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Preparation Of Ferrocene Derivatives Of Niobium IV

A.W.M. Abdulla
Department of Chemistry,College of Education -Ibn Al.Haetham,
University of Baghdad

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Abstract

This study included the preparation of the dihalogens -1,3 metalla-2[3] ferrocenophanes like Cp_2NbS_2Fc,$(tBuCp)_2NbS_2Fc$,Cp_2NbSe_2Fc and $(tBuCp)_2NbSe_2Fe$ where (Fc=ferrocence) These complexes has been prepared from the reaction of $(R)_2$ $NbCl_2$ with $FCLiM_2$, where(R=Cp,tBuCp) (M = S,Se) under refluxing in toluene,the reaction was carried under Argon atmosphere .

These complexes were characterized by elemental microanalysis ,Masse spectra scopy, nuclear magnetic resonance (^{1}HNMR) and melting points .

Key words: Ferrocene , Niobium ,Selenium , Sulfur ,Inert Atmosphere Organometalic complexes

Introduction

The early studies consist the reaction of the compounds as follows

$$2MeCpli + NbCl_4 \longrightarrow (MeCp)_2 NbCl_2 \text{ [1]}$$

And products like $(MeCp)_2NbOCl$,$(iPrCp)_2$ $NbOCl$. $CpNbCl_4$ etc, by other side ferrocene has much derivatives with transition metals like Zr,Ti,Hf,Co,Mn and many others [2] To understand the Niobium compounds properties we must know something about it physical properties like density mpc bpc covalent diameter as follows 8.57 2470 4927 0.134 In base temperature Niobium becomes super conductor, Niobium halogene derivatives as Niobium tetra chloride which react with ferrocene to produce the complexes of our work . Ferrocene has two iso energetic [3] conformations eclipsed and staggered [3][4]. but the x-ray and electron diffraction indicate an eclipsed conformation , the rotation barrier about the iron- Cp ring axis is very weak (2-5kcal.mole), thus the rotation about that axes is,so in fluid solution we find only one 1,1disubstituted isomer [5,6] , because the free rotation makes all position on the first ring equivalent to the second ring

The ferrocene molecular orbital diagram shows various metal ring interactions , (Cp → Fe) ,λ(Cp → Fe) and (Cp → Fe) so the reaction of dichaleogene with (Ti,Zr,Hf) underegoes all the important reactions of the early works [7,8].

But reaction between niobium derivatives and ferrocene derivative are not found , so our work focus to prepare new complexes of ferrocene Niobium derivatives.

Results and dissuasion

To obtain these complexes we follow the procedure bellow

$$(RCp)_2NbCl_2 + Fc(MH)_2 \longrightarrow (RCp)_2NbM_2Fc$$

$$Cp_2NbCl_2 + Fc(MH)_2 \longrightarrow Cp_2NbM_2Fc$$

R = +Bu Fc = Ferrocen
Cp = C_5H_5 M = S,Se

NMR Study

In $CdCl_3$ we get a clear signals which assist groups of massive
For the ferrocene between two to four ,there is a variety of chemical displacement without any change of the morphology of the NMR spectrum [10] , the comparison between the spectrums of (S) and (Se) complexes leads to the fact that there is a displacement toward the faible field of the forrocenic massives [11] of (S) complexes than that of(Se) . The effect of the free electron pair [12] of (S) or (Se) toward the other (H) atom of C5H5 ring neighbor at the proton , we constat that the ring torsion is due to the steric [13,14]

Experiments

All the complexes performed under Inert gas
preparation of

A. **Cp_2NbS_2Fc** :-To a solution of FcS_2 Li Tmeda (0.7)gm(1.8)m mol in (20) ml of toluene /THF (2/1) , a solution of Cp_2NbCl_2 (0.5) gm (1.7) m mol in (20)ml of toluene was added , the mixture was refluxed for (30) minutes with stringing an orange crystal obtained (0.55)gm yield (60%) mp 260 dec
B. **Cp_2NbSe_2Fc** :-To a solution of $FcSeH_2$ A (0.42)gm (1.2)ml in (30ml) of (n) toluene a solution of Cp_2NBCl_2 (0.34)gm (1.18)m mol in (20) ml of toluene was added , the maximum was refluxed for (2) hours with stirring , an orange crystals obtained (0.42)gm (61%) yield mp mp260 C
C. **$(tBuCp)_2NbS_2Fc$**:- To a solution of (0.4) gm (01.1)m mol of $(tBuCp)_2NbCl_2$ and (0.3) gm (1.1) m mol of FcS_2H_2 was added then o.56 ml of Net_3 in 50 ml of toluene , the mixture was stirred at 70 C for 3 hour , the product was isolated by chromatography , after recrystallization in hexane, we obtained red crystals (0.3)gm 18yeild F 260
D. **$(tB4Cp)_2NbSe_2Fc$** :-To a solution of (0.5)gm (1.2)m mol of $(tB4Cp)_2NbCl_2$ and (0.4)gm (1.1)m mol of $FcSeH_2$ In 50 ml toluene/THF (2/I)then o.65 ml of Net3 was added the mixture stirred at 88 C for 3 hours , the product was isolated by chromatography after rercystalisation in hexane weobtained orange crystals f 260 C 56% yield 50% (0.5)gm (0.7) m mol

Instruments:

mpc by electro thermal digital mp apparatus
TLC: glass plats coated with merckgelC.F.250 silica gel
NMR Joel fx(100) of Fourier trans former
Chromatography kiesel gel type 3300 (70 ev at 200C)
Analysis CNRS France

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Table(1): ^{1}HNMR spectral data for ligands and complexe (chemical shift) δ in p.p.m

Complex	Cp	C_5H_5
Cp_2NbS_2fc	5.9(5)	5.2(1) 4.5(1) 4.0(2)
Cp_2NbSe_2fc	5.92(5)	4.94(1) 4.38(1) 4.31(1) 4.1(1)
Complex	tBu	Cp + C_5H_4
$(tBuCp)_2NbSe_2fe$	1.15(9) 6.42(1)	576(2) 5.6(1) 5.3 (1) 5.4 (1) 4(1)
$(tBaCp)_2NbSe2fe$	1.13(9) 5.62(1) 5.01(1)	4.98(1) 4.1(1) 4.0(1)

Table (2): physical properties

Compound	mp	color	weight of Nb chloride	weight of Fc M2Li	Yield
Cp_2 $NbSe_2Fc$	260>	Orange	0.52gm	0.74	60%
Cp_2NbSe_2Fc	260>	Orange	0.42gm	0.42	61%
$(tBuCp)_2Cp_2NbSe_2Fc$	260>	Red	0.7gm	0.54	48%
$(tBuCp)_2Cp_2NbSe_2Fc$	260>	Orange	0.37gm	0.41gm	50%

Table (3): masse spectral data for the complexes

Cp_2NbSe_2Fc	470(m^+) 450(C_2H4FeS^+) 253(m^+) $(CpNbSCp)^+$
Cp_2NbSe_2Fc	566(m+) 314 $(C_{10}H8Fe\ Se)^+$ 222$(CpH_{10}Nb)^+$ 184 $(C_{10}H8Fe)^+$
$(tB4Cp)_2NbSe_2Fc$	582 (m+)561$(m\text{-}tB4Cp)^+$
$(tBuCp)_2NbSe_2Fc$	(678(m+),266($C_{10}H8FeSe$)

Table (4) :Analytical and physical data for ligands and complexes

Cp_2NbSe_2Fc	$C_2OH_{18}FeFe_2Nb$	Calc C43% 4.29 Nb 17 found C 42.55% H3.01Nb 16.8
$(tBuCp_2)$ $NbSe_2Fc$	$C_2OH34FeSe_2Nb$	Calc C 49.18% H5.94 found C 49.76 % H4.91
$(tBuCp)_2Nb$ Se_2Fc	$C_2OH_{18}FeS_2Nb$	Calc C 50% H3.8 Nb 1.97 found C 50.8 H3.9 Nb=19.72

Table (5) :The solubility of prepared complexes

Cp_2NbS_2Fc	water	CH3OH	C2H5OH	toluene	THF	hexane	ether
Cp_2NbS_2Fc	÷	+	+	÷	+	-	-
$(tBuCp)_2NbS_2Fc$	÷	+	+	÷	+	-	-
$(tBuCp)_2NbSe_2Fe$	-	÷	÷	÷	+	-	-
$(tBuCp)_2NbSe_2Fe$	-	÷	+	÷	+	÷	-

Soluble (+) Insoluble (-) Sparingly (÷)

Chemicals used in this work and their suppliers

NO material	**Company**	**Purity %**
1-Ferrocene	**Merck**	**99**
2- TMEDA	**B.D.H**	**99**
3- bUli	**B.D.H**	**99**
4-Cp2NbCl2	**Riedel-Ochean**	**99**
5-Toluene	**Fluka**	**99**
6- THF	**Fluka**	**99**
7- (tBuCp)2NbCl2	**Merck**	**99**
8-Hexane	**Merck**	**99**
9- Sulfur	**B.D.H**	**99**
10- Selenium	**B.D.H**	**99**
Fc (ScH)2	**Merck**	**99**

تحضير مشتقات الفيروسين للنيوبيوم IV

عبد الواحد محجوب عبد الله
قسم الكيمياء، كلية التربية - ابن الهيثم ،جامعة بغداد

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الخلاصة

تضمن البحث تحضير معقدات ثنائي كلورو 1و3ميتالا 2[3] فيروسينوفان مثل
$Cp_2NbS_2Fc,(tBuCp)_2 NbS_2Fc$, $Cp_2NbSeFc(tBuCp)_2NbSe_2Fc$ (هو الفيروسين Fc)
تم الحصول على هذه المعقدات من مفاعلة معقدات كلوريدات النيوبيوم مع معقد ثنائي ليثيوم الفيروسين لعنصري الكبريت والسليكون وباستخدام التصعيد بوجود التولوين كوسطاً للتفاعل مع اضافة ثنائي مثيل اثيل ثنائي امين (TMEDA)،وتحت جو من غاز خامل هو الاركون شُخِصت هذه المعقدات باستخدام التحليل الدقيق للعناصر (CHN) وطيف الرنين النووي المغناطيسي (^1H) وطيف الكتلة مع درجة الانصهار

الكلمات المفتاحية :-فيروسين ، نيوبيوم ، سلينيوم ، كبريت ، غاز خامل ، معقدات عضوية معدنية

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