Inorganica Chimica Acta, 161 (1989) 11–12

The Reactions of $(\eta\text{-}C_5H_5)_2Ti(SR)_2$ with Benzyl Bromide and Bromine to Give Sulfides and Disulfides, Respectively

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(Received January 30, 1989)

In the course of studies [1] directed towards the synthesis of catenated polysulfur ligands of the type RSS^-, characterization of the complexes formed via chemical derivation became necessary. For complexes of the type $Cp_2Ti(SR)(S_xR)$, where $x \neq 1$, it is difficult [2] to determine x by spectroscopic techniques and elemental analysis can sometimes be misleading [3]. Therefore the reactivities of the parent complexes $Cp_2Ti(SR)_2$ with benzyl bromide and with bromine have been investigated. In addition to being useful for the above purposes, such studies are of interest with respect to the development of new sulfur-transfer reagents – an area of some activity. Diatomic sulfur has been generated from titanium and zirconium pentasulfides [4]. The complex $(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2]$ reacts with alkyl halides to give a mixture of sulfides and disulfides [5]. The compound bis(tributyltin)sulfide is a versatile sulfur-transfer reagent [6]. Finally, bisthiolato platinum complexes react with alkyl halides to give sulfides [7]. We find that complexes of the type $Cp_2Ti(SR)_2$ can be used to prepare sulfides or disulfides selectively.

The bisthiolato titanium complexes were prepared from Cp_2TiCl_2, which is readily available, via well-known procedures [8]. Subsequent reactions were conducted under nitrogen with isolation of the products in air. The products were characterized by comparison of ^1H NMR spectra, GC retention times and, where necessary, GC–mass spectra to those of authentic samples. The reactions are summarized in Table 1.

$$Cp_2Ti(SR)_2 + Br_2 \longrightarrow Cp_2TiBr_2 + RSSR \qquad (1)$$

In a typical reaction with bromine (eqn. (1)), $Cp_2Ti(SCH_2Ph)_2$ (1.0 g, 2.3 mmol), suspended in hexanes (30 ml), was treated with Br_2 (123 μl, 2.4 mmol) and the reaction stirred for 15 min. The purple slurry immediately became brown in colour. The brown precipitate was collected on a filter in air and dried to give mostly Cp_2TiBr_2 in high yield. The yellow filtrate contained $(PhCH_2)_2S_2$ which was isolated in moderate yield upon removal of the hexanes. GC analysis of the filtrates for $R = CH_2Ph$ and Ph revealed a large peak for the appropriate disulfides, with minute amounts of RSR, RBr and RSH. The NMR spectra of all the products gave peaks for only the pure disulfides. The non-optimized yields were generally moderate and, in the case of $R = CHMe$ and $(CH_2)_3Me$, only fair due to evaporation of the volatile disulfides upon evaporation of the hexanes. The reaction proceeded somewhat more slowly for R = Ph and $CHMe_2$, as indicated by the detection of $Cp_2Ti(SR)_2$ and $Cp_2Ti(SR)Br$ in the NMR spectra of the Cp_2TiBr product. The reaction proceeds to completion upon longer stirring. The reaction with $R = (CH_2)_3Me$ was stirred overnight to give Cp_2TiBr_2 quantitatively.

$$Cp_2Ti(SR)_2 + 2PhCH_2Br \longrightarrow Cp_2TiBr_2 + 2PhCH_2SR \qquad (2)$$

In a typical reaction with benzyl bromide (eqn. 2)), $Cp_2Ti(SCH_2Ph)_2$ (1.0 g, 2.4 mmol) in toluene (80 ml) was treated with $PhCH_2Br$ (0.59 ml, 5.0 mmol) and refluxed with stirring under nitrogen for 4.5 h. The purple solution became red in colour. Upon cooling, the solution was evaporated to dryness on a rotatory evaporator. The residue was extracted

TABLE 1. Reactions of $Cp_2Ti(SR)_2$ with Br_2 and $PhCH_2Br$

R	Reagent	Solvent	Time (h)	Product (yield %)
CH_2Ph	Br_2	hexanes	0.25	$(PhCH_2)_2S_2$ (52)
CH_2Ph	$2PhCH_2S$ phthalimide	CH_2Cl_2	14	$(PhCH_2)_2S_2$ (46)
Ph	Br_2	hexanes	0.25	Ph_2S_2 (51)
$CHMe_2$	Br_2	hexanes	0.25	$(Me_2CH)_2S_2$ (31)
$(CH_2)_3Me$	Br_2	hexanes	0.25	$(Me(CH_2)_3)_2S_2$ (56)
CH_2Ph	$2PhCH_2Br$	toluene	4.5	$(PhCH_2)_2S$ (58)
Ph	$2PhCH_2Br$	toluene	4.5	$PhCH_2SPh$ (79)
$CHMe_2$	$2PhCH_2Br$	toluene	4.5	$PhCH_2SCHMe_2$ (52)
$(CH_2)_3Me$	$2PhCH_2Br$	toluene	4.5	$PhCH_2S(CH_2)_3Me$ [a]

[a] Sample lost during work-up.

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0020-1693/89/$3.50

with 30 ml dry hexanes and filtered. The brown insoluble material on the fritte was Cp_2TiBr_2. The filtrate was evaporated to give an oil which crystallized to give $(PhCH_2)_2S$ (0.59 g, 58%). The isolated sulfides were spectroscopically pure. Neither phenyl bromide nor n-butyl bromide reacted with $Cp_2Ti(SCH_2Ph)_2$ under these reaction conditions. Alkyl iodides are expected to be more reactive than the bromides [7].

The complex $Cp_2Ti(SCH_2Ph)_2$ reacts with *N*-(benzylthio)phthalimide [3] in CH_2Cl_2 at ambient temperature to give $(PhCH_2)_2S_2$ after work-up. The titanium-containing products decomposed upon work-up to give phthalimide and intractable polymers. Presumably, the phthalimido group initially transferred to the metal atom, as has been observed previously [9, 10]. Attempts to prepare $Cp_2Ti(phthalimido)_2$ from Cp_2TiCl_2 and potassium phthalimide gave phthalimide and insoluble polymers.

The complexes $Cp_2Ti(SR)_2$ are versatile sulfur-transfer reagents, being selective precursors of sulfides and disulfides upon treatment with phenylmethyl bromide and bromine, respectively.

Acknowledgements

Support for this research from the Natural Sciences and Engineering Council of Canada and the Quebec Department of Education is gratefully acknowledged. S. M. thanks the Canadian Commonwealth Scholarship and Fellowship Plan for a predoctoral scholarship.

References

1 A. Shaver and J. Hartgerink, *Can. J. Chem., 65* (1987) 1190.

2 A. Shaver, J. M. McCall, P. H. Bird and N. Ansari, *Organometallics, 2* (1983) 1894.

3 A. Shaver and J. M McCall, *Organometallics, 3* (1984) 1823.

4 D. N. Harpp and J. G. MacDonald, *J. Org. Chem., 53* (1988) 3812.

5 D. N. Harpp and J. G. MacDonald, *Tetrahedron Lett., 25,* (1984) 703.

6 D. N. Harpp and M. Gingras, *J. Am. Chem. Soc., 110,* (1988) 7737.

7 P. C. B. Page, S. S. Klair, M. P. Brown, M. M. Harding, C. S. Smith, S. J. Maginn and S. Mulley, *Tetrahedron Lett., 29* (1988) 4477.

8 (a) R. S. P. Coutts, J. R. Surtees, J. M. Swan and P. C. Wailes, *Aust. J. Chem., 19* (1966) 1377; (b) S. A. Giddings, *Inorg. Chem., 6* (1967) 849; (c) H. Köpf and M. Schmidt, *Z. Anorg. Allg. Chem., 340* (1965) 139.

9 A. Shaver and R. D. Lai, *Inorg. Chem., 27* (1988) 4664.

10 P. M. Treichel, P. C. Nakagaki and K. J. Haller, *J. Organometal. Chem., 327* (1987) 327.