# SYNTHESIS AND CHARACTERIZATION OF FLUORUS RHODOXIMES*

*Florlu Rodoksim Sentezleri Ve Yapılarının Aydınlatılması*

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**ABSTRACT**

In this study, Vic-dioxime type ligands such as bis[(3-trifluoromethyl) phenylamino]glyoxime($H_2L^1$),bis[(3,5ditrifluoromethyl)phenylamino]glyoxime ($H_2L^2$), and their Rh(III) complexes have been synthesized. The ligands and their metal complexes have been characterized using by $^1$H-NMR, $^{19}$F-NMR, FT-IR and elemental analysis.

**Key Words:** Vic-dioxime, Rhodoxime, Metal Complexes

**ÖZET**

Bu çalışmada, vic-dioksim tipi ligandlardan bis[(3-trifloro metil)fenilamino] glioksim, bis[3,5-ditrifloro metil)fenilamino]glioksim ligandları ve bu ligandların Rh(III) kompleksleri sentezlenmiştir. Ligandların ve metal komplekslerin yapıları elementel analiz, $^1$H-NMR, $^{19}$F-NMR ve FT-IR spektrumları alınarak aydınlatılmıştır.

**Anahtar Kelimeler:** Vic-dioksim, Rodoksim, Metal Kompleks

## Introductıon

During the past decades, there has been a great deal of interest in the synthesis and characterization of transition metal *vic*-dioxime complexes because of exceptional stability and unique electronic properties. These complexes find a number of applications; in particular, they have been used as reagents in analytical chemistry for quantitative, qualitative, spectrophotometric analysis and aqueous-phase extraction of metal ions.

Since the first preparation of organorhodoximes [Rh(dmgH)$_2$(L)R] (L=py; R=Me; Et, $CH_2CH_2CN$) by Weber and Schrauzer in 1970, there have been synthesized numerous organorhodoximes with various axial bases (L=$PPh_3$, $PMe_3$, $H_2O$, py, …) and a wide variety of organo ligands (R=alkyl, aryl, vinyl, alkynyl, allenyl, functionalized organo ligands) Recently, dinuclear oligo-methylene bridged complexes [Rh]-$(CH_2)_n$-[Rh] (n=2-5) and a vinylene bridged complex, [{K(MeOH)$_2$}$_2${($PPh_3$)(dmg)(dmgH)Rh-CH=CH-Rh(dmg)(dmgH)($PPh_3$)}], were also prepared and characterized by NMR spectroscopy and by X-ray structure analysis. Especially the triphenylphosphine complexes [Rh]-R were used to study the structural and the NMR trans influence of R with the bond length d(Rh-P) and the coupling constant J($^{103}$Rh, $^{13}$C), respectively, as measure.

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The present paper reports the synthesis of fluorinated *vic*-dioxime derivative ligands and their $Rh^{III}$ complexes. The ligands and the metal complexes have been characterized using by FT-IR, $^{1}$H-NMR, $^{19}$F-NMR and elemental analysis.

**Results and dıscussıon**

The main focus of this work is the design and synthesizing of fluorinated *vic*-dioxime derivative ligands and their $Rh^{III}$ complexes. General procedure for preparation of ligands **($H_2L^{1,2}$)** and their $Rh^{III}$ complexes **(4a-b)** is shown in Scheme. Analytical and spectroscopic data for the ligands and their $Rh^{III}$ complexes are given in experimental section. The elemental analysis data of the synthesized ligands and their $Rh^{III}$ complexes are in agreement with the theoretical values.

**NMR Spectra**

The $^{1}$H NMR spectra of ligands (**$H_2L^{1,2}$**) showed singled peaks at δ = 10.67, and 9.8 ppm respectively, that assigned as oxime OH protons. This assignment was further substantiated by disappearance of the corresponding OH peaks when ligands underwent deuterium exchange. The N-H and Ar-H peaks of ligands were observed in agreement with the literature data, at $\delta$ = 8.4, 6.9-7.4 ppm and at $\delta$= 9.1, 6.9-8.1 ppm, respectively. The N-H and Ar-H peaks of the $Rh^{III}$ complexes were observed **(4a-b)** at $\delta$= 8.5, 6.6-7.8 ppm and at $\delta$= 9.5, 6.9-7.8 ppm, respectively. The $^{19}$F NMR spectra of the ligands showed one peak at around $\delta$= -61.8 ppm and at $\delta$= -63.25 ppm. The $^{19}$F NMR spectra of the $Rh^{III}$ complexes were observed at $\delta$= -61.4 ppm and at $\delta$= -61.6 ppm.

**Infrared Spectra**

The FT-IR spectra of the **$H_2L^{1,2}$** show a strong bands at $v$= 1656-1615 $cm^{-1}$ and 1779 $cm^{-1}$ assignable to imin (C=N) group. This bands are shifted to the $v$= 1540, 1598 $cm^{-1}$ and at $v$= 1619 $cm^{-1}$ region respectively in the complexes **(4a-b)** due to the coordination of the *vic*-dioxime ligands through the imin nitrogen. For the ligands, show the strong OH stretching bands at $v$= 3380-3100 $cm^{-1}$ and at $v$= 2850-3500 $cm^{-1}$. The FT-IR spectra of the **$H_2L^{1,2}$** show bands at $v$= 950, 933 $cm^{-1}$ and at $v$= 946 $cm^{-1}$ assignable to N-O group. This bands are shifted to the $v$= 1000 $cm^{-1}$ and at $v$= 1009 $cm^{-}$1 region respectively in the complexes **(4a-b).**

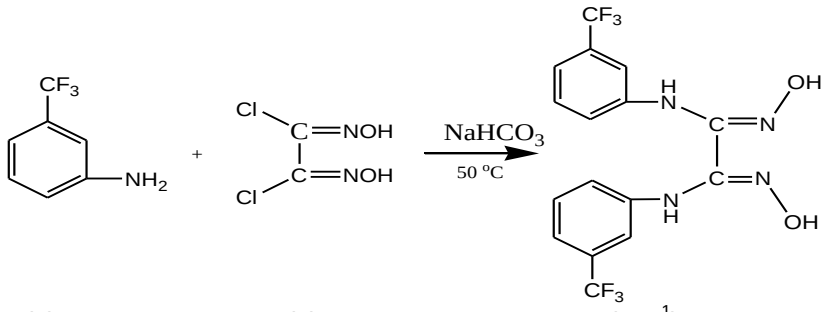
**Experimental**

All chemicals were of reagent grade quality and used further purifications. Bis(3-methylphenylamino)glyoxime ($H_2L$) and its $Rh^{III}$ complex were prepared according to the literatures, and used for compare with the synthesized flourus ligands and complexes solubility. The $^{1}$H-NMR and $^{19}$F-NMR spectra were obtained on a Bruker-Advance DPX 400 spectrometer in DMSO-$d_6$ with $CDCl_3$ as internal standard. IR spectra were recorded on a Perkin Elmer Mattson 1000 FT-IR spectrometer as KBr pellets in range 4000-500 $cm^{-1}$. Elemental analyses were recorded on a LECO CHNS-932 analyzer and Hitachi 180-80 polarized Zeeman

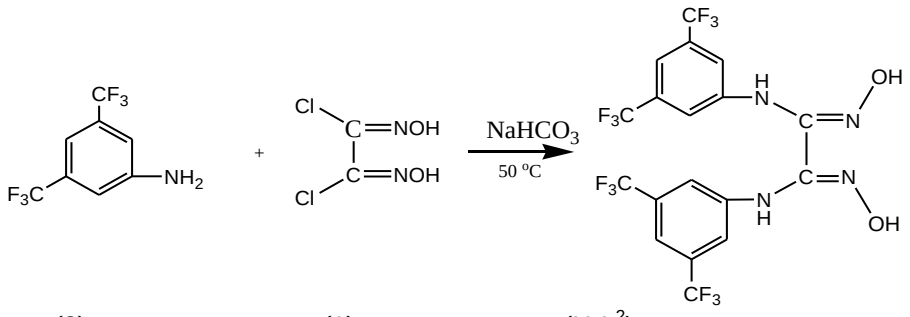
Atomic Absorption spectrometer. Melting point was determined on a Gallenkamp apparatus in a sealed capillary and is uncorrected.

**General Procedure for Preparation of Ligands**

For preparation of ligands a solution of 0.78 g (0.005 mol) dichloroglyoxime (1) in 20 mL EtOH was added 0.01 mol the 3-(trifluoromethyl)anilyn (2) or 3,5-(trifluoromethyl)anilyn (3). 1.02 g NaHCO3 was added this solution. The reaction mixture was stirred for 3 h at the 50 oC in the reflux. The product ($H_2L^{1,2}$) was separated by filtration, and then dried in vacuum. The crude product was recrystallized.



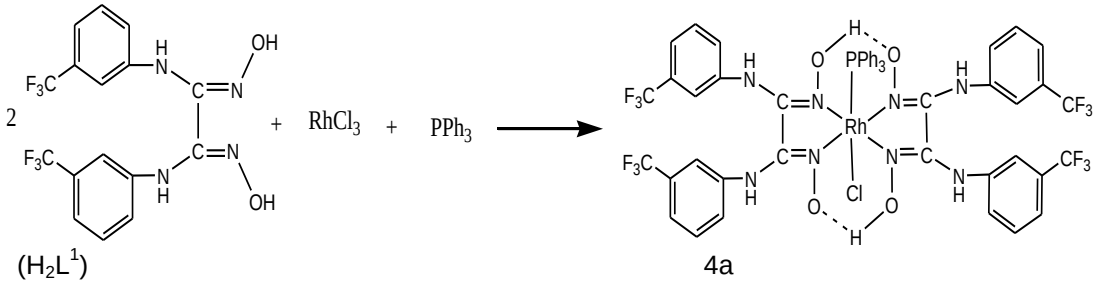

(2) (1) ($H_2L^1$)

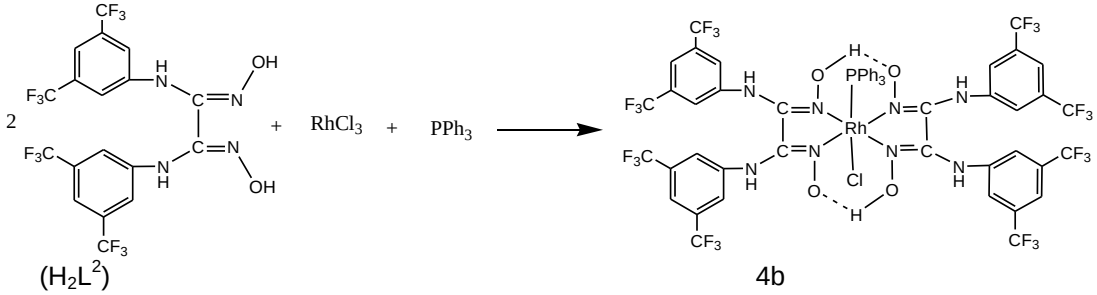



(3) (1) ($H_2L^2$)

**General Procedure for Preparation of Complexes**

For preparation of complexes a solution of 0.086 g, (4.1x10-4 mol) RhCl3 in 15 mL H2O was added to a solution of the corresponding ligands 0.33g (8.2x10-4 mol) in 20 mL EtOH at room temperature. The reaction mixture was stirred for 5 min. The mixture was added a solutıon of 0.107 g (4.1x10-4 mol) PPh3 in 15 mL hot EtOH. The mixture was concentrated to 15 mL to precipitate out of complexes from the solution as yellow solid. The crude product was recrystallized .




**Bis[(3-trifluoromethyl)phenylamino]glyoxime ($H_2L^1$).** Yield 0.77 g, 38 %, m.p. 190 $^oC$ (dec). Anal. Calc'd for $C_{16}H_{12}F_6N_4O_2$: C, 47.29; H, 2.95; N, 13.79 %. Found: C, 47.36; H, 3.30; N, 13.87 %. $^1$H-NMR (DMSO, 400 MHz, ppm): δ=10.67 (s, 2H, C=N-OH), 8.4 (s, 2H, N-H), 6.9-7.4 (m, 8H, Ar-H). $^{19}$F-NMR ($CDCl_3$, 376 MHz, ppm): δ= -61.8 (s, 3F, m-$CF_3$-Ph). FT-IR (KBr pellets, $cm^{-1}$): 3380-3100 (O-H), 3407 (N-H), 1497-1446 (Ar-H), 1656, 1615 (C=N), 950, 933 (N-O).

**Bis[(3,5-ditrifluoromethyl)phenylamino]glyoxime ($H_2L^2$).** Yield 1.29 g, 48 %, m.p. 217.5 $^oC$ (dec). Anal. Calc'd for $C_{18}H_{10}F_{12}N_4O_2$: C, 39.85; H, 1.85; N, 10.33 %. Found: C, 40.62; H, 2.28; N, 11.32 %. $^1$H-NMR ($CDCl_3$, 400 MHz, ppm): δ= 9.8 (s, 2H, C=N-OH), 9.1 (s, 2H, N-H), 6.9-8.1 (m, 8H, Ar-H). $^{19}$F-NMR ($CDCl_3$, 376 MHz, ppm): δ= -63.25 (s, 3F, 3,5-$CF_3$-Ph). FT-IR (KBr pellets, $cm^{-1}$): 2850-3500 (O-H), 3440 (N-H), 1630, 1473 (Ar-H), 1779 (C=N), 946 (N-O).

**[Rh($HL^1$)$_2$] (4a).** Yield 0.17 g, 34 %. $C_{50}H_{37}F_{12}N_8O_4PClRh$: $^1$H-NMR (DMSO, 400 MHz, ppm): δ= 8.5 (s, 2H, NH), 6.6-7.8 (m, 8H, Ar-H). $^{19}$F-NMR (DMSO, 376 MHz, ppm): δ= -61.4 (s, 3F, m-$CF_3$-Ph). FT-IR (KBr pellets, $cm^{-1}$): 3420 (N-H), 1485 (Ar-H), 1540,1598 (C=N), 1437 (O-H--O), 1000 (N-O).

**[Rh($HL^2$)$_2$] (4b).** Yield 0.14 g, 28 %. Anal. Calc'd for $C_{54}H_{33}F_{24}N_8O_4PClRh$: $^1$H-NMR (DMSO, 400 MHz, ppm): δ= 9.5 (s, 2H, N-H), 6.9-7.8 (m, 8H, Ar-H). $^{19}$F-NMR

(DMSO, 376 MHz, ppm): δ= -61.6 (s, 3F, 3,5-$CF_3$-Ph). FT-IR (KBr pellets, $cm^{-1}$): 3435 (N-H), 1619 (C=N), 1541, 1471 (Ar-H), 1437 (O-H--O), 1009 (N-O).

| Compound | MW | Solubility | |
|---|---|---|---|
| | | mg/L | (mol/L) |
| **$H_2L$** | 298 | 74 | $2.48x10^{-4}$ |
| **$H_2L^1$** | 406 | 256 | $6.31x10^{-4}$ |
| **$H_2L^2$** | 406 | 210 | $5.17x10^{-4}$ |
| **$H_2L^3$** | 542 | 656 | $1,21x10^{-3}$ |
| **4 a** | 652 | 28 | $4.29x10^{-5}$ |
| **4 b** | 868 | 82 | $9.44x10^{-5}$ |
| **4 c** | 868 | 70 | $8.06x10^{-5}$ |
| **4 d** | 1140 | 126 | $1.11x10^{-4}$ |

**Conclusıons**

This work reports a convenient method for synthesis of trifluoromethyl substituted *vic*-dioxime derivatives ligands and their Rh(III) complexes. The ligands and the metal complexes have been characterized using by FT IR, $^1$H-NMR, $^{19}$F-NMR.

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