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SELENIUM AND TELLURIUM DERIVATIVES OF DI-π-CYCLOPENTADIENYL-TITANIUM(IV) AND -ZIRCONIUM(IV)

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Summary

The complexes $(\pi\text{-}C_5H_5)_2TiL_2$ (L = $SeCH_3$, $SeCH_2C_6H_5$, SeC_6H_5, $SeC_6H_4CH_3\text{-}p$, TeC_6H_5, and $TeC_6H_4CH_3\text{-}p$) and $(\pi\text{-}C_5H_5)_2ZrL_2$ (L = SeC_6H_5, $SeC_6H_4CH_3\text{-}p$, and TeC_6H_5) have been prepared. Some properties as well as the IR and NMR spectra of these complexes are described.

Introduction

In previous work, we described the synthesis of, and the donor properties of the Group VI atom in, $\pi\text{-}C_5H_5\cdot Ni\cdot P(n\text{-}C_4H_9)_3\cdot EC_6H_4X$ (E = S, Se Te) [1,2]. The unambiguous conclusion about the Ni—E bond character in these complexes suggested that further investigation of the donor properties of the Group VI atom might be necessary. Emphasis at this stage may be put on the preparation and characterization of complexes with selenium and tellurium ligands since these have been rather neglected in studies of transition metal complexes, although the donor properties of sulfur-containing ligands have been much investigated [3].

Titanium(IV) and zirconium(IV), which have no *d* electrons, should not be able to enter into d_π—d_π back-bonding with the Group VI donor atom and the behavior of $(\pi\text{-}C_5H_5)_2Ti(IV)$ and $(\pi\text{-}C_5H_5)_2Zr(IV)$ groups would give valuable information about the donor properties of Group VI atom. We now report the new synthesis and some properties of the selenium and tellurium derivatives of di-π-cyclopentadienyl-titanium(IV) and -zirconium(IV).

Results and discussion

It is known that $(\pi\text{-}C_5H_5)_2Ti(SeR)_2$ can be obtained from the reaction of $(\pi\text{-}C_5H_5)_2TiCl_2$ (I) with HSeR (R = C_2H_5, C_6H_5) in the presence of NEt_3 [4], or from the reaction of $(\pi\text{-}C_5H_5)_2Ti$ with RSeSeR (R = C_6H_5) [5]. We have found that the reaction of (I) with RSeMgBr in THF gives dark green crystals of $(\pi\text{-}C_5H_5)_2Ti(SeR)_2$ (II) in good yields, according to eqn. (1).

$$\underset{(I)}{(\pi\text{-}C_5H_5)_2TiCl_2} + 2RSeMgBr \rightarrow \underset{(II)}{(\pi\text{-}C_5H_5)_2Ti(SeR)_2} + 2MgBrCl \qquad (1)$$

$(R = CH_3, CH_2C_6H_5, C_6H_5, C_6H_4CH_3\text{-}p)$

Similarly, the red-brown tellurium derivatives $(\pi\text{-}C_5H_5)_2Ti(TeR)_2$ (III) ($R = C_6H_5$, $C_6H_4CH_3\text{-}p$) are obtained in good yields from the reaction of (I) with RTeMgBr. The physical properties of complexes (II) and (III) are shown in Table 1.

The new tellurium complexes reported are the first examples of compounds in which this chalcogen is a donor atom for cyclopentadienyltitanium compounds.

It is interesting to find out whether the above procedure is applicable to the synthesis of selenium and tellurium derivatives of di-π-cyclopentadienylzirconium. However, our attempts to prepare them were unsuccessful; a red powder, insoluble in all solvents, was obtained with both reagents of the type REMgBr (E = Se, Te). The IR spectra are similar to that of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (IV) with no band characteristic of R. Unfortunately, efforts to characterize this red product failed because of its insolubility in all solvents. However, (IV) reacted with RELi (E = Se, Te) to give yellow solids or red crystals in good yields, according to eqn. (2).

$$\underset{(IV)}{(\pi\text{-}C_5H_5)_2ZrCl_2} + 2RELi \rightarrow (\pi\text{-}C_5H_5)_2Zr(ER)_2 + 2LiCl \qquad (2)$$

$[(V)\ E = Se,\ R = C_6H_5, C_6H_4CH_3\text{-}p;$

$(VI)\ E = Te,\ R = C_6H_5]$

The physical properties of complexes (V) and (VI) are shown in Table 2.

The selenium and tellurium complexes of zirconium isolated herein are the first examples of compounds in which there exist zirconium—selenium and zirconium—tellurium bonds.

The complexes (II), (III), (V) and (VI) are soluble in organic solvents such as benzene, toluene, THF and carbon disulfide, but insoluble in methanol, ethanol, n-hexane and petroleum ether. The complexes (II) and (V) are stable

TABLE 1

SOME PROPERTIES OF $(\pi\text{-}C_5H_5)_2TiL_2$

L	Color.	M.p. (°C)	^1H NMR (τ) (ppm)[b]		
			C_5H_5	C_6H_4	$CH_3(CH_2)$
$SeCH_3$	Green	210 - 211	4.03(s, 10)		7.36(s, 6)
$SeCH_2C_6H_5$	Green	169 - 171	3.96(s, 10)	2.75 - 3.10(m, 10)	5.61(s, 4)
SeC_6H_5	Green	153 - 155[a]	4.14(s, 10)	2.42 - 2.62 and 2.70 - 2.94(m, 10)	
$SeC_6H_4CH_3\text{-}p$	Green	183 - 185	4.18(s, 10)	2.40(d, J 8.0Hz, 4), 3.03(d, 4)	7.69(s, 6)
TeC_6H_5	Brown	123 - 126	4.15(s, 10)	2.26 - 2.50 and 2.72 - 2.98(m, 10)	
$TeC_6H_4CH_3\text{-}p$	Brown	165 - 167	4.18(s, 10)	2.48(d, J 8.0Hz, 4), 2.98(d, 4)	7.59(s, 6)

[a] Ref. 4 gives 120 - 122°. [b] Measured in CS_2 using TMS as internal reference. Multiplicity of peaks: s, singlet: d, doublet: m, multiplet.

TABLE 2

SOME PROPERTIES OF $(\pi\text{-}C_5H_5)_2ZrL_2$

L	Color.	M.p. (°C)	${}^1H$ NMR (τ) (ppm)^a		
			C_5H_5	C_6H_4	CH_3
SeC_6H_5	Yellow	134 - 136	4.17(s, 10)	2.40 - 2.54 and 2.78 - 2.93(m, 10)	
$SeC_6H_4CH_3$-*p*	Yellow	148 - 150	4.19(s, 10)	2.63(d, *J* 8.0Hz, 4), 3.06(d, 4)	7.72(s, 6)
TeC_6H_5	Red	118 - 120	4.18(s, 10)	2.30 - 2.38 and 2.70 - 2.92(m, 10)	

^{a}Measured in CS_2 using TMS as internal reference: Multiplicity of peaks: s, singlet: d, doublet: m, multiplet.

in air for long periods, although solutions in benzene decompose in air after about one day for (II), or about three days for (V). The complexes (III) and (VI) are unstable in air, and solutions in benzene decompose in air after only one minute for (III), or about two hours for (VI). Thus it seems that $(\pi\text{-}C_5H_5)_2Ti$ and $(\pi\text{-}C_5H_5)_2Zr$ groups form more stable compounds with selenium- than with tellurium-containing ligands. This result corresponds with that for $\pi\text{-}C_5H_5\cdot Ni\cdot P(n\text{-}C_4H_9)_3\cdot EC_6H_4X$ (E = Se, Te) [2], but is in marked contrast with that for $\pi\text{-}C_5H_5\cdot Fe\cdot(CO)_2\cdot EC_6H_5$ [6] and $\pi\text{-}C_5H_5\cdot Mo\cdot(CO)_3\cdot EC_6H_5$ [7]. On the other hand, the $(\pi\text{-}C_5H_5)_2Zr$ moiety seems to form more stable compounds with RE (E = Se, Te) groups than the $(\pi\text{-}C_5H_5)_2Ti$ moiety does, indicating that the $(\pi\text{-}C_5H_5)_2Zr$ group is a softer acid than the $(\pi\text{-}C_5H_5)_2Ti$ group.

The IR spectra of (II), (III), (V) and (VI) showed the normal vibrations of the $\pi\text{-}C_5H_5$ group and substituents R at their usual wave numbers, with an especially strong band for the C—H out-of-plane deformations of the $\pi\text{-}C_5H_5$ group in the range of 800 - 810 cm^{-1}.

The NMR spectra of (II), (III), (V) and (VI) are shown in Tables 1 and 2. Resonances due to the phenyl and methyl protons occurred at the expected positions. The π-cyclopentadienyl protons gave peaks at about τ 4.15 ppm with the exception of those of the L = $SeCH_3$ or $SeCH_2C_6H_5$ groups in the complexes (II), which absorbed at τ 4.03 or 3.96 ppm. It is known that the ${}^1H$ chemical shift of the $\pi\text{-}C_5H_5$ group in π-cyclopentadienylmetal compounds is closely related to the charge density on the transition metal [8]. In view of this, it is suggested that the $SeCH_3$ and $SeCH_2C_6H_5$ groups withdraw more electrons from titanium than other RE (E = Se, Te) groups in the complexes (II) and (III). On the basis of Giddings' hypothesis [9], this result suggests that the $SeCH_3$ and $SeCH_2C_6H_5$ groups are more able to enter into titanium—selenium π-bond formation than are the SeC_6H_4X and TeC_6H_4X groups, for which titanium—selenium or titanium—tellurium π-bond formation would be hindered by the bulky phenyl groups. Little useful information about the comparative donor properties of selenium and tellurium could be obtained from the data of ${}^1H$ chemical shifts for the $\pi\text{-}C_5H_5$ group, because the difference of the shifts between L = SeC_6H_5 (or $SeC_6H_4CH_3$-*p*) and L = TeC_6H_5 (or $TeC_6H_4CH_3$-*p*) in the complexes (II) and (III), or between L = SeC_6H_5 and L = TeC_6H_5 in the complexes (V) and (VI) is too small (Tables 1 and 2). However, the great difference in stability between the selenium and tellurium derivatives of di-π-cyclopentadienyltitanium(IV) and -zirconium(IV) appears to suggest that a difference in the donor ability of selenium and tellurium does exist.

Experimental

All experiments were carried out in an atmosphere of dry nitrogen. Solvents were purified by conventional methods: before use they were freed from oxygen by degassing and saturating with nitrogen. The starting materials were prepared according to published procedures [10]. IR spectra were measured with a Hitachi EPI—S2 spectrometer. NMR spectra were measured by means of a JEOL-JNM-4H-100NMR spectrometer.

Preparation of $(\pi\text{-}C_5H_5)_2Ti(ER)_2$ *(E = Se, Te)*

To a Grignard reagent prepared from methyl bromide (1.14 g), magnesium (0.28 g) and THF (30 ml) was added selenium (0.79 g) under nitrogen while stirring. After five hours of stirring, the yellow solution formed was added with stirring to a suspension of $(\pi\text{-}C_5H_5)_2TiCl_2$ (1.25 g) in THF (30 ml). A deep green solution resulted. After stirring for two hours, the solvent was removed under reduced pressure to leave a green residue. Recrystallization from benzene—methanol gave 1.45 g (yield 79%) of dark green crystals. A similar procedure was used for the preparation of the other selenium and tellurium derivatives. Yield, analysis and molecular weight data are collected in Table 3.

Preparation of $(\pi\text{-}C_5H_5)_2Zr(ER)_2$ *(E = Se, Te)*

To a phenyllithum reagent prepared from bromobenzene (1.88 g), lithum (0.20 g) and ether (40 ml) was added selenium (0.79 g) under nitrogen while stirring. After six hours of stirring, the resulting white solution was added to a suspended solution of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (1.46 g) in benzene (30 ml) with stirring at 0°. A yellow solution formed. After stirring for two hours, the solvent was removed under reduced pressure to leave a yellow residue. After the residue was reduced at 100°/1.0 mm, the for five hours cooling gave 2.13 g (yield 80%) of yellow solid. A similar procedure was used for the preparation of the

TABLE 3

Compound	Yield (%)	Analysis found (calcd.)(%)		Mol. wt. found[a] (calcd.)
		C	H	
$(\pi\text{-}C_5H_5)_2Ti(SeCH_3)_2$	79	39.56 (39.34)	4.41 (4.37)	337 (366)
$(\pi\text{-}C_5H_5)_2Ti(SeCH_2C_6H_5)_2$	80	55.59 (55.37)	4.63 (4.63)	
$(\pi\text{-}C_5H_5)_2Ti(SeC_6H_5)_2$	83	53.65 (53.88)	4.03 (4.08)	465 (490)
$(\pi\text{-}C_5H_5)_2Ti(SeC_6H_4CH_3\text{-}p)_2$	81	55.59 (55.37)	4.52 (4.63)	
$(\pi\text{-}C_5H_5)_2Ti(TeC_6H_5)_2$	80	44.63 (44.88)	3.19 (3.40)	572 (588)
$(\pi\text{-}C_5H_5)_2Ti(TeC_6H_4CH_3\text{-}p)_2$	78	46.10 (45.83)	3.88 (3.90)	
$(\pi\text{-}C_5H_5)_2Zr(SeC_6H_5)_2$	80	48.23 (49.53)	3.91 (3.95)	512 (533)
$(\pi\text{-}C_5H_5)_2Zr(SeC_6H_4CH_3\text{-}p)_2$	82	51.47 (51.34)	4.38 (4.25)	
$(\pi\text{-}C_5H_5)_2Zr(TeC_6H_5)_2$	77	41.84 (41.88)	3.25 (3.17)	617 (630)

[a] Cryosopic in C_6H_6.

p-tolyl selenide derivative, and phenyl telluride derivative, which was recrystallized from benzene—n-hexane. Yield, analysis and molecular weight data are collected in Table 3.

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