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# Studies on the reactions of transition metal hydrides with heterocumulenes

## VI *. Reaction of $Cp_2Zr(H)Cl$ with RNCS ($R = C_6H_5$, $2\text{-}C_{10}H_7$, $c\text{-}C_6H_{11}$ and $n\text{-}C_4H_9$)

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**Abstract**

The novel N,S-containing zirconacycle complexes $Cp_2ZrCl[SC(H)NR]$ (**1a**, $R = C_6H_5$; **1b**, $R = 2\text{-}C_{10}H_7$; **1c**, $R = c\text{-}C_6H_{11}$; **1d**, $R = n\text{-}C_4H_9$) were obtained by insertion reactions of $Cp_2Zr(H)Cl$ with RNCS. **1(a–d)** could react further with $Cp_2Zr(H)Cl$ to yield a sulphur-bridging complex $(Cp_2ZrCl)_2S$ (**2**) and a Schiff base $RN{=}CH_2$. The crystal structure of **1a** has been determined by X-ray analysis.

### 1. Introduction

The activation of some unreactive small molecules, such as $N_2$, CO and $CO_2$, by organo-transition-metal complexes has long been considered to be effective. Investigations into the reactions of heterocumulenes with organometallic complexes can contribute to a better understanding of the activation and the application of carbon dioxide for building up certain large organic molecules. Although the reactions of heterocumulenes with late-transition-metal complexes have been extensively investigated [1], little is known of the chemical behaviour of heterocumulenes towards early-transition-metal complexes [2]. We have already reported the reactions of $Cp_2Zr(H)Cl$ and $Cp_2ZrH_2$ with RNCO and $Cp_2MH_2$ (M = Zr, Hf) with $CS_2$ and RNCS [3]. In this paper the reactions of $Cp_2Zr(H)Cl$ with aryl and alkyl isothiocyanates, the X-ray structure of the novel complex $Cp_2ZrCl[SC(H)NC_6H_5]$ (**1a**), and a new type of desulphurization reaction of **1** with $Cp_2Zr(H)Cl$ are reported.

### 2. Results and discussion

A mixture of $Cp_2Zr(H)Cl$ and RNCS ($R = C_6H_5$, $2\text{-}C_{10}H_7$, $c\text{-}C_6H_{11}$ and $n\text{-}C_4H_9$) in a molar ratio of 1:1 reacted smoothly in THF at room temperature. The N,S-containing zirconacycle complexes $Cp_2ZrCl[SC(H)NR]$ (**1a–d**) were mainly formed by the insertion of RNCS into the Zr–H bond in $Cp_2Zr(H)Cl$. When the isolated products **1(a–d)** were treated with a further mole of $Cp_2Zr(H)Cl$, or $Cp_2Zr(H)Cl$ with RNCS in a molar ratio of 2:1 $Cp_2Zr(H)Cl$ : RNCS, a new type of desulphurization reaction occurred, and a sulphur-

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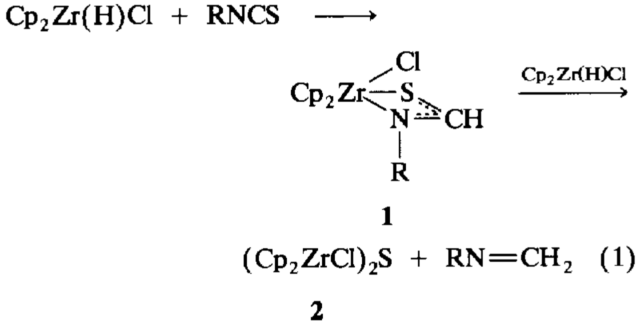
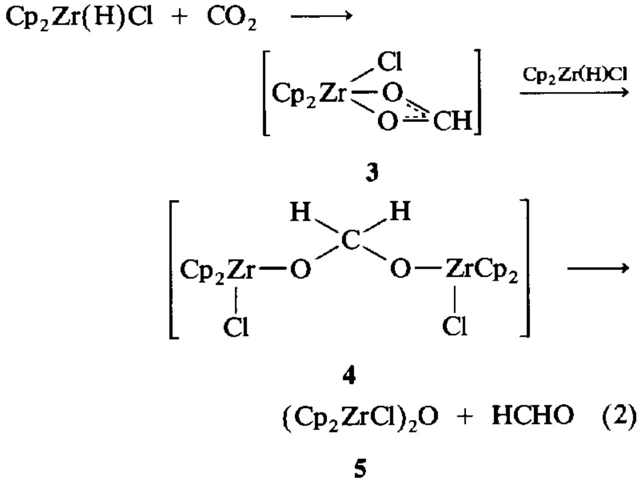
bridging homobinuclear complex $(Cp_2ZrCl)_2S$ (**2**) and a Schiff base $RN{=}CH_2$ were obtained (eqn. (1)).



$R = C_6H_5$ (**1a**), $2\text{-}C_{10}H_7$ (**1b**), $c\text{-}C_6H_{11}$ (**1c**),
$n\text{-}C_4H_9$ (**1d**)

Floriani *et al.* reported [4] that $CO_2$ can be reduced to formaldehyde by $Cp_2Zr(H)Cl$ under moderate conditions, and the mechanism of this reaction has been investigated in recent years [5]. It has been assumed that the reaction pathway relates to two intermediates **3** and **4** (eqn. (2)), but so far neither of them has been isolated.



The isolation and identification of **1** obtained from the reaction of $Cp_2Zr(H)Cl$ with RNCS gives strong support for the above hypothetical mechanism. It was found that when n-butyl isothiocyanate was used as an organic substrate, the yield of equimolecular adduct **1d** was much lower than that of **1a–c**. With $CS_2$ as a substrate the equimolecular adduct "$Cp_2ZrCl[SC(H)S]$" (**6**) could not be isolated even when the reaction was conducted between −30 and −40°C, and only complex **2** was obtained. The results suggest that in the above reaction systems, when the 4-membered zirconacycle complex $Cp_2ZrCl[YC(H)X]$ has a thioformamido ligand (X = NR, Y = S), it is more stable than the analogous complex with a dithioformate ligand (X = Y = S) or with a formate ligand (X = Y = O). A plausible explanation is that for complex **1** when the R group in the ligand $[SC(H)NR]^-$ is sufficiently bulky, further reaction could be prevented, but for **3** and **6** the outside oxygen or sulphur atom is very easily attacked by another molecule of $Cp_2Zr(H)Cl$ to give the oxygen- or sulphur-bridging complex.

TABLE 1. IR, $^1H$ and $^{13}C$ NMR spectral data for **1**

| Product | $\nu(C{=}N)$ (KBr, $cm^{-1}$) | $\delta_H(S\text{-}C(H)\text{-}NR)$ ($CDCl_3$, ppm) | $\delta_C(S\text{-}C(H)\text{-}NR)$ ($CHCl_3$, ppm) |
|---|---|---|---|
| **1a** | 1562 (s) | 9.10 (s) | 183.19 (d) |
| **1b** | 1567 (s) | 9.21 (s) | 179.33 (d) |
| **1c** | 1565 (s) | 8.89 (s) | 179.95 (d) |
| **1d** | 1535 (s) | 8.79 (s) | 183.19 (d) |

The characteristic data of the N,S-containing 4-membered metallacycle complexes in IR and $^1H$ NMR spectra have been reported [6]. The IR spectra of the chelate thioformamido complexes show a $\nu(C{=}N)$ band at *ca.* 1500–1570 $cm^{-1}$. The signal arising from the central proton of the chelate thioformamido ligand $[SC(H)NR]^-$ is located in the low field region (*ca.* $\delta$ 8.08–10.5 ppm) of $^1H$ NMR spectra. The characteristic data of **1** in the IR and $^1H$ NMR spectra (Table 1) coincide with those of the late-transition-metal complexes containing a chelate thioformamido ligand.

For products **1a**, **1c** and **1d**, only a single signal of the cyclopentadienyl ligands appeared in each $^1H$ NMR spectrum. However, in the $^1H$ NMR spectrum of **1b** there were two signals at 6.22 and 6.30 ppm. The intensities of the signals suggest that each represents one cyclopentadienyl ligand. The reason might be that the large bulk of the 2-naphthyl group in **1b** influences the protons of the two cyclopentadienyl ligands to different extents, and results in different chemical shifts in the $^1H$ NMR spectrum.

The crystal structure of **1a** has been determined (Fig. 1). The main bond distances and important bond angles are given in Tables 2 and 3, and the atomic coordinates are listed in Tables 4 and 5. The analogous crystal structures of $CpZrAr_2[SC(Ar)NCH_2C_6H_4]$ (Ar = $p\text{-}CH_3C_6H_4$) [7] and $Cp_2ZrMe[OC(Me)NPh]$ [8] have been reported in recent years. Both of the complexes are formed by the insertion of RNCX (X = O, S) into the Zr–C bond. To our knowledge, however, the X-ray structure of an N,S-containing zirconacycle complex such as **1** has not yet been reported.

The molecule of **1a** has no symmetry operation. The Cl atom is just within the least-squares plane with the ring formed by ZrNC(0)S atoms. The deviations of atoms from this least-squares plane are as follows: Cl, 0.0091; Zr, −0.0199; N, 0.0273; S, 0.0042; C(0), −0.0206 Å. However, the plane of the phenyl ring is not in the same least-squares plane with the

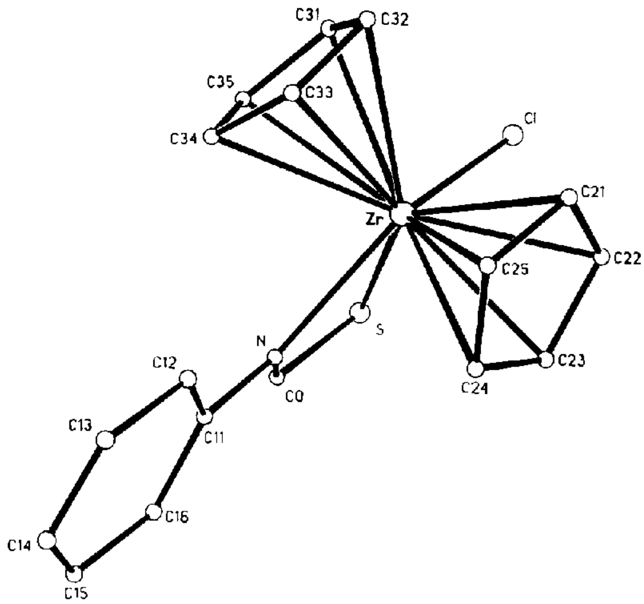


Fig. 1. Molecular structure of $Cp_2\overline{ZrCl[SC(H)N}C_6H_5]$ (**1a**) viewed from the plane defined by Zr, S, C(0) and N atoms. Hydrogen atoms are omitted.

ZrNC(0)SCl atoms, the dihedral angle between these two planes being 9.6°. The plane formed by two Cp(centroid) ligands and a zirconium atom is almost perpendicular to that of the ZrNC(0)SCl atoms (89.90°). The two Cp rings are eclipsed and the Cp(centroid)–Zr–Cp(centroid) angle is 130.0°. The angle between the normals and the least-squares plane of the cyclopentadienyl ligands is 127.1°.

The average length of the Zr–C(Cp) bonds (2.53 Å) in **1a** is greater (2.49 Å) than in $Cp_2ZrCl_2$, while the Zr–Cl bond (2.58 Å) in the former is longer (2.44 Å) than in the latter [9]. In the ZrNC(0)S ring, the bond lengths of Zr–N (2.41 Å) and Zr–S (2.66 Å) are, respectively, longer than the normal ones of Zr–N (2.1–2.2 Å) [10] and Zr–S (*ca.* 2.55 Å) [11] in zirconocene complexes with a coordination number of 4. The lengthening of all these bonds of Zr–X (X = N, S, Cl and Cav(Cp)) in **1a** may result from the sterical crowding of the ligands in **1a** with a coordination

TABLE 2. Bond lengths (Å) in **1a**

| Bond | Distance (Å) | Bond | Distance (Å) |
|---|---|---|---|
| Zr–S | 2.659(4) | C(11)–C(12) | 1.381(18) |
| Zr–N | 2.408(9) | C(12)–C(13) | 1.362(20) |
| Zr–Cl | 2.580(3) | C(13)–C(14) | 1.348(16) |
| S–C(0) | 1.700(15) | C(14)–C(15) | 1.420(23) |
| N–C(0) | 1.284(20) | C(15)–C(16) | 1.375(21) |
| N–C(11) | 1.438(7) | C(11)–C(16) | 1.381(18) |
| Zr–C(21) | 2.485(14) | C(21)–C(22) | 1.342(20) |
| Zr–C(22) | 2.509(14) | C(22)–C(23) | 1.392(19) |
| Zr–C(23) | 2.533(13) | C(23)–C(24) | 1.407(19) |
| Zr–C(24) | 2.540(13) | C(24)–C(25) | 1.403(19) |
| Zr–C(25) | 2.507(14) | C(21)–C(25) | 1.405(19) |
| Zr–C(31) | 2.533(15) | C(31)–C(32) | 1.409(32) |
| Zr–C(32) | 2.544(15) | C(32)–C(33) | 1.401(22) |
| Zr–C(33) | 2.478(15) | C(33)–C(34) | 1.432(21) |
| Zr–C(34) | 2.580(13) | C(34)–C(35) | 1.451(21) |
| Zr–C(35) | 2.582(15) | C(31)–C(35) | 1.431(23) |

TABLE 3. Selected bond angles (°) in **1a**

| Angle | Magnitude (°) | Angle | Magnitude (°) |
|---|---|---|---|
| S–Zr–Cl | 75.4(1) | S–Zr–C(21) | 137.2(3) |
| Cl–Zr–N | 135.9(3) | N–Zr–C(21) | 122.3(4) |
| S–Zr–N | 60.6(3) | S–Zr–C(22) | 106.3(4) |
| Zr–S–C(0) | 81.0(5) | N–Zr–C(22) | 116.9(4) |
| Zr–N–C(0) | 10.3(8) | S–Zr–C(23) | 86.7(3) |
| Zr–N–C(11) | 136.8(9) | N–Zr–C(23) | 85.3(4) |
| S–C(0)–N | 118.0(0) | S–Zr–C(24) | 102.7(3) |
| C(0)–N–C(11) | 122.9(11) | N–Zr–C(24) | 70.2(4) |
| Cl–Zr–C(21) | 86.6(3) | S–Zr–C(25) | 134.9(3) |
| Cl–Zr–C(22) | 72.5(4) | N–Zr–C(25) | 91.9(4) |
| Cl–Zr–C(23) | 91.1(3) | S–Zr–C(31) | 105.3(5) |
| Cl–Zr–C(24) | 122.0(3) | N–Zr–C(31) | 117.8(4) |
| Cl–Zr–C(25) | 120.8(3) | S–Zr–C(32) | 137.4(5) |
| Cl–Zr–C(31) | 73.5(5) | N–Zr–C(32) | 124.6(4) |
| Cl–Zr–C(32) | 88.4(4) | S–Zr–C(33) | 134.4(4) |
| Cl–Zr–C(33) | 120.1(4) | N–Zr–C(33) | 93.8(4) |
| Cl–Zr–C(34) | 123.4(3) | S–Zr–C(34) | 101.7(3) |
| Cl–Zr–C(35) | 92.2(4) | N–Zr–C(34) | 70.7(4) |
| N–C(11)–C(12) | 121.7(11) | S–Zr–C(35) | 85.1(3) |
| N–C(11)–C(16) | 120.9(13) | N–Zr–C(35) | 85.8(4) |

TABLE 4. Atomic coordinates ($\times 10^4$) in **1a** and isotropic thermal parameters

| Atom | *x* | *y* | *z* | *U* [a] |
|---|---|---|---|---|
| Zr | 217(1) | 387(1) | 7529(1) | 30(1) |
| S | −1400(3) | 1361(2) | 7321(2) | 55(2) |
| Cl | −1024(3) | −268(2) | 8598(2) | 47(1) |
| N | 221(9) | 1595(6) | 6521(6) | 38(4) |
| C(0) | −672(12) | 1862(9) | 6586(9) | 59(6) |
| C(11) | 912(11) | 1987(8) | 5940(7) | 42(5) |
| C(12) | 1820(12) | 1600(3) | 5786(3) | 45(6) |
| C(13) | 2475(12) | 1954(7) | 5227(7) | 47(6) |
| C(14) | 2274(12) | 2709(7) | 4793(8) | 52(7) |
| C(15) | 1358(14) | 3140(8) | 4971(9) | 69(7) |
| C(16) | 706(10) | 2735(3) | 5536(7) | 47(5) |
| C(21) | 1521(11) | 213(8) | 8619(8) | 46(5) |
| C(22) | 840(12) | 731(9) | 8989(8) | 46(6) |
| C(23) | 755(10) | 1558(8) | 8592(8) | 41(5) |
| C(24) | 1483(11) | 1549(8) | 7959(8) | 45(6) |
| C(25) | 1951(10) | 714(9) | 7964(9) | 51(5) |
| C(31) | −222(18) | −1163(9) | 6995(11) | 66(7) |
| C(32) | 781(16) | −1199(10) | 7212(9) | 59(7) |
| C(33) | 1182(11) | −622(10) | 6604(10) | 57(6) |
| C(34) | 478(11) | −252(9) | 6029(8) | 52(6) |
| C(35) | −471(11) | −579(10) | 6310(10) | 55(7) |

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

TABLE 5. Coordinates of H atoms in **1a** ($\times 10^3$) and isotropic thermal parameters

| Atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| H(12) | 1993 | 1067 | 6089 | 40 |
| H(13) | 3090 | 1654 | 5137 | 45 |
| H(14) | 2725 | 2941 | 4381 | 53 |
| H(15) | 1222 | 3700 | 4701 | 57 |
| H(16) | 95 | 3085 | 5644 | 54 |
| H(31) | −688(72) | −1435(59) | 7223(53) | 3(33) |
| H(22) | 540(71) | 503(61) | 9346(58) | 15(30) |
| H(0) | −993(87) | 2313(62) | 6153(61) | 99(37) |
| H(21) | 892 | −322 | 8712 | 37 |
| H(25) | 2438 | 633 | 7565 | 84 |
| H(33) | −775 | −471 | 6512 | 12 |
| H(24) | 1582 | 1938 | 7587 | 28 |

number of 5. The length of the C(0)–S bond (1.70 Å) in **1a** is between those of the single bond (C–S, 1.81 Å) and the double bond (C=S, 1.61 Å ) in organic compounds [12]. Compared with a normal C=N double bond (1.27 Å) [12], the C(0)–N bond (1.284 Å) is also somewhat longer. The length of the C(0)–X (X = S, N) bond shows that an unlocated $\pi$-bond is formed in the bidentate ligands $(S{=}C(H){=}NR]^-$ of **1a**. The band $\nu(C{=}N)$ at 1535–1567 $cm^{-1}$ in the IR spectra of **1(a–d)** has apparently shifted to a lower wavenumber than that for the normal band of $\nu$(C=N) (*ca.* 1630–1660 $cm^{-1}$). This corresponds to the results of X-ray studies.

The process of reaction of $Cp_2Zr(H)Cl$ with RNCS was detected by the ESR technique at different temperatures (−150 to 25°C). It was found that during the reaction process ESR signals appeared, the intensities of which first rose and then fell with reaction time. At the end of the reaction the signals disappeared. The signal for the reaction of $Cp_2Zr(H)Cl$ with $C_6H_5NCS$ centred on a $g$ value of 1.999, but no signal was found during the similar reaction process of $Cp_2Zr(H)Cl$ with RNCO by the ESR method at −150 to 35°C. Up to now there have been very few reports on the reactions of zirconium complexes with organic substrates via a radical mechanism without light or thermal excitation. According to the ESR spectra of the above reactions, a new mechanism in the field of zirconium chemistry has been proposed, namely that in the reaction of $Cp_2Zr(H)Cl$ with RNCS the Zr–H bond is cleaved homolytically and a transient $Zr^{III}$ species is formed. The cleavage might be induced by the pre-coordination of the lone pair electrons on the sulphur atom of RNCS to the zirconium centre.

## 3. Experimental details

All operations and reactions were carried out under an atmosphere of purified nitrogen. Solvents were distilled before use. IR spectra were recorded with a Perkin–Elmer 683 spectrometer. $^1H$ and $^{13}C$ NMR spectra were taken with an FT-Varian 80A apparatus. MS spectra were obtained on a Hitachi M80 mass spectrometer. The $Cp_2Zr(H)Cl$ complex and RNCS ($R = C_6H_5$, c-$C_6H_{11}$ and n-$C_4H_9$) were all obtained commercially. 2-$C_{10}H_7NCS$ was prepared as in the literature [13].

### 3.1. *Reaction of $Cp_2Zr(H)Cl$ with RNCS ($R = C_6H_5$, 2-$C_{10}H_7$, c-$C_6H_{11}$ and n-$C_4H_9$) in a molar ratio of 1:1*

Phenyl isothiocyanate (0.36 ml, 3.0 mmol) was dropped into a suspension of $Cp_2Zr(H)Cl$ (0.78 g, 3.0 mmol) in THF (20 ml) at 10°C. The solid dissolved within a few minutes to form a clear light yellow solution. After stirring for 20 min the solvent was removed *in vacuo*. The oily residue was extracted with toluene (20 ml) and the undissolved residue was filtered out. With the addition of n-hexane (2 ml), the resulting solution gave colourless crystals on standing overnight at 0°C. Recrystallization of the product from toluene/n-hexane afforded **1a** with a yield of 280 mg (68%).

**1a**: Anal. Found: C, 51.65; H, 4.06; N, 3.43%. Calc. for $C_{17}H_{16}NSClZr$: C, 51.95; H, 4.07; N, 3.56%. IR (KBr, $cm^{-1}$): $\nu$(C=N) 1562s. $^1H$ NMR ($CDCl_3$): $\delta$ 6.34 (10H, s, 2Cp), 7.14–7.37 (5H, m, $C_6H_5$), 9.10 (1H, s, $N{=}C(H){=}S$) ppm. $^{13}C$ NMR ($CHCl_3$): $\delta$ 113.09 (d, Cp), 121.66 (d, $C_6H_5$), 126.34 (d, $C_6H_5$), 129.50 (d, $C_6H_5$), 183.19 (d, $N{=}C(H){=}S$) ppm.

Similar reactions of $Cp_2Zr(H)Cl$ with 2-naphthyl isothiocyanate and cyclohexyl isothiocyanate in THF gave colourless needle crystals of **1b** and **1c** in 60–70% yield, respectively.

**1b**: Anal. Found: C, 56.12; H, 4.23; N, 3.41%. Calc. for $C_{21}H_{18}NSClZr$: C, 56.92; H, 4.07; N, 3.17%. IR (KBr, $cm^{-1}$): $\nu$(C=N) 1567s. $^1H$ NMR ($CDCl_3$): $\delta$ 6.22 (5H, s, Cp), 6.30 (5H, s, Cp), 7.24–7.83 (7H, m, $C_{10}H_7$), 9.21 (1H, s, $N{=}C(H){=}S$) ppm. $^{13}C$ NMR ($CHCl_3$): $\delta$ 113.33 (d, $C_{10}H_7$), 114.01 (d, Cp), 114.44 (d, $C_{10}H_7$), 116.94 (d, $C_{10}H_7$), 125.96 (d, $C_{10}H_7$), 127.48 (d, $C_{10}H_7$), 127.83 (d, $C_{10}H_7$), 130.17 (d, $C_{10}H_7$), 179.33 (d, $N{=}C(H){=}S$) ppm.

**1c**: Anal. Found: C, 51.16; H, 5.60; N, 3.59%. Calc. for $C_{17}H_{22}NSClZr$: C, 51.15; H, 5.52; N, 3.51%. IR (KBr, $cm^{-1}$): $\nu$(C=N) 1565s. $^1H$ NMR ($CDCl_3$): $\delta$ 1.10–2.10 (10H, m, $5CH_2$), 3.15 (1H, m, N–CH), 6.20 (10H, s, 2Cp), 8.88 (1H, s, $N{=}C(H){=}S$) ppm. $^{13}C$ NMR ($CHCl_3$): $\delta$ 25.42 (t, $CH_2$), 25.78 (t, $CH_2$), 34.07 (t, $CH_2$), 62.00 (d, CH), 112.66 (d, Cp), 179.95 (d, $N{=}C(H){=}S$) ppm.

Under the same conditions, similar adducts could not be isolated from the reactions of $Cp_2Zr(H)Cl$ with n-butyl isothiocyanate and carbon disulphide. Only

$(Cp_2ZrCl)_2S$ (**2**) was obtained as light yellow crystals. The reaction of $Cp_2Zr(H)Cl$ with an excess of n-$C_4H_9$ NCS was carried out in toluene at $-10$°C. The equimolecular adduct **1d** was obtained in 35% yield. But with $CS_2$ as a substrate the adduct could not be isolated even when the reaction was carried out at $-40$°C.

**1d**: Anal. Found: C, 48.32; H, 5.43; N, 3.26%. Calc. for $C_{15}H_{20}NSClZr$: C, 48.33; H, 5.42; N, 3.75%. IR (KBr, $cm^{-1}$): $\nu$(C=N) 1535s. $^1$H NMR ($CDCl_3$): $\delta$ 0.95 (3H, t, $CH_3$), 1.20–1.80 (4H, m, $2CH_2$), 3.38 (2H, t, N–$CH_2$), 6.20 (10H, s, 2Cp), 8.79 (1H, s, N$=$C($H$)$=$S) ppm. $^{13}$C NMR ($CHCl_3$): $\delta$ 13.64 (q, $CH_3$), 20.48 (t, $CH_2$), 33.44 (t, $CH_2$), 56.71 (t, N–$CH_2$), 113.08 (d, Cp), 183.19 (d, N$=$$C$(H)$=$S) ppm.

### *3.2. Reaction of* **1(a–d)** *and* $Cp_2Zr(H)Cl$ *in a molar ratio of 1:1*

A mixture of **1** (1.0 mmol) and $Cp_2Zr(H)Cl$ (1.0 mmol) in THF (10 ml) was stirred for 30 min. After removal of the solvent *in vacuo*, the residue was extracted with toluene (10 ml). Light yellow crystals of $(Cp_2ZrCl)_2S$ (**2**) were obtained from the toluene filtrate in 72–80% yield. A Schiff base $RN{=}CH_2$ (yield, 60–75%) and a very small amount of $RN(H)CH_3$ were identified in the solution by GC-MS spectroscopy.

**2**: Anal. Found: C, 44.46; H, 3.88%. Calc. for $C_{20}H_{20}SCl_2Zr$: C, 44.01; H, 3.69%. IR (KBr, $cm^{-1}$): $\nu$(ZrSZr) 736m. $^1$H NMR ($CDCl_3$): $\delta$ 6.26 (s, Cp) ppm. $^{13}$C NMR ($CHCl_3$): $\delta$ 113.20 (d, Cp) ppm.

### *3.3. Reaction of* $Cp_2Zr(H)Cl$ *with RNCS* $(R = C_6H_5$, $2\text{-}C_{10}H_7$, $c\text{-}C_6H_{11}$ *and* $n\text{-}C_4H_9)$ *in a molar ratio of 2:1* $(Cp_2Zr(H)Cl:RNCS)$

RNCS (1.0 mmol) was dropped into the suspension of $Cp_2Zr(H)Cl$ (2.0 mmol) in THF under the same conditions as above. The mixture was stirred for 1 h at room temperature. From the resulting green–yellow solution **2** was isolated in 75–85% yield. The corresponding Schiff base $RN{=}CH_2$ (yield: 62–80%) in solution was also identified from GC–M S spectra. When **2** was hydrolysed, $H_2S$ escaped and $(Cp_2ZrCl)_2)O$ was formed.

### *3.4. X-ray study of* **1a**

Crystal size: 0.24 × 0.12 × 0.40 mm. Diffracted intensities were collected on a Nicolet XRD four circle diffractometer at room temperature, a graphite monochromator, Mo K$\alpha$ radiation, a scan range $3° \le 2\theta \le 48°$ and a scan mode $\omega$–$2\theta$ at variable speeds. The crystal of **1a** is orthorhombic, space group *Pcab*, $a = 13.611$; $b = 14.956$; $c = 15.787$ Å; $V = 3213.7$ Å$^3$; $Z = 8$; $D_c = 1.62$ $gcm^{-3}$. Of the 2502 reflections measured, 2233 reflections with $I \ge 3\sigma(I)$ were used. The structure was solved by heavy-atom methods. Hydrogen atoms were included in the refinement with fixed positional and isotropic thermal parameters. Least-squares refinement converged to a final value of $R = 0.038$ $(R = \Sigma(|F_o - F_c|)/F_o)$.

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