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SELENIUM AND TELLURIUM DERIVATIVES OF DI-π-CYCLOPENTADIENYL-VANADIUM(IV), -NIOBIUM(IV), -MOLYBDENUM(IV) AND -TUNGSTEN(IV)

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Summary

The preparation and some properties of (π-C_5H_5)$_2$VL_2 (L = SeC_6H_5 and $SeC_6H_4CH_3$-*o*), (π-C_5H_5)$_2$NbL_2 (L = SeC_6H_5 and TeC_6H_5), (π-C_5H_5)$_2$MoL_2 (L = $SeCH_3$, SeC_6H_5, TeC_6H_5 and $TeC_6H_4CH_3$-*p*) and (π-C_5H_5)$_2$WL_2 (L = $SeCH_3$, SeC_6H_5, TeC_6H_5 and $TeC_6H_4CH_3$-*p*) are described.

Introduction

We previously reported concerning the preparation of, and the donor properties of selenium and tellurium in (π-C_5H_5)$_2$M(ER)$_2$ (M = Ti or Zr, E = Se or Te and R = alkyl or aryl) [1]. The equivocal conclusion about the donor properties of selenium and tellurium in these complexes suggested that further investigation of the donor properties of selenium and tellurium might be necessary. Although the donor properties of sulfur in (π-C_5H_5)$_2$M(SR)$_2$ (M = V [2], Nb [3], Mo and W [4]) have been investigated, the properties of selenium and tellurium derivatives of those type complexes have not been studied.

The chemical behavior of (π-C_5H_5)$_2$M (M = V, Nb, Mo or W) moieties might give valuable information about the donor properties of selenium and tellurium by comparison with the behavior of (π-C_5H_5)$_2$M (M = Ti or Zr) groups. We now describe the synthesis and some properties of the selenium and tellurium derivatives of di-π-cyclopentadienyl-vanadium(IV), -niobium(IV), -molybdenum(IV) and -tungsten(IV).

Results and discussion

Treatment of the complex (π-C_5H_5)$_2$MCl_2 (M = V or Nb) with arylselenolithium, RSeLi, afforded the complexes (π-C_5H_5)$_2$M(SeR)$_2$ in good yields, according to eqn. 1.

$$(\pi\text{-}C_5H_5)_2MCl_2 + 2RSeLi \rightarrow (\pi\text{-}C_5H_5)_2M(SeR)_2 + 2LiCl \qquad (1)$$

$$\text{(I)}\quad M = V,\ R = C_6H_5,\ C_6H_4CH_3\text{-}o$$

$$\text{(II)}\quad M = Nb,\ R = C_6H_5$$

Similarly, the green tellurium derivative $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$ (III) was obtained in good yield from the reaction of $(\pi\text{-}C_5H_5)_2NbCl_2$ with C_6H_5TeLi. The properties of complexes I, II and III are shown in Table 1. The selenium and tellurium derivatives of niobium isolated are the first such derivatives of a cyclopentadienylniobium compound.

The complexes $(\pi\text{-}C_5H_5)_2MCl_2$ (M = Mo or W) reacted with REMgBr (E = Se or Te) to give the compounds $(\pi\text{-}C_5H_5)_2M(ER)_2$ in good yields, according to eqn. 2. The data for complexes IV, V, VI and VII are listed in Table 2.

$$(\pi\text{-}C_5H_5)_2MCl_2 + 2REMgBr \rightarrow (\pi\text{-}C_5H_5)_2M(ER)_2 + 2MgBrCl \qquad (2)$$

$$\text{(IV)}\quad M = Mo,\quad E = Se,\quad R = CH_3,\ C_6H_5$$

$$\text{(V)}\quad M = W,\quad E = Se,\quad R = CH_3,\ C_6H_5$$

$$\text{(VI)}\quad M = Mo,\quad E = Te,\quad R = C_6H_5, C_6H_4CH_3\text{-}p$$

$$\text{(VII)}\quad M = W.\quad E = Te,\quad R = C_6H_5, C_6H_4CH_3\text{-}p$$

Complexes I, II and III are soluble in organic solvents such as benzene, dichloromethane, carbon disulfide and THF, but insoluble in alcohol, n-hexane and petroleum ether. Complexes IV, V, VI and VII are moderately soluble in dichloromethane, chloroform, acetone and DMSO, but insoluble in other common organic solvents. All the above complexes react with concentrated hydrochloric acid to give the parent dichloride. With methyl iodide, II, III, IV, V, VI and VII react to give the respective $(\pi\text{-}C_5H_5)_2MI_2$, with exception of $(\pi\text{-}C_5H_5)_2\text{-}Mo(SeCH_3)_2$, which gives the ionic complex $[(\pi\text{-}C_5H_5)_2Mo(SeMe_2)I]^+I^-$. This green complex is soluble in polar solvents such as alcohol and acetone. The conductivity of its solution (2.55×10^{-4} *M*) in nitromethane was consistent with that of a 1/1 electrolyte.

Complexes I, II and III are unstable in air and their solutions in benzene decompose in air immediately. The complexes IV, V, VI and VII are quite stable in air, although their solutions in dichloromethane decompose after about two days for IV and V, or about one day for VI and VII. Thus it seems that $(\pi\text{-}C_5H_5)_2Mo$ and $(\pi\text{-}C_5H_5)_2W$ groups form more stable compounds with selenium-

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF $(\pi\text{-}C_5H_5)_2ML_2$ (M = V, Nb)

Compound	Yield (%)	Colour	M.p. (°C)	Analysis found (calcd.) (%) C	H
$(\pi\text{-}C_5H_5)_2V(SeC_6H_5)_2$	75	Green	126-130	53.85(53.54)	4.02(4.06)
$(\pi\text{-}C_5H_5)_2V(SeC_6H_4CH_3\text{-}o)_2$	79	Green	143-146	55.46(55.27)	4.56(4.61)
$(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$	80	Moss-green	137-142	42.18(41.70)	3.12(3.16)
$(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$	68	Dark-green	101-105	49.75(49.34)	3.77(3.74)

TABLE 2

ANALYTICAL DATA AND SOME PROPERTIES OF (π-C_5H_5)$_2$$ML_2$ (M = Mo, W) [a]

Compound	Yield	M.p.	Analysis found (calcd.) (%)		^{1}H NMR (τ) (ppm)		
	(%)	(°C)	C	H	C_5H_5	C_6H_4	CH_3
(π-C_5H_5)$_2$Mo($SeCH_3$)$_2$	81	197-198	35.01(34.78)	3.68(3.86)	4.80(s,10) [b]		8.45(s,6)
(π-C_5H_5)$_2$Mo(SeC_6H_5)$_2$	79	230-231	48.97(49.07)	3.88(3.72)	4.78(s,10) [b]	2.63-3.03(m,10)	
(π-C_5H_5)$_2$Mo(TeC_6H_5)$_2$	75	198-199	41.90(41.51)	3.08(3.14)	4.72(s,10) [b]	2.50-3.15(m, 10)	
(π-C_5H_5)$_2$Mo($TeC_6H_4CH_3$-p)$_2$	73	192-194	43.58(43.37)	3.58(3.61)	4.68(s,10) [c]	2.31(d,$J_{8.0}$Hz,4), 3.01(d,4)	
(π-C_5H_5)$_2$W($SeCH_3$)$_2$	77	207-207	28.27(28.68)	3.16(3.19)	4.69(s,10) [c]		7.47(s,6)
(π-C_5H_5)$_2$W(SeC_6H_5)$_2$	80	231-232	42.65(42.17)	3.04(3.20)	4.64(s,10) [c]	2.30-3.08(m) [e]	
(π-C_5H_5)$_2$W(TeC_6H_5)$_2$	71	212-213	36.87(36.46)	2.55(2.76)	4.66(s,10) [c]	2.10-2.95(m) [e]	
(π-C_5H_5)$_2$W($TeC_6H_4CH_3$-p)$_2$	79	212-214	38.18(38.29)	3.09(3.19)	4.69(s,10) [c]	2.31(d,$J_{8.0}$Hz,4) 3.02(d,4)	
[(π-C_5H_5)$_2$Mo($SeMe_2$)I]$^+$I$^-$ [f]	60	> 260	24.45(24.45)	2.58(2.71)	4.26(s,10) [d]		7.58(s,6)

[a] All compounds are brown. [b] Measured in $(CD_3)_2SO$ using TMS as internal standard; multiplicity of peaks: s, singlet; d, doublet; m, multiplet. [c] In $CDCl_3$. [d] In CD_3OD. [e] Overlapped by signals of $CDCl_3$ protons. [f] Molar conductivity in nitromethane of 2.55×10^{-4} M solution was 50.9 Ω^{-1} cm^2/mole.

than with tellurium-containing ligands. This result corresponds with that found for $(\pi\text{-}C_5H_5)NiP(n\text{-}C_4H_9)_3EC_6H_4X$ (E = Se, Te) [5] and $(\pi\text{-}C_5H_5)_2M(ER)_2$ (M = Ti, Zr) [1], but is in marked contrast with that observed for $(\pi\text{-}C_5H_5)Fe(CO)_2EC_6H_5$ [6] and $(\pi\text{-}C_5H_5)Mo(CO)_3EC_6H_5$ [7].

^1H NMR spectra of the complexes I, II and III could not be obtained for the paramagnetic vanadium(IV) and niobium(IV) compounds. The ^1H NMR spectral data of IV, V, VI and VII are shown in Table 2. Resonances due to the phenyl and methyl protons occurred at the expected positions. The π-cyclopentadienyl protons gave peaks at around τ 4.70 ppm. Little useful information about the comparative donor properties of selenium and tellurium could be obtained from the ^1H chemical shifts for $\pi\text{-}C_5H_5$ group, which can afford useful information about their properties [8], because the differences of shifts between the selenium ligands and the tellurium ligands in the complexes IV, V, VI and VII is too small (Table 2). Studies of the donor properties of Group VIB elements in the type $(\pi\text{-}C_5H_5)_2ML_2$ (M = Ti, Zr, V, Nb, Mo and W; L = Group VIB atoms) will be reported later.

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 complexes $(\pi\text{-}C_5H_5)_2VCl_2$ [9], $(\pi\text{-}C_5H_5)_2NbCl_2$ [10] and $(\pi\text{-}C_5H_5)_2MCl_2$ (M = Mo, W) [11] were prepared using published procedures. IR spectra were measured by a Hitachi EPI-S2 spectrometer. NMR spectra were measured by means of a JEOL-JNM-4H-100NMR spectrometer. Conductivities were measured by the Wheatstone bridge method.

Preparation of $(\pi\text{-}C_5H_5)_2VL_2$ (L = SeC_6H_5 or $SeC_6H_4CH_3\text{-}o$ and $(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$

To phenyllithium prepared from 1.88 g (0.12 mol) of bromobenzene, 0.20 g (0.029 mol) of lithium and ether (40 ml) was added 0.79 g (0.01 mol) of selenium under nitrogen while stirring. After six hours of stirring at room temperature the colorless solution which resulted was added to a syspension of 1.25 g (0.005 mol) of $(\pi\text{-}C_5H_5)_2VCl_2$ in benzene (40 ml) with stirring at 0°C. After three hours of stirring at room temperature a green-black solution formed. The solvent was removed under reduced pressure to leave a black residue. Recrystallization of the latter from benzene—methanol gave 1.54 g (yield 75%) of dark green crystals. A similar procedure was used for the preparation of $(\pi\text{-}C_5H_5)_2V(SeC_6H_4CH_3\text{-}o)_2$ and $(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$. Yields and analyses are collected in Table 1.

Preparation of $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$

To phenyllithium prepared from 1.88 g (0.012 mol) of bromobenzene, 0.20 g (0.029 mol) of lithium and ether (40 ml) was added 1.27 g (0.01 mol) of tellurium under nitrogen while stirring. After two hours of refluxing, the grey solution which formed was added to a suspension of 1.72 g (0.005 mol) of $(\pi\text{-}C_5H_5)_2NbCl_2$ in benzene (40 ml) with stirring at 0°C. After three hours of stirring at room temperature, a green solution formed. The solvent was removed under reduced pressure to leave a green residue. Recrystallization of the latter from benzene—methanol gave 2.51 g (yield 80%) of green crystals.

Preparation of $(\pi\text{-}C_5H_5)_2ML_2$ *(M = Mo or W; L =* $SeCH_3$ *or* SeC_6H_5*)*

To the Grignard reagent prepared from 1.14 g (0.012 mol) of methyl bromide, 0.29 g (0.012 mol) of magnesium in THF (30 ml), was added 0.79 g (0.01 mol) of selenium under nitrogen while stirring. After five hours of stirring at room temperature the yellow solution which formed was added with stirring to a suspension of 1.48 g (0.005 mol) of $(\pi\text{-}C_5H_5)_2MoCl_2$ in THF (30 ml). After one day of stirring at room temperature, a brown solution formed. The solvent was removed under reduced pressure and the brown residure extracted with dichloromethane. The brown solution was chromatographed on a 2×30 cm alumina column. Elution with dichloromethane gave a brown eluate from which the solvent was removed, leaving a brown residue. This was recrystallized from dichloromethane—n-hexane to yield brown crystals (1.68 g, yield 81%). A similar procedure was used for the preparation of the other $(\pi\text{-}C_5H_5)_2M(SeR)_2$ (R = CH_3 or C_6H_5). Yields and analyses are collected in Table 2.

Preparation of $(\pi\text{-}C_5H_5)_2ML_2$ *(M = Mo or W; L =* TeC_6H_5 *or* $TeC_6H_4CH_3$*-p*

To the Grignard reagent prepared from 1.88 g (0.012 mol) of bromobenzene, 0.29 g (0.012 mol) of magnesium in THF (30 ml), was added 1.27 g (0.01 mol) of tellurium under nitrogen while stirring. After twelve hours of stirring at room temperature the grey solution which formed was added with stirring to a suspension of 1.48 g (0.005 mol) of $(\pi\text{-}C_5H_5)_2MoCl_2$ in THF (30 ml). After ten hours of stirring at room temperature a brown solution formed. The solvent was removed under reduced pressure and the brown residue was extracted with dichloromethane. The brown solution was chromatographed on a 2×30 cm alumina column and eluted with dichloromethane to give a brown band. The solvent was removed and the residue was recrystallized from dichloromethane—n-hexane to give brown crystals (2.38 g, yield 75%). A similar procedure was used for the preparation of the other $(\pi\text{-}C_5H_5)_2M(TeR)_2$ (R = C_6H_5 or $C_6H_4CH_3$-*p*) Yields and analyses are shown in Table 2.

Reaction of $(\pi\text{-}C_5H_5)_2NbL_2$ *(L =* SeC_6H_5 *and* TeC_6H_5*) with MeI*

$(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$ (0.8 g, 0.0015 mol) in benzene (15 ml) was treated with methyl iodide (2.28 g, 0.016 mol). After one hour of standing at room temperature, dark red crystals began to precipitate. After twelve hours of standing at room temperature the crystals were separated, washed with ether and dried to give 0.56 g of dark red crystals. Analysis, infrared spectrum and melting point of this material were identical with those of $(\pi\text{-}C_5H_5)_2NbI_2$ [12]. Similarly, $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$ reacted with MeI to give 0.60 g (yield 84%) of $(\pi\text{-}C_5H_5)_2NbI_2$.

Reaction of $(\pi\text{-}C_5H_5)_2Mo(SeCH_3)_2$ *with MeI*

$(\pi\text{-}C_5H_5)_2Mo(SeCH_3)_2$ (0.6 g, 0.0015 mol) in CH_2Cl_2 (50 ml) was treated with methyl iodide (2.28 g, 0.016 mole). After one hour of standing at room temperature the green crystals were separated, washed with CH_2Cl_2 and ether. and dried to give 0.70 g (yield 60%) of $[(\pi\text{-}C_5H_5)_2Mo(SeMe_2)I]^+I^-$. Analysis,

^{1}H NMR spectral data and conductivity of its solution ($2.55\ 10^{-4}\ M$) in nitromethane are collected in Table 2.

Reaction of $(\pi\text{-}C_5H_5)_2MoL_2$ *(L =* SeC_6H_5*,* TeC_6H_5 *and* $TeC_6H_4CH_3\text{-}p$*) with MeI*

$(\pi\text{-}C_5H_5)_2Mo(SeC_6H_5)_2$ (0.8 g, 0.0015 mol) in CH_2Cl_2 (50 ml) was treated with methyl iodide (2.28 g, 0.016 mole). After two days of standing at room temperature dark green crystals were separated, washed with ether and dried to give 0.47 g of green crystals. This compound was characterized by analysis, infrared spectrum and melting point, and shown to be identical with $(\pi\text{-}C_5H_5)_2MoI_2$ [11]. Similarly, $(\pi\text{-}C_5H_5)_2MoL_2$ (L = TeC_6H_5 and $TeC_6H_4CH_3\text{-}p$) reacted with MeI to give 0.53 g (74%) and 0.55 g (77%) of $(\pi\text{-}C_5H_5)_2MoI_2$, respectively.

Reaction of $(\pi\text{-}C_5H_5)_2WL_2$ *(L =* $SeCH_3$*,* SeC_6H_5*,* TeC_6H_5 *and* $TeC_6H_4CH_3\text{-}p$*) with MeI*

$(\pi\text{-}C_5H_5)_2W(SeCH_3)_2$ (0.75 g, 0.0015 mol) in CH_2Cl_2 (50 ml) was treated with methyl iodide (2.28 g, 0.016 mol). After twelve hours of standing at room temperature dark green crystals were separated, washed with ether and dried to give 0.68 g of green crystals identical in analysis, infrared spectrum and melting point with $(\pi\text{-}C_5H_5)_2WI_2$ [11]. Similarly, $(\pi\text{-}C_5H_5)_2WL_2$ (L = SeC_6H_5, TeC_6H_5 and $TeC_6H_4CH_3\text{-}p$) reacted with MeI to give 0.56 g (66%), 0.67 g (79%) and 0.68 g (80%) of $(\pi\text{-}C_5H_5)_2WI_2$, respectively.

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