from which the last traces of SO_2 could be removed only by heating to 70° for several hours under vacuum. The sulphite was off-white in colour and hygroscopic. (Found: C, 33.4; H, 2.9; S, 18.2; Zr, 24.9. $C_{10}H_{10}O_5S_2Zr$ calcd.: C, 32.86; H, 2.76; S, 17.54; Zr, 24.96%.)

The same product was obtained when [(π-C_5H_5)$_2$ZrCl]$_2$O was treated with SO_2 at room temperature for several days. The SO_2 solution remained clear for 20–30 min and then slowly formed a gel. Continuous extraction with THF in a Soxhet apparatus for several hours left the pure sulphite undissolved.

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