Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

INSERTION REACTIONS OF DICYCLOPENTADIENYLDIMETHYLZIRCONIUM AND RELATED CYCLOPENTADIENYL COMPOUNDS WITH SULPHUR DIOXIDE AND NITRIC OXIDE

P. C. WAILES, H. WEIGOLD AND A. P. BELL
C.S.I.R.O., Division of Applied Chemistry, Box 4331, G.P.O., Melbourne (Australia)

(Received June 30th, 1971)

SUMMARY

The reactions of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ are characterized by lability of the methyl groups, one or both of which may be displaced by reaction with hydrogen, phenylacetylene, methanol or lead chloride. Sulphur dioxide will insert between both methyl groups and the zirconium atom and also between one of the cyclopentadienyl ligands and the metal atom. Nitric oxide will insert between one of the methyls and the zirconium leading to a novel zirconium complex of methylnitrosohydroxylamine. Insertion reactions of SO_2 and NO were also observed with the monomethyl derivative $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$, and with $(C_5H_5)_4Zr$.

INTRODUCTION

Since the first stable alkylzirconium compounds were prepared in the early 1960's many more have been isolated. However, to date, very little work has been published on the reactions and reactivity of the zirconium–carbon linkage. In this paper the preparation of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ is reported and some of its reactions and the reactions of several related cyclopentadienyl derivatives of both titanium and zirconium are discussed.

RESULTS AND DISCUSSION

Dicyclopentadienyldimethylzirconium, $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (I), was prepared from $(\pi\text{-}C_5H_5)_2ZrCl_2$ and methyllithium. In contrast to the thermal instability of the corresponding titanium derivative[1], the dimethylzirconium compound is stable to heat and is best purified by sublimation under high vacuum at 100–110°. Although stable towards dry oxygen and carbon dioxide, (I) is very sensitive to hydroxylic compounds and so is hydrolysed in air giving methane and oxygen-bridged compounds such as $[(C_5H_5)_2ZrCH_3]_2O$ and $[(C_5H_5)_2ZrO]_n$ which react further, losing cyclopentadiene and giving mixtures of products.

In like manner the methyl group of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ (II) is hydrolytically unstable but in this case the well known oxide $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$[2] is the stable end-product. This behaviour contrasts sharply with the great stability of $(\pi\text{-}C_5H_5)_2$-

TABLE 1

NMR SHIFTS FOR $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (RELATIVE TO TMS)

Solvent	$\delta(C_5H_5)$ (ppm)	$\delta(CH_3)$ (ppm)
C_6D_6	5.80	−0.14
C_6F_6	6.05	−0.57
$CHCl_3$	6.08	−0.39
CH_2Cl_2	6.08	−0.40
Cyclohexane	6.03	−0.33
C_5D_5N	6.12	−0.18

$Ti(CH_3)_2$ towards water and alcohols[1]. Both the zirconium and titanium dimethyl derivatives are quite soluble in petroleum and all common organic solvents. The chemical shifts of the cyclopentadienyl protons in the NMR spectrum of (I) remain almost constant in all solvents except benzene. The large upfield shift observed in this solvent appears to be a general phenomenon occurring with all of the dicyclopentadienyltitanium and -zirconium derivatives studied. The positions of the C_5H_5 and CH_3 protons in the NMR spectra of (I) in a variety of solvents are shown in Table 1. The infrared spectrum of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (KCl disc) is shown in Fig. 1.

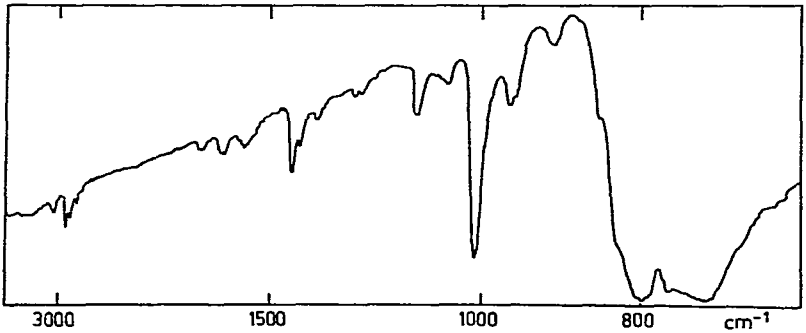


Fig. 1. Infrared spectrum (KCl disc) of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (I).

Reaction with hydrogen

While $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ reacts with hydrogen in solution to give titanocene[1] and in the solid state to give $[(\pi\text{-}C_5H_5)_2TiH]_2$[3],$(\pi\text{-}C_5H_5)_2Ti(Cl)CH_3$ did not react even in petrol at 100–120°. The corresponding monomethylzirconium chloride compound was also inert to hydrogen but the dimethyl derivative was hydrogenated in petrol above 110°. The crimson coloured product contained one methyl group per zirconium and analyzed approximately for $[(\pi\text{-}C_5H_5)_2ZrCH_3]_2$. Since the infrared spectrum showed the normal bands associated with symmetrically bonded cyclopentadienyl groups, the methyl groups are probably bridging.

Reaction with phenylacetylene

With phenylacetylene in boiling toluene over a period of one day $(\pi\text{-}C_5H_5)_2$-$Zr(CH_3)_2$ reacted slowly to give, besides the starting material, both the mono- and diacetylide, presumably with elimination of methane.

Reaction with methanol

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ with methanol proceeded readily with elimination of methane and the formation of methoxides. If the reaction was carried out stoichiometrically in deuterochloroform using methanol diluted with the same solvent, the initial product was the monomethoxide (III).

$$(\pi\text{-}C_5H_5)_2Zr(CH_3)_2 + CH_3OH \xrightarrow{\text{fast}} \underset{\text{(III)}}{(\pi\text{-}C_5H_5)_2Zr(OCH_3)CH_3} + CH_4$$

The methoxide (III) was identified by its NMR spectrum, in which the C_5H_5 protons showed as a sharp singlet at δ 6.22 ppm (relative intensity 10). Two other bands were present each of relative intensity 3 at δ 3.78 ppm (due to the OCH_3 group) and at δ 0.04 ppm (due to the CH_3 bonded to zirconium).

Addition of a second equivalent of methanol was followed by a slow decrease in the intensity of the bands due to $(\pi\text{-}C_5H_5)_2Zr(OCH_3)CH_3$ and the appearance of two new bands at δ 6.02 and 3.81 ppm due to the dimethoxide. Surprisingly the peak at δ 0.04 ppm due to the $ZrCH_3$ group was still observable even after several hours. In fact a white precipitate identified as the tetramethoxide $Zr(OCH_3)_4$, formed during this period. It is apparent that alcoholysis of the $Zr{-}C_5H_5$ bonds, presumably in the dimethoxy derivative, occurred at a rate comparable with that of the reaction of the $ZrCH_3$ groups in $(\pi\text{-}C_5H_5)_2Zr(OCH_3)CH_3$ with methanol*.

Reaction with lead dichloride

In chloroform or benzene at room temperature $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ was found to react with $PbCl_2$ to give firstly $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ and then $(\pi\text{-}C_5H_5)_2ZrCl_2$. During the reaction metallic lead was precipitated. By observation of changes in the NMR spectrum of the reaction mixture it was established that formation of the monomethyl product was quite fast, in fact the presence of metallic lead was noted after mixing the solid reactants. Further reaction of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ with $PbCl_2$ was slow and appreciable amounts of the dichloride were present only after reaction periods in excess of 1 day. In fact it was possible to convert the dimethyl derivative almost quantitatively to the monomethylzirconium chloride by vigorous stirring over one hour with a stoichiometric amount of $PbCl_2$. One more peak at δ 0.74 ppm in $CDCl_3$ appears in the NMR spectrum at a growth rate comparable with that of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$. The presence of two satellite peaks approximately 31 Hz either side of the main resonance indicates the presence of a methyllead compound, in particular $Pb(CH_3)_4$. The reaction scheme is shown below:

$$4(\pi\text{-}C_5H_5)_2Zr(CH_3)_2 + 2\,PbCl_2 \xrightarrow{\text{fast}} 4\underset{\text{(II)}}{(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3} + Pb + Pb(CH_3)_4$$

$$4(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3 + 2\,PbCl_2 \xrightarrow{\text{slow}} 4(\pi\text{-}C_5H_5)_2ZrCl_2 + Pb + Pb(CH_3)_4$$

---

* Activation of $Zr{-}C_5H_5$ bonds to hydrolytic type cleavage by the presence of alkoxy groups on zirconium has been established in previous papers[4,5].

The amount of lead required by this scheme could be recovered at the end of each reaction.

Reactions with sulphur dioxide

When $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ was dissolved in SO_2 at solid CO_2/EtOH temperatures and the SO_2 was allowed to evaporate, the yellow product obtained corresponded in analysis to $(C_5H_5)_2Zr(CH_3)_2 \cdot 3SO_2$. The compound was not a sulphite and not an adduct of SO_2. The infrared spectrum of the product in nujol mull or in KCl disc showed a broad strong band between 1100 and 800 cm^{-1} associated with S–O stretches and C_5H_5 vibrations and similar to the spectrum of $\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)Cl$[5]. From this data and by analogy with the reactions of SO_2 with $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ and $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ reported in a previous paper[5], the product now obtained was considered to be $\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)_2$ (IV). Insertion of SO_2 between the zirconium and the cyclopentadienyl ligand occurred even when reaction and removal of SO_2 were carried out at $-78°$. The insolubility of the compound in non-interacting solvents meant that its NMR spectrum could not be measured and attempts to obtain the spectrum in liquid SO_2 were hampered by further reaction with this solvent. At room temperature in liquid SO_2 a yellow precipitate formed from which sulphur dioxide was liberated on treatment with sulphuric acid. The infrared spectrum showed broad strong absorption between 1100 and 850 cm^{-1}, while the band at 800 cm^{-1} usually very strong in most cyclopentadienyl compounds, was quite weak. From this data the complex was considered to be an *O*-sulphinatozirconium sulphite (V) formed according to the scheme:

$$(\pi\text{-}C_5H_5)_2Zr(CH_3)_2 + 3\,SO_2 \xrightarrow[<-10°]{\text{liq. }SO_2} \underset{\text{(IV)}}{\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)_2} \xrightarrow[20°]{\text{liq. }SO_2}$$

$$\rightarrow \underset{\text{(V)}}{(C_5H_5SO_2)_2ZrSO_3} + (CH_3)_2SO$$

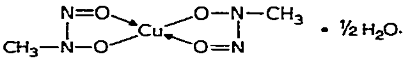
As added proof that insertion between a metal and a cyclopentadienyl ligand can occur, it is pertinent to mention that SO_2 will insert into $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$, as described in a previous paper[5], and also into tetracyclopentadienylzirconium. In the solid state the latter compound has three cyclopentadienyl ligands π-bonded and one σ-bonded[6]. In liquid SO_2 at room temperature $(C_5H_5)_4Zr$ was converted to the *O*-sulphinato derivative $C_5H_5(C_5H_5SO_2)_3Zr$, the infrared spectrum of which was similar to those of all other $C_5H_5SO_2Zr$ compounds.

Reactions with nitric oxide

While there are now numerous examples of insertion of SO_2 into a metal–alkyl bond, there are very few corresponding cases of NO insertion. Perhaps one of the first experiments was that of Frankland in 1856 who reacted NO with dimethyl- and diethylzinc[7]. The complexes formed were probably of the type $RZn(NO)_2R$*. Later, in 1903, Sand and Singer[8] isolated the compound $C_6H_5N(NO)OH$ from the reaction of nitric oxide with a phenyl Grignard reagent, while the methyl derivative led to a copper complex to which they assigned the structure (VI).

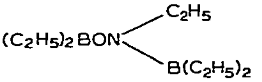
---

* Calculated from Frankland's elemental analyses. His assignment of the formula $C_4H_5ZnNO_2$ to the ethyl derivative was based on atomic weights not acceptable now.



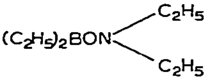
(VI)

More recently Brois[9] (1964) and Inatome and Kuhn[10] (1964) treated trialkylborons with nitric oxide. At −30° the product was the *N*-bonded complex $(C_2H_5)_2$-$BN(NO)OC_2H_5$ (VII). Structural proof came from the NMR chemical shift of the unique ethyl group (CH_2, δ 4.15; CH_3, δ 1.73 ppm, neat) together with the similarities of the infrared spectrum to those of nitrosamines and the fact that N_2O was obtained on treatment with concentrated sulphuric acid. When the reaction was carried out at 70°, a reversal of the mode of insertion was found as the compounds isolated were (VIII) and (IX):



(VIII)

NMR (neat): δ 3.27 (CH_2), 1.10 ppm (CH_3)



(IX)

NMR (neat): δ 2.65 (CH_2), 1.00 ppm (CH_3)

When NO was bubbled through a solution of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ in light petroleum at room temperature a white precipitate was obtained. Analysis suggested that two NO groups were incorporated in the molecule. The NMR spectrum in deuterobenzene consisted of three sharp singlets, one of relative intensity 10 at δ 5.78 ppm due to the C_5H_5 protons, and two of relative intensity 3 at δ 3.03 and 0.55 ppm, which were ascribed to two different methyl groups. The corresponding δ values in deuterochloroform were 5.88, 3.83 and 0.14 ppm. The peak at 0.55 ppm in deuterobenzene was presumably due to a methyl group attached directly to the metal, since in the NMR spectrum of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ in deuterobenzene the methyl band is found at δ 0.32 ppm, while for the corresponding titanium compound the band is at δ 0.70 ppm. The infrared spectrum (Fig. 2) differed appreciably from that of the

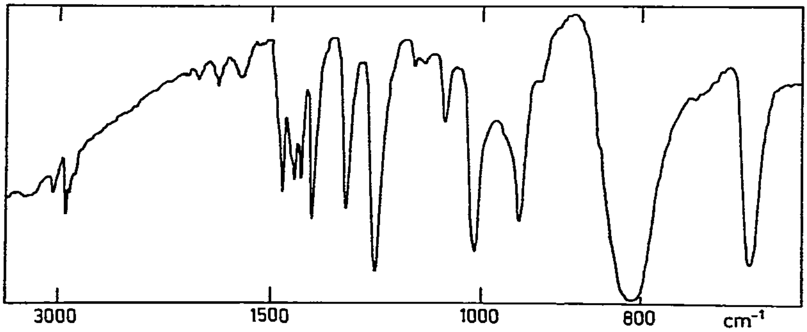
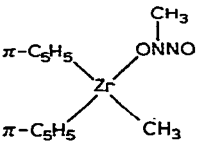
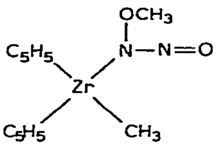


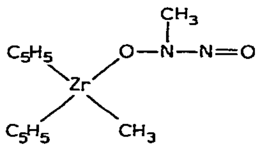
Fig. 2. Infrared spectrum (KCl disc) of



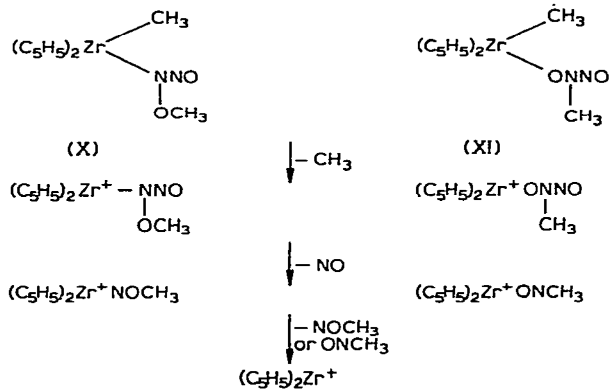
(XI)

dimethyl derivative and indicated that the compound was not a metal nitrosyl. The two possible structures (X) and (XI) were therefore considered for this compound:


(X)


(XI)

Since the methyl group involved in the reaction had its NMR resonance at δ3.03 ppm it was not possible to assign it with confidence to either an OCH_3 or an NCH_3 group. The mass spectrum, at the mildest inlet temperatures obtainable, showed no strong peaks at mass numbers below 100, so that no peaks could be assigned to species containing OCH_3 or NCH_3 groups. The breakdown pattern of the compound was explicable using either structure (X) or (XI), *viz.*:



The only other zirconium-containing species found were $C_5H_5ZrO^+$ and $C_3H_3ZrO^+$, which may well have been formed by partial hydrolysis of a $ZrCH_3$ group during transfer of the compound into the spectrometer inlet. This is supported by the fact that in the mass spectrum of $(\pi\text{-}C_5H_5)_2ZrCl(N_2O_2CH_3)$, the parent peak together with $C_5H_5ZrCl(N_2O_2CH_3)^+$, $(C_5H_5)_2ZrCl^+$ and $C_5H_5ZrCl(NOCH_3)^+$ were found but not $C_5H_5ZrO^+$ or $C_3H_3ZrO^+$.

As in the case of the alkylboron compounds, treatment with 12 *N* H_2SO_4 at refluxing temperature for 3 h gave N_2O, identified by its infrared spectrum, and no NO. As this could not be taken as a definite indication of one structure or the other, one of the ligands was synthesized. Methylhydroxylamine hydrochloride, CH_3-$NHOH \cdot HCl$, was nitrosylated at −5° in the presence of copper sulphate to protect the hydroxyl group. The copper complex so obtained, which analyzed for the anhydrous form of (VI), showed an infrared spectrum virtually identical with that of the zirconium compound, if the cyclopentadienyl absorption is taken into account (Fig. 3). Furthermore on hydrolysis of the copper complex with 50% H_2SO_4, N_2O was formed and again no NO was detected. On this basis structure (XI) was assigned to the zirconium complex. This is of course what one would intuitively expect as

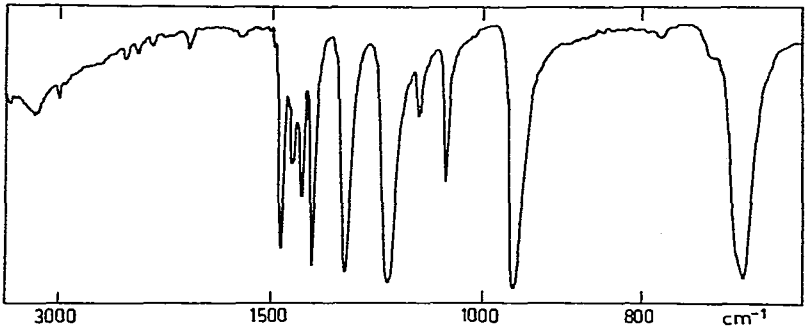
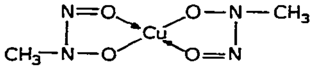


Fig. 3. Infrared spectrum (KCl disc) of



(VI)

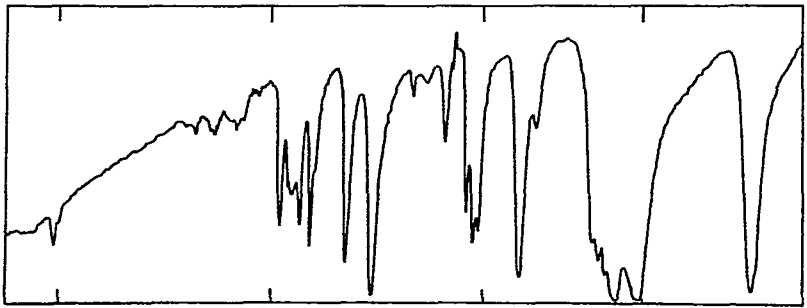
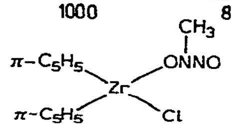


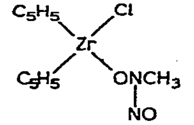
Fig. 4. Infrared spectrum (KCl disc) of



(XII)

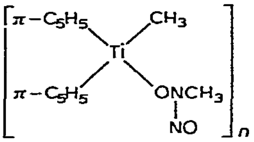
zirconium in general appears to prefer bonding through oxygen rather than through nitrogen.

Attempts to insert NO between the second methyl group and the zirconium by treatment of a solution of $(\pi\text{-}C_5H_5)_2Zr(CH_3)N_2O_2CH_3$ with NO over several hours were not successful, even at reflux temperature in benzene or in higher-boiling solvents. The monomethylzirconium chloride, $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$, on the other hand was readily converted to the corresponding nitrosylated complex (XII) by treatment of a benzene solution with nitric oxide. The infrared spectrum of (XII) was almost identical with that of the dimethylzirconium product (Fig. 4). The lack of reactivity of $(\pi\text{-}C_5H_5)_2Zr(CH_3)N_2O_2CH_3$ with NO is paralleled in the titanium case. Dicyclopentadienyldimethyltitanium reacts with nitric oxide in benzene at room temperature to give (XIII) the infrared spectrum of which was similar to that of the corresponding zirconium compound.



(XII)

NMR $(CDCl_3)$: δ 6.14 (C_5H_5), δ 3.84 ppm (CH_3)
(C_6D_6) : δ 6.04 (C_5H_5), δ 2.89 ppm (CH_3)



(XIII)

The molecular weight of (XIII) in boiling tetrahydrofuran was concentration-dependent, varying between an initial value of 740 and increasing to 1050 at concentrations of approximately 16 g/l. This may well be indicative of a trimer (mol.wt. 805) $\rightleftharpoons$ tetramer (mol.wt. 1087) equilibrium. The NMR spectrum of the compound was complicated by the polymerization which caused some precipitation in the solvent used (benzene-d_6). The proton chemical shifts were at approximately δ 0.8 ppm ($TiCH_3$), δ 3.05 ppm (NCH_3) with a broad complex band between δ 5.5 and 6.5 ppm (C_5H_5).

Attempts to insert NO into the titanium compound $(\pi\text{-}C_5H_5)_2Ti(Cl)CH_3$ were unsuccessful, even at elevated temperatures.

Tetracyclopentadienylzirconium also reacts with nitric oxide but as yet a product sufficiently pure for identification has not been obtained. Investigation of this and other reactions of NO with alkyl and aryl derivatives of titanium and zirconium is being continued.

EXPERIMENTAL

General

All manipulations of solid materials were carried out in a nitrogen-filled glove box and all reactions were performed in a stream of purified argon. Analyses for carbon and hydrogen were determined by the Australian Microanalytical Service, C.S.I.R.O. and University of Melbourne, on pelleted samples sealed in aluminium capsules. Metal was determined by ashing sulphated pellets of each compound. NMR spectra were measured on Varian T60 or HA 100 instruments. Nitric oxide (Matheson) was passed through a solid CO_2/ethanol trap before use. Sulphur dioxide (B.D.H.) was used without further purification.

Preparation of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$

To a stirred suspension of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (18.0 g, 61.6 mmole) in diethyl ether (100 ml) at room temperature was added methyllithium solution (145 ml of 0.85 *M* solution, 123.2 mmole, in diethyl ether) over 1 h. (The CH_3Li is best prepared from CH_3Cl rather than CH_3I, as the LiCl precipitates from the reaction mixture making subsequent purification easier.) After stirring overnight the mixture was filtered under argon and the filtrate was evaporated to dryness under reduced pressure. After two sublimations at 100–110°/10^{-4} mm, pure $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ was obtained as a colourless solid (11.4 g, 73 % yield) which softened at 150° and melted with decomposition at 190°. (Found: C, 57.7; H, 6.4; Zr, 36.8 %; mol. wt. in boiling benzene, 253. $C_{12}H_{16}Zr$ calcd.: C, 57.31; H, 6.42; Zr, 36.26 %; mol.wt., 251.5.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with* H_2

The dimethylzirconium compound was heated under reflux in light petroleum (b.p. 110–120°) while hydrogen was bubbled through the solution. The colour changed to crimson and after $\frac{1}{2}$ h the product was isolated by evaporation of solvent. (Found: C, 56.1; H, 6.1; Zr, 36.4; methane on hydrolysis, 1.0 mole/mole; mol.wt. in boiling benzene, 404. $C_{12}H_{16}Zr$ calcd.: C, 55.89; H, 5.54; Zr, 38.54%; methane on hydrolysis, 1.0 mole/mole; mol.wt., 473.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with* $PbCl_2$

$(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.26 g, 5.0 mmole) was dissolved in benzene (50 ml) and lead chloride (0.70 g, 2.5 mmole) was added with stirring. The colour of the solution darkened immediately due to the formation of metallic lead. After stirring for several hours the mixture was filtered and solvent removed under reduced pressure to give a cream-coloured solid identical in NMR and infrared spectra with $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$[11]. (Found: Zr, 33.3%. $C_{11}H_{13}ClZr$ calcd.: Zr, 33.57%.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with* SO_2

(*a*). *At low temperature.* Sulphur dioxide (approx. 15 ml) was condensed on to $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.5 g) contained in a Schlenk flask cooled in solid CO_2/ethanol. All of the solid dissolved to give a yellow solution. SO_2 was allowed to evaporate and the last traces were removed under reduced pressure giving bright yellow solid $\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)_2$, which was insoluble in all common organic solvents. (Found: C, 31.0; H, 3.6; S, 22.4; Zr, 20.0. $C_{12}H_{16}O_6S_3Zr$ calcd.: C, 32.48; H, 3.63; S, 21.68; Zr, 20.55%.)

The same product was obtained when the reaction and removal of SO_2 were carried out at −78°.

(*b*). *At room temperature.* SO_2 (10–15 ml) was condensed on to $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.5 g) contained in a tube which was then sealed with a Teflon-stemmed stopcock. After 1–2 h at room temperature an off-white precipitate formed. Excess SO_2 was syphoned off and the product, $(C_5H_5SO_2)_2ZrSO_3$, was dried under reduced pressure. (Found: C, 28.0; H, 3.4; S, 22.4; Zr, 21.6. $C_{10}H_{10}O_7S_3Zr$ calcd.: C, 27.96; H, 2.35; S, 22.39; Zr, 21.23%.)

Reaction of $(C_5H_5)_4Zr$ *with* SO_2

$(C_5H_5)_4Zr$ (0.7 g) was stirred in a sealed tube (as in preceding experiment) with liquid SO_2 (10 ml) at room temperature for 2 days. The clear supernatant liquid was removed and the light brown precipitate was dried under reduced pressure giving $C_5H_5Zr(O_2SC_5H_5)_3$. (Found: C, 43.0; H, 3.7; S, 16.9; Zr, 16.5. $C_{20}H_{20}O_6S_3Zr$ calcd.: C, 44.17; H, 3.71; S, 17.69; Zr, 16.77%.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with NO*

NO was bubbled through a solution of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.5 g) in light petroleum (40 ml, b.p. 30–40°) at room temperature. After 5–10 min a white precipitate appeared and passage of NO was continued for 30 min. The precipitate was collected by filtration, washed with petrol and dried under vacuum giving $(\pi\text{-}C_5H_5)_2Zr(CH_3)\text{-}N_2O_2CH_3$. (Found: C, 46.2; H, 5.3; N, 8.8; Zr, 29.5; mol.wt. in boiling THF, 329. $C_{12}H_{16}N_2O_2Zr$ calcd.: C, 46.26; H, 5.18; N, 8.99; Zr, 29.27%; mol.wt., 311.5.) Hydrolysis of this compound with boiling 12 *N* H_2SO_4 over 3 h gave a mixture of nitrous oxide, methane and ethane, identified from their infrared spectra. No other nitrogen-containing gases were present.

Preparation of $Cu(O_2N_2CH_3)_2$

Benzophenone oxime was methylated with dimethyl sulphate to give *N*-methylbenzophenone oxime[12]. Hydrolysis of the oxime with concd. HCl after the method of Kjellin[13] yielded *N*-methylhydroxylamine hydrochloride. Nitrosylation of the hydrochloride in the presence of copper sulphate[14] gave the purple copper complex, which was collected by filtration, washed with water and dried under vacuum over P_2O_5. (Found: C, 11.2; H, 2.8; N, 25.7. $C_2H_6CuN_4O_4$ calcd.: C, 11.25; H, 2.83; N, 26.23%.) This complex is paramagnetic with μ_{eff} varying from 1.89 B.M. at room temperature to 1.82 B.M. at 90K and having a θ value of -8°*. The g value of the powdered sample was found to be 2.284.

Reaction of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ *with NO*

Nitric oxide was bubbled through a solution of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ (2 g) in benzene (40 ml) at room temperature for 2 h. The solution was reduced to dryness giving $(\pi\text{-}C_5H_5)_2Ti(CH_3)N_2O_2CH_3$ as a pale brown powder. (Found: C, 53.6; H, 5.2; N, 9.2; Ti, 17.2. $C_{12}H_{16}N_2O_2Ti$ calcd.: C, 53.74; H, 6.01; N, 10.44; Ti, 17.86%.) The compound can be made also using light petroleum (b.p. 30–40°) as solvent, from which the product precipitates during the course of the reaction.

Reaction of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$[11,5] *with NO*

The reaction was carried out exactly as for the dimethyltitanium compound above giving $(\pi\text{-}C_5H_5)_2Zr(Cl)N_2O_2CH_3$ as a pale brown solid which could be crystallized from benzene/light petroleum. (Found: C, 39.5; H, 4.0; Cl, 10.6; N, 7.9; Zr, 27.4; mol.wt. in boiling THF, 350. $C_{11}H_{15}ClN_2O_2Zr$ calcd.: C, 39.81; H, 3.95; Cl, 10.68; N, 8.44; Zr, 27.48%; mol.wt., 331.9.)

REFERENCES

1 K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, 654 (1962) 8.
2 A. F. Reid, J. S. Shannon, J. M. Swan and P. C. Wailes, *Aust. J. Chem.*, 18 (1965) 173.
3 J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 91 (1969) 7301.
4 P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, 24 (1970) 413.
5 P. C. Wailes, H. Weigold and A. P. Bell, *J. Organometal. Chem.*, in press.
6 V. I. Kulishov, E. M. Brainina, N. G. Bokiy and Yu. T. Struchkov, *J. Chem. Soc. D*, (1970) 475.
7 E. Frankland, *Justus Liebigs Ann. Chem.*, 99 (1856) 342.
8 J. Sand and F. Singer, *Justus Liebigs Ann. Chem.*, 329 (1903) 190.
9 S. J. Brois, *Tetrahedron Lett.*, (1964) 345.
10 M. Inatome and L. P. Kuhn, *Boron–Nitrogen Chemistry*, A.C.S. Monograph No. 42, Amer. Chem. Soc., New York, 1964, p. 183.
11 J. R. Surtees, *Chem. Commun.*, (1965) 567.
12 L. Semper and L. Lichtenstadt, *Ber. Deut. Chem. Ges.*, 51 (1918) 928.
13 C. Kjellin, *Ber. Deut. Chem. Ges.*, 26 (1893) 2377.
14 B.A.S.F., *Brit. Pat.*, 815,537 (1959); *Chem. Abstr.*, 54 (1960) 3270*h*.

---

* Using the formula $\mu_{eff}=2.83\sqrt{\chi_A\cdot(T-\theta)}$