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PREPARATION OF ORGANOCHALCOGEN-BRIDGED DINUCLEAR COMPLEXES OF TITANIUM OR NIOBIUM AND IRON OR COBALT

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Summary

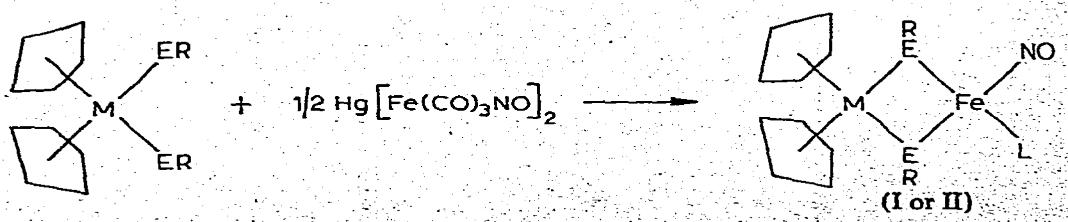
Organochalcogen-bridged heteronuclear complexes $(\pi\text{-}C_5H_5)_2Ti(ER)_2Fe(NO)_2$ (ER = SCH_3, SC_6H_5, $SeCH_3$, SeC_6H_5 or TeC_6H_5), $(\pi\text{-}C_5H_5)_2Nb(ER)_2Fe(NO)(CO)$ (ER = SC_6H_5, SeC_6H_5 or TeC_6H_5) and $(\pi\text{-}C_5H_5)_2Nb(ER)_2Co(CO)_2$ (ER = SC_6H_5, SeC_6H_5 or TeC_6H_5) have been prepared.

Introduction

Although heteronuclear transition metal complexes containing bridging organothio-ligands have been known for nearly five years [1-4], organochalcogen-bridged dinuclear complexes of titanium or niobium and iron or cobalt have received little attention. In continuation of a series of studies on the chemical reactivities and donor properties of chalcogen atoms in transition metal complexes containing Group VIb elements [5-8], we report here the preparation of new complexes of type $(\pi\text{-}C_5H_5)_2Ti(ER)_2Fe(NO)_2$, $(\pi\text{-}C_5H_5)_2Nb(ER)_2$-$Fe(NO)(CO)$ and $(\pi\text{-}C_5H_5)_2Nb(ER)_2Co(CO)_2$ (E = S, Se or Te).

Results and discussion

$Hg[Fe(CO)_3NO]_2$ reacted slowly at room temperature in acetone with two



(I or II)

(I: M = Ti; L = NO; ER = SCH_3, SC_6H_5, $SeCH_3$, SeC_6H_5, TeC_6H_5)
(II: M = Nb; L = CO; ER = SC_6H_5, SeC_6H_5, TeC_6H_5)

TABLE 1

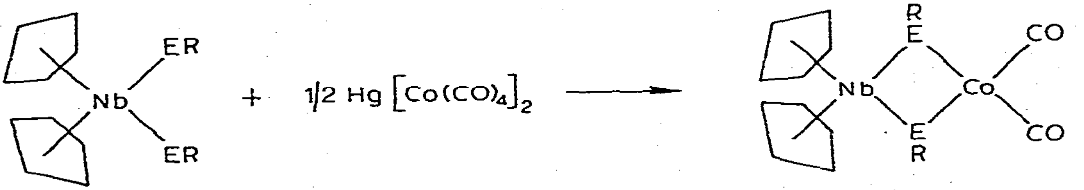
SOME PROPERTIES OF COMPOUNDS I-III

Compound	Color	M.p.[c] (°C)	ν(NO) or ν(CO)[d] (cm^{-1})	^{1}H NMR (τ ppm)		
				C_5H_5	C_6H_5	CH_3
$(\pi\text{-}C_5H_5)_2Ti(SMe)_2Fe(NO)_2$	Violet	231-232	1672s, 1715s	4.44-4.84(m)		7.62(s)[e]
$(\pi\text{-}C_5H_5)_2Ti(SPh)_2Fe(NO)_2$[a]	Violet	209-210	1670s, 1705s	4.71(s)	2.52-2.82(m)[e]	
$(\pi\text{-}C_5H_5)_2Ti(SeMe)_2Fe(NO)_2$	Blue	217-218	1670s, 1715s	4.61(s), 4.71(s), 4.85(s)		7.72(s), 7.84(s)[e]
$(\pi\text{-}C_5H_5)_2Ti(SePh)_2Fe(NO)_2$	Blue	182-183	1688s, 1706s	4.48(s), 4.58(s), 4.80(s)	2.50-2.80(m)[f]	
$(\pi\text{-}C_5H_5)_2Ti(TePh)_2Fe(NO)_2$[b]	Green	156-157	1675s, 1708s	4.68(s), 4.71(s), 4.83(s)	2.60-2.84(m)[f]	
$(\pi\text{-}C_5H_5)_2Nb(SPh)_2Fe(NO)(CO)$	Brown	175-176	1605s, 1847s			
$(\pi\text{-}C_5H_5)_2Nb(SePh)_2Fe(NO)(CO)$	Brown	156-157	1610s, 1845s	4.31(s), 4.58(s), 4.64(s) 4.78(s), 4.93(s), 5.21(s)	2.50-2.74(m)[g]	
$(\pi\text{-}C_5H_5)_2Nb(TePh)_2Fe(NO)(CO)$	Brown	170-171	1623s, 1845s	4.64(s), 4.83(s), 4.90(s) 5.07(s), 5.25(s), 5.31(s)	2.50-2.74(m)[g]	
$(\pi\text{-}C_5H_5)_2Nb(SPh)_2Co(CO)_2$	Brown	173-175	1855s, 1910s			
$(\pi\text{-}C_5H_5)_2Nb(SePh)_2Co(CO)_2$	Brown	136-138	1850s, 1909s	4.64(s), 4.98(s), 5.34(s)	2.44-2.89(m)[g]	
$(\pi\text{-}C_5H_5)_2Nb(TePh)_2Co(CO)_2$	Brown	157-160	1859s, 1911s	4.73(s), 4.99(s), 5.31(s)	2.45-2.85(m)[g]	

[a] Mol. wt. found: 561 (calcd.: 512) by cryoscopy in C_6H_6. [b] Mol. wt. found: 681 (calcd.: 703) by cryoscopy in C_6H_6. [c] With decomposition. [d] KBr disc. [e] In $CDCl_3$. [f] In $(CD_3)_2CO$. [g] In $(CD_3)_2SO$.

molar equivalents of $(\pi\text{-}C_5H_5)_2Ti(ER)_2$ to give $(\pi\text{-}C_5H_5)_2Ti(ER)_2Fe(NO)_2$ (I). Also, the reaction of one mole of the former with two moles of $(\pi\text{-}C_5H_5)_2Nb(ER)_2$ yielded brown complexes, $(\pi\text{-}C_5H_5)_2Nb(ER)_2Fe(NO)(CO)$ (II). The physical properties of complexes I and II are shown in Table 1.

On the other hand, no heteronuclear complex could be obtained from the reaction of $Hg[Co(CO)_4]_2$, which is isoelectronic with $Hg[Fe(CO)_3NO]_2$, with $(\pi\text{-}C_5H_5)_2Ti(ER)_2$, but it did react in acetone with two molar equivalents of $(\pi\text{-}C_5H_5)_2Nb(ER)_2$ to give brown complexes, $(\pi\text{-}C_5H_5)_2Nb(ER)_2Co(CO)_2$ (III). The data for complexes (III) are also collected in Table 1.



(III)

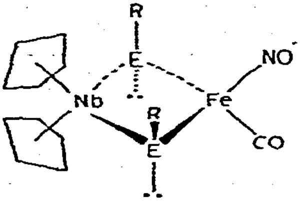
$(ER = SC_6H_5\text{ , }SeC_6H_5\text{ , }TeC_6H_5)$

Qualitatively, the rate of formation of I ($R = C_6H_5$), II or III was observed to increase in the order of $E = S < Se < Te$. A similar trend was observed with I ($R = CH_3$). These results might be explained in terms of the nucleophilicity of E which increases in the order $S < Se < Te$. $Hg[Fe(CO)_3NO]_2$ seems to react more quickly with $(\pi\text{-}C_5H_5)_2Ti(ECH_3)_2$ (for a given E) than with $(\pi\text{-}C_5H_5)_2Ti(EC_6H_5)_2$, which corresponds with the relative rates of reaction of $(\pi\text{-}C_5H_5)_2Ti(SR)_2$ ($R = CH_3$, C_6H_5) with $(\text{norbornadiene})M(CO)_4$ (M = Cr, Mo, W) [2].

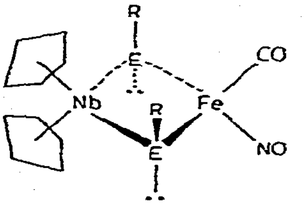
The complexes I, II and III are stable under nitrogen, but solutions in DMSO decompose in air immediately. II and III are more stable than the parent complexes $(\pi\text{-}C_5H_5)_2Nb(ER)_2$, both in solution and in the solid state when exposed to air.

The IR spectra of I exhibited two strong bands due to the stretching frequencies of the nitrosyl groups in the range of 1670-1715 cm^{-1}. In the IR spectra of II and III, there was one strong band at around 1610 cm^{-1} due to a N—O stretching vibration, another at around 1840 cm^{-1} attributable to a C—O stretching frequency for II, and two strong C—O stretching frequencies at around 1850 and 1910 cm^{-1} for III (see Table 1).

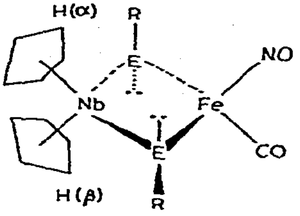
The NMR spectra of I, II and III are shown in Table 1, but we could not obtain those for $ER = SC_6H_5$ in II and III because of solubility problems, Three separate singlets due to the π-cyclopentadienyl protons for I ($ER = SeCH_3$, SeC_6H_5 or TeC_6H_5) and III ($ER = SeC_6H_5$ or TeC_6H_5) might be attributed to *cis/trans* isomerism in solution, in which the former affords two peaks and the latter one peak [2]. Furthermore, showing two separate singlets for the methyl protons for I ($ER = SeCH_3$) would correspond with one peak due to the *cis* form and one attributable to the *trans* form. The π-cyclopentadienyl protons of II ($ER = SeC_6H_5$ or TeC_6H_5) gave six peaks at around τ4.70 ppm. This result may be understood if the complexes are present as *cis* (IIa_1, IIa_2) and *trans* (IIb) isomers in solution. IIa_1 and IIa_2 each should afford two peaks. In IIb, H(α) is in a different environment from H(β), since the electronic effects of a nitrosyl group differ from those of a carbonyl group. Therefore, IIb would give two signals.



(IIa$_1$)



(IIa$_2$)



(IIb)

One singlet of the π-cyclopentadienyl protons for I (ER = SC_6H_5) might be interpreted in terms of interconversion between the *cis* and the *trans* form, or in terms of presence of the *trans* form. But we could not interpret the complexed multiplet due to the π-cyclopentadienyl protons and one singlet due to the methyl protons for I (ER = SCH_3).

Complexes II and III are diamagnetic, which suggests that the niobium is bonded to the iron or cobalt.

Experimental

All experiments were carried out in an atmosphere of dry nitrogen. Solvents were purified by conventional methods: freed from oxygen by degassing and saturating with nitrogen. The complexes $(\pi\text{-}C_5H_5)_2Ti(ER)_2$ (ER = SCH_3 [9], SC_6H_5 [10], $SeCH_3$, SeC_6H_5 and TeC_6H_5 [7]), $(\pi\text{-}C_5H_5)_2Nb(ER)_2$ (ER = SC_6H_5 [4], SeC_6H_5 and TeC_6H_5 [8]), $Hg[Fe(CO)_3NO]_2$ [11] and $Hg[Co(CO)_4]_2$ [12] were prepared using published procedures. IR spectra were measured by a Hitachi EPI-S2 spectrometer. NMR spectra were measured by means of a JOEL-JNM-100 NMR spectrometer.

Reaction of $(\pi\text{-}C_5H_5)_2Ti(SCH_3)_2$ with $Hg[Fe(CO)_3NO]_2$

To a solution of $(\pi\text{-}C_5H_5)_2Ti(SCH_3)_2$ (0.27 g, 1 mmol) in acetone (30 ml) was added $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) whilst stirring. Periodic withdrawal of small samples for IR spectra showed that after 10 h of stirring $Hg[Fe(CO)_3NO]_2$ no longer was present in the violet solution. The reaction mixture was filtered and solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from acetone/n-hexane to give 0.08 g [21% yield based on $(\pi\text{-}C_5H_5)_2Ti(SCH_3)_2$] of violet crystals, m.p. (dec.) 231-232°C. (Found: C, 37.49; H, 4.16; N, 7.25. $C_{12}H_{16}FeN_2O_2S_2Ti$ calcd.: C, 37.11; H, 4.12; N, 7.22%.)

Reaction of $(\pi\text{-}C_5H_5)_2Ti(SC_6H_5)_2$ with $Hg[Fe(CO)_3NO]_2$

A similar reaction using $(\pi\text{-}C_5H_5)_2Ti(SC_6H_5)_2$ (0.39 g, 1 mmol) and $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) after 18 h gave 0.10 g (20% yield) of violet crystals, m.p. (dec.) 209-210°C. (Found: C, 51.84; H, 3.84; N, 5.41. $C_{22}H_{20}FeN_2O_2S_2Ti$ calcd.: C, 51.56; H, 3.91; N, 5.47%.)

Reaction of $(\pi\text{-}C_5H_5)_2Ti(SeCH_3)_2$ with $Hg[Fe(CO)_3NO]_2$

A similar reaction using $(\pi\text{-}C_5H_5)_2Ti(SeCH_3)_2$ (0.37 g, 1 mmol) and $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) after 4 h gave 0.10 g (22% yield) of blue crystals, m.p. (dec.) 217-218°C. (Found: C, 29.82; H, 3.67; N, 5.95. $C_{12}H_{16}FeN_2O_2Se_2Ti$ calcd.: C, 29.88; H, 3.32; N, 5.81%.)

Reaction of $(\pi\text{-}C_5H_5)_2Ti(SeC_6H_5)_2$ with $Hg[Fe(CO)_3NO]_2$

A similar reaction using $(\pi\text{-}C_5H_5)_2Ti(SeC_6H_5)_2$ (0.49 g, 1 mmol) and $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) after 15 h gave 0.12 g (20% yield) of blue crystals, m.p. (dec.) 182-183°C. (Found: C, 43.95; H, 3.32; N, 4.74. $C_{22}H_{20}FeN_2O_2Se_2Ti$ calcd.: C, 43.57; H, 3.30; N, 4.63%.)

Reaction of $(\pi\text{-}C_5H_5)_2Ti(TeC_6H_5)_2$ with $Hg[Fe(CO)_3NO]_2$

A similar reaction using $(\pi\text{-}C_5H_5)_2Ti(TeC_6H_5)_2$ (0.59 g, 1 mmol) and $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) after 2 h gave 0.17 g (24% yield) of green crystals, m.p. (dec.) 156-157°C. (Found: C, 37.16; H. 3.01; N, 3.68. $C_{22}H_{20}FeN_2O_2Te_2Ti$ calcd.: C, 37.55; H, 2.84; N, 3.98%.)

Reaction of $(\pi\text{-}C_5H_5)_2Nb(SC_6H_5)_2$ with $Hg[Fe(CO)_3NO]_2$

$(\pi\text{-}C_5H_5)_2Nb(SC_6H_5)_2$ (0.44 g, 1 mmol) and $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) were refluxed in acetone (100 ml) for 2 h. The original red color of the starting materials changed gradually to brown and a gray precipitate separated. The reaction mixture was filtered and solvent was removed from the filtrate under reduced pressure to leave a brown solid. The solid was washed with benzene and ether, and dried under vacuum to give 0.41 g [75% yield based on $(\pi\text{-}C_5H_5)_2Nb(SC_6H_5)_2$] of a brown solid, m.p. (dec.) 175-176°C. (Found: C, 49.94; H, 3.57; N, 2.57. $C_{23}H_{20}FeNNbO_2S_2$ calcd.: C, 49.73; H, 3.60; N, 2.52%.)

Reaction of $(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$ with $Hg[Fe(CO)_3NO]_2$

$(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$ (0.54 g, 1 mmol) and $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) were refluxed in acetone (100 ml) for 1 h. The solution turned from red to brown and a gray precipitate separated. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from DMSO/diethyl ether to give 0.45 g (70% yield) of brown crystals, m.p. (dec.) 156-157°C. (Found: C, 42.14; H, 2.86; N, 2.18. $C_{23}H_{20}FeNNbO_2Se_2$ calcd.: C, 42.52; H, 3.08; N, 2.16%.)

Reaction of $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$ with $Hg[Fe(CO)_3NO]_2$

To a solution of $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$ (0.63 g, 1 mmol) in acetone (50 ml) was added dropwise a solution of $Hg[Fe(CO)_3NO]_2$ (0.27 g, 0.5 mmol) in acetone (50 ml). After 1 h of stirring at room temperature, the solution turned from green to brown and a gray precipitate separated. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from DMSO/diethyl ether to give 0.60 g (80% yield) of brown crystals, m.p. (dec.) 170-171°C. (Found: C, 36.73; H, 2.51; N, 2.00. $C_{23}H_{20}FeNNbO_2Te_2$ calcd.: C, 37.00; H, 2.68; N, 1.87%.)

Reaction of $(\pi\text{-}C_5H_5)_2Nb(SC_6H_5)_2$ with $Hg[Co(CO)_4]_2$

$(\pi\text{-}C_5H_5)_2Nb(SC_6H_5)_2$ (0.44 g, 1 mmol) and $Hg[Co(CO)_4]_2$ (0.27 g, 0.5 mmol) were refluxed in acetone (100 ml) for 2 h. The original red color of the starting materials turned gradually to brown and a gray precipitate separated. The reaction mixture was filtered and solvent was removed from the filtrate under reduced pressure to leave a brown solid. The solid was washed with benzene and ether, and dried under vacuum to give 0.39 g [70% yield based on $(\pi\text{-}C_5H_5)_2Nb(SC_6H_5)_2$] of brown solid, m.p. (dec.) 173-175°C. (Found: C, 52.29; H, 3.82; S, 11.55. $C_{24}H_{20}CoNbO_2S_2$ calcd.: C, 51.80; H, 3.60; S, 11.51%.)

Reaction of $(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$ with $Hg[Co(CO)_4]_2$

$(\pi\text{-}C_5H_5)_2Nb(SeC_6H_5)_2$ (0.54 g, 1 mmol) and $Hg[Co(CO)_4]_2$ (0.27 g, 0.5 mmol) in acetone (100 ml) were stirred for 15 h at room temperature. The solution turned gradually from red to brown and a gray precipitate separated. The reaction mixture was filtered and solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from DMSO/diethyl ether to give 0.48 g (74% yield) of brown crystals, m.p. (dec.) 136-138°C. (Found: C, 44.09; H, 3.18. $C_{24}H_{20}CoNbO_2Se_2$ calcd.: C, 44.30; H, 3;08%.)

Reaction of $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$ with $Hg[Co(CO)_4]_2$

A similar reaction using $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$ (0.63 g, 1 mmol) and $Hg[Co(CO)_4]_2$ (0.27 g, 0.5 mmol) for 2 h gave 0.67 g (90% yield) of brown crystals, m.p. (dec.) 157-160°C. (Found: C, 38.40; H, 2.68. $C_{24}H_{20}CoNbO_2Te_2$ calcd.: C, 38.59; H, 2.76%.)

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