Synthesis and Reactivity of 2-Azabutadiene Functionalizes. Complexation and Luminescence properties

Amira Ben Esseghaier*, Moheddine Askri

Laboratory of Heterocyclic Chemistry Natural Products and Reactivity/LCHPNR, Department of Chemistry,
University of Monastir, Faculty of Science of Monastir, 5000 Monastir, Tunisia

(Received: 03 June 2016, accepted: 29 June 2016)

Abstract: During this work, we are interested in the synthesis of π-conjugated azadienic ligand, and their coordination study to two transition metals Rhenium and Ruthenium; we report also in this paper, the luminescence properties of some mono and binuclear complexes of Re(I) with 2-azabutadiene [1], furthermore, the study of their reactivity toward some nucleophiles. Ligand and complexes structures have been confirmed by IR, ^{1}H and ^{13}C NMR spectroscopic data.

Key words: 2-azabutadienes ; cycloaddition; rhenium; ruthenium; luminescence.

INTRODUCTION

The 1.3-dipolar cycloaddition reaction is a very appreciated access road to offered a big variety of pentagonal cycles for two or three heteroatom [2,3]. Numerous theoretical and experimental studies were conducted to understanding chemo, regio and stereoselectivity of cycloaddition reactions. In the other hand, azabutadienes are a very important class of molecule due to their interesting properties derived from their entirely conjugate structure, which makes it able to be complexed to a large range of metals [4,5], also their ability to be used as a dienophile in same cycloaddition reaction. In addition, azabutadienes is very effective in Diels-Alder reaction [6], especially, when they are strengthened by a powerful electro-donors substituents.

In this context, we report first, the synthesis of a new azadienic ligand and their reactivity study towards some nucleophiles, further we present their electrochemical properties. [7-10] In a second part, we describ their complexation with two metals: Re (I) and Ru (II), last we record their luminescence properties [11,12] in the solution and solid state.

EXPERIMENTAL

1. Apparatus

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent containing TMS (tetramethylsilane) on a Bruker 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75.47 MHz). The chemical shifts (δ) are reported in ppm relative to TMS (internal reference). For the ^{1}H NMR, the multiplicities of signals are indicated by the following abbreviations: s: singlet. m: multiplet.

IR spectra were registered with a device SHIMADZU (Infra-Rouge spectra was registered on a device of total reflection limited for solids and on a KBr pellet for liquids).

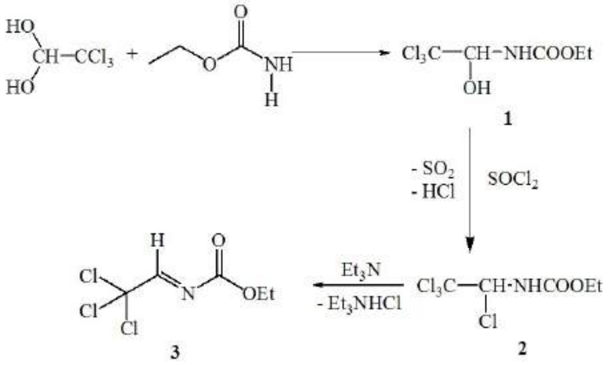
The UV-visible spectrum was recorded in the range between 200-400 nm with an UV JENWAY 6405 spectra photometer equipped with a stoppered quartz cell with 1.0 cm optical path length.

2. Synthesis of the imine

The first synthesis of anhydrochloralurethane was brought back by Moscheles in 1891 [13]. Later, Feist reveal that it wasn't the appropriate products but it's about another compound with the structure

---

[*] Corresponding author, e-mail address : amoura0811@hotmail.fr ; moheddine.askri@fsm.rnu.tn



Scheme 1: Synthesis of anhydrochloralurethanes.

(ROOC-NH-CH(CCl_3)$_2$) [14]. In 1968, the first authentic preparation of *N*-ethoxycarbonyl-*N*-(2.2.2-trichloroethylidene)amine was realized by ulrich and coll [15], as well in three stages starting from carbamic acid ethyl ester.

The first step is almost quantitative (95 %), same for the second (99 %) herein, the yield of the last one is about 48 %.

Ethyl N-(1-hydroxy.2.2.2-trichloroethyl) carbamate (1) :

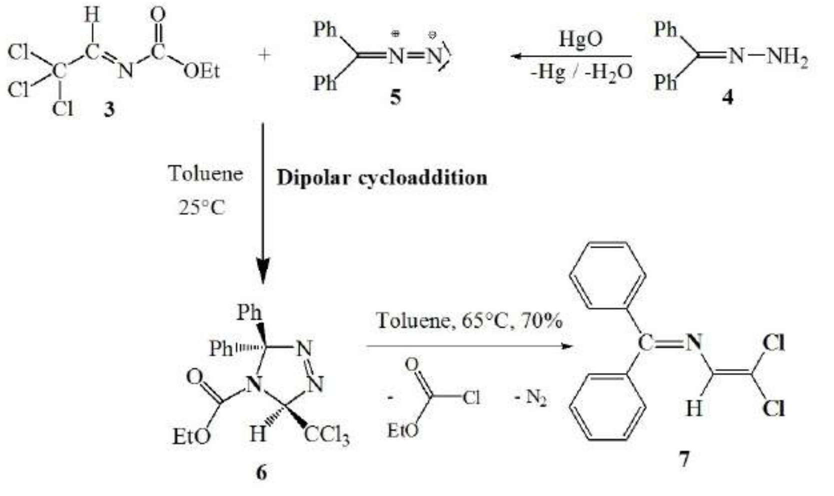
In an erlenmeyer ground of 250 mL, we introduce carefully 0.12 mol of chloral hydrate and 0.12 mol of urethane, the mixture is maintained under agitation during 1 hour until total liquefaction Then, 6.6 mL of concentrated hydrochloric acid are added. The mixture becomes confused then a precipitate of white color appears and becomes more marked with the addition of acid. Trained product is filtered and washed with cold distilled water up to neutral pH. After drying at 100°C in the steam room during a night, we obtain the desired product as a white powder with a yield of 95%.

Ethyl N-(1.2.2.2-tetrachloroethyl)carbamate (2) *:*

In a two-necked flask of 1 liter equipped with a gas trap, we introduce 0.098 mol of ethyl N-(1-hydroxy.2.2.2-trichloroethyl) carbamate (1), in 600 mL of an equivalent mixture of dichloromethane and toluene with a dropping funnel a mixture of 0.108 mol of thionyl chloride and 2 mL of pyridine diluted in 50 mL of toluene was added drop wise to the reaction mixture. Then the mixture was carried in reflux for 3 hours. Then the solvent is evaporated and the solid is dried under vacuum. After three extraction with 100 mL of dichloro-methane, draying under Na_2SO_4, and removing the solvent, we obtain compound **2** from a beige solid with a yield of 99%.

N-ethoxycarbonyl N-(2.2.2-trichloroehylidene) amine (3):

In a two nicked flask of 500 mL, 0.075 mol of N-(1.2.2.2-tetrachloroehyl ethyl carbamate (2) are solubilized in a mixture of 50 mL of dichloromethane and 150 mL of toluene. With a dropping funnel, 13 mL of $N(Et)_3$ are added drop wise in the reaction mixture. The white powder salt thus formed should be removed. Then the solution was concentrated in the rotary evaporator and cooled at 0°C over a night, the precipitate is again filtered then the solvent is evaporated. The raw



**4.4-Dichloro-1.1-Diphenyl-2-Aza
-1.3-Butadiene**

Scheme 2: Synthesis of 4.4-Dichloro-1.1-Diphenyl-2-Aza-1.3-Butadiene liquid is distilled under vacuum by means of a device " KUGELROHR ", 0.047 mole of the pure product in the form of a colorless liquid is obtained under a pressure of 0.18 mbar at 120°C.

3. Cycloaddition of diazomethane with imine

Imine was widely used as reactive dipolarophile in dipolar cycloaddition reaction to form heterocyclic compounds. During this study, the unexpected formation of 4.4-dichloro-1.1-diphenyl-2-azabuta-1.1-diene obtained by cycloaddition of diphenyl-diazomethane with imine in toluene at 65°C was described and discussed. It should be noted that the same reaction at room temperature was mentioned in the literature and lead to triazoline compound.

The hydrazones $Ar_2C=N-NH_2$ were prepared according to the literature and converted to Ar_2N_2 using yellow HgO [16-18].

Synthesis of triazoline: 5-trichloromethyl-2.2-diphenyl-1-ethoxycarbonyl-Δ^3-1.3.4-triazoline (6):

A Mixture of 1.86 mmol of diphenyldiazomethane **(5)** and 1.83 mmol N-ethoxycarbonyl N-(2.2.2-trichloroethylidene) amine **(3)** in 10 mL of toluene was stirring at room temperature during 2 days. The residue is filtered and washed with hexane. After vacuum drying 0.51 g of white powder are isolated. Note: after 4 days a change of the product color can be remarked, which turns from white to beige, indicating his decomposition. The product obtained was confirmed by IR, ^{1}H and ^{13}C NMR analysis.

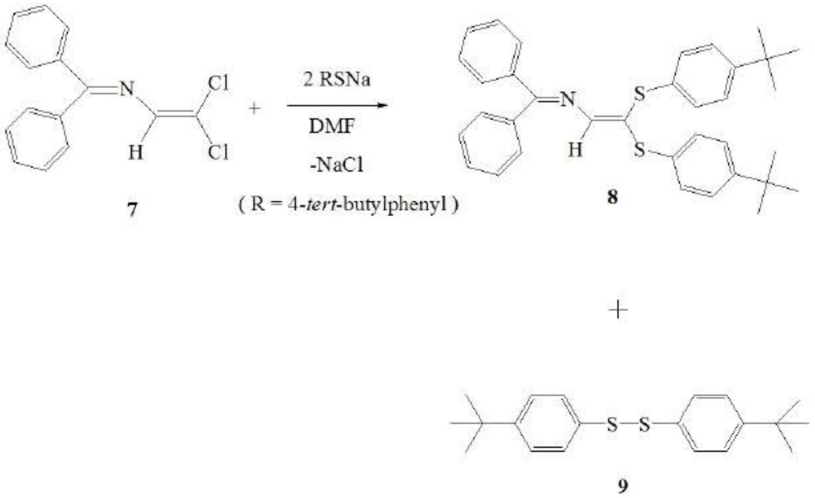
Reaction at 65°C: 4.4-dichloro-1.1-diphenyl-2-azabuta-1.3-diene (7):

In an erlenmeyer of 250 mL containing 0.018 mol of diphenyldiazomethane **2** dissolves in 40 mL of toluene, 0.018 mol N-ethoxycarbonyl N-(2.2.2-trichloroethylidene) amine **(1)** was added**.** Reaction mixture was carried at 60°C for 24 hours. Toluene was then evaporated and residual liquid of yellow color is precipitated into 10 mL of cooled ethanol. The precipitate is filtered then purified by chromatography using a mixture of petroleum ether dichloromethane (70/30) as eluent. 2.8 g of light yellow powder were obtained with 70 % yields. The product obtained was confirmed by IR, ^{1}H and ^{13}C NMR analysis.

4. Reactivity of 2-azabutadienes towards the thiolates of sodium

In previous studies, several strategies were developed for the synthesis of 2-azabuta-1.3-dienes substituted by thiolates group (-SR). In this context, we were interested in the development of a new π- conjugated dithioethers azadienic ligand. We recently reported the synthesis of $[(RS)_2C=CH-N=CPh_2]$, obtained by the reaction of $Cl_2C=CH-N=CPh_2$ (7) with an excess of 4-^{t}butylbenzenethiol from sodium in DMF at room temperature [17]. In these conditions, the reaction was incomplete. Indeed, we isolated the bisubstituted product $[(PhS)(Cl)C=C(H)-N=CPh_2]$ **8** accompanied with the dimmer **9** (scheme 3). After purification on column of silica in a mixture of hexane dichloro (80/20), the bisubstituted compound **8** is isolated in the form of a viscous yellow color liquid.

In a Schlenck-tube, we introduce 2.3 mmol of 4-*t*-butylbenzenethiol into 5 mL of anhydrous di-methylformamide, then adds 0.5 g of sodium, the mixture was stirring until total disappearance of



Scheme 3: Synthesis of 4.4-di*para*-^{t}butylphenylthio-1.1-diphenyl-2-azabuta-1.3-diene **8**

metal. Then, 1.086 mmol of 4.4-dichloro-1.1-diphenyl-2-azabuta-1.3-diene **(7)** was added. The reaction mixture was stored at room temperature for 24h. Then poured into water (100mL) and extracted with diethyl ether (150mL), organic solution was washed three times with water, dried over anhydrous sodium sulfate and evaporate. Finaly, the residue was purified by chromatography on column of silica gel using as eluent a mixture of hexane dichloro (80/20). 0.36 g of a yellow solid were obtained with a 70 % yield and 0.050g of the dimere. The product obtained was confirmed by IR, ^{1}H and ^{13}C NMR analysis.

5. Coordination of 2-azabutadienes to ReBr $(CO)_5$ and $RuCl(CO)_5$ complex

Carbonyl complexes of rhenium were very widely studied [20,21]. The carbonyl complexes of [MX $(CO)_3L$] (M = Re or Ru, X = Cl or Br and L = 8) was prepared by reacting ligand with the precursor mononuclear cell MX $(CO)_5$ (M = Re; X = Br) in the chloroform at 60°C or with the dimmer [MX $(CO)_3L]_2$ (M = Ru; X = Cl) in CCl_4 at room temperature. The complex mononuclear *fac*-[MX $(CO)_3L)$] were isolated in the form of a yellow powder stable in air with yields from 40 to 60 %.

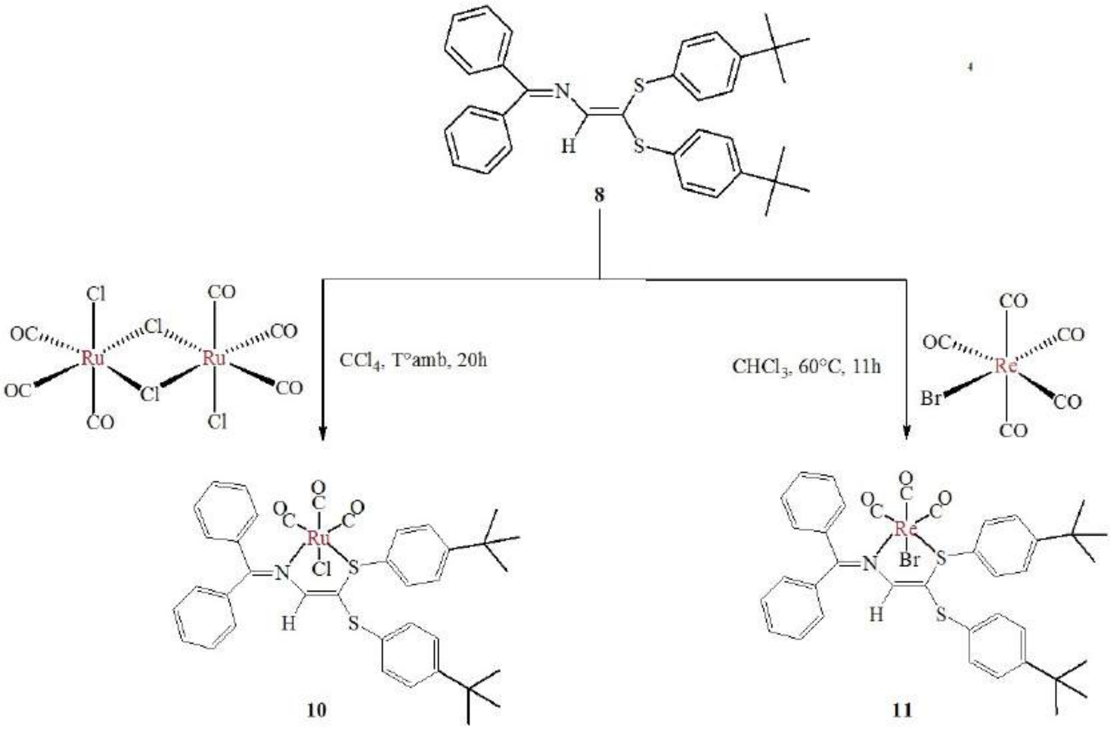
[RuCl(CO)$_3$L] : (10). In a Schlenck-tube containing 0.225 mmol of ligand **L(8)** dissolved in 3 mL of CCl_4, 0.112 mmol of the dimmer $[RuCl(CO)_3]_2$ was added. Then the reaction mixture is carried at room temperature. After 20 hours, the product precipitate by centrifugation then dried under vacuum. 0.045 g of a yellow solid are obtained with 40% yield. The product obtained was confirmed by IR, ^{1}H and ^{13}C NMR analysis.

[ReBr(CO$)_3$L$^]$: (11). In a Schlenck-tube containing 0.633mmol of the ligand **L(8)** dissolved in 3 mL of chloroform, 0.633 mmol of the precursor mononuclear ReBr(CO$)_5$ was added. Then the reaction mixture was carried at 50°C. After 17 hours, the precipitate is got back by centrifugation then dried under vacuum. 0.400 g of a yellow solid are obtained with 60% yield. The product obtained was confirmed by IR, ^{1}H and ^{13}C NMR spectra.

RESULTS AND DISCUSSION

1. ^{1}H , ^{13}C NMR and infrared of different compounds

The ^{1}H and ^{13}C NMR spectra of different products have been studied in $CDCl_3$ and are characterized with their assignments.



Scheme 4: Synthesis of complex.

1.1. Ethyl N-(1-hydroxy.2.2.2-trichloroethyl) carbamate (1)

Yield = 95%; MP: 116±1°C; IR-TF(ATR): υ(cm^{-1}) = 1530(s), 1676(s), 1705(s), 1728(s) (C=O), 2988 (m), 3287(m) (N-H), 3399(s) (O-H).

1.2. Ethyl N-(1.2.2.2-tetrachloroethyl)carbamate (2):

Yield = 99%; MP: 69±1°C; IR-TF(ATR): υ(cm^{-1}) = 1053(m). 1246(s), 1315(s), 1489(m), 1524(s), 1707(s), 1728(s) (C=O), 3291(m) (N-H).

1.3. N-ethoxycarbonyl N-(2.2.2-trichloroehylidene) amine (3):

Yield = 48%; IR-TF (KBr): υ(cm^{-1}) = 1240(s), 1279(m), 1340(m), 1477(m), 11499(m), 1685(m) (C=N), 1741(s)(C=O), 3031(m), 3061(m); ^{1}H NMR ($CDCl_3$): δ(ppm) = 1.40 (t, ^{3}J=6.8Hz.-CH_3). 4.36 (q, ^{3}J=6.8Hz. -CH2-). 8.17(s, H-C=N); ^{13}C NMR {^{1}H} ($CDCl_3$): δ(ppm) = 14.0 (-CH_3), 64.2 (-CH_2), 92.5 (C=N), 160.3 (CCl_3), 162.09(C=O).

1.4. Benzophenone hydrazone (4):

Yield= 97%; MP: 109±1°C; IR-TF(ATR): υ(cm^{-1}) = 1064(s), 1176(m), 1336(m),1443(m), 1491(m), 1573(m), 1609(m) (C=N), 3054(m), 3271(m), 3423(s).

1.5. Diphenyldiazomethane (5):

Yield=86%; IR-TF(ATR) :υ(cm^{-1}) = 1031(w), 1075(w), 1444(w),1495(m), 1577(w),1594(m), 2037(s) (C=N_2).

1.6. 5-trichloromethyl-2.2-diphenyl-1-ethoxycarbonyl-Δ^3-1.3.4-triazoline (6) :

Yield=70%; IR-TF(ATR): υ(cm^{-1}) = 1043(m), 1124(m), 1206(m), 1323(s) (C-O), 1375 (m),1401 (m), 1448 (m), 1708(s) (C=O), 2954(w); ^{1}H NMR ($CDCl_3$): δ(ppm) = 0.65 (3H , $CO_2CH_2C\underline{H_3}$), 3.40-4.00 (2H, $CO_2C\underline{H_2}CH_3$), 6.60-7.90 (m, 11H, 10 Ar-$\underline{H}$ + $\underline{H_a}$); ^{13}C NMR {^{1}H} ($CDCl_3$) : δ(ppm) = 13.2 ($CO_2CH_2\underline{C}H_3$), 62.8 ($CO_2\underline{C}H_2CH_3$), 96.2($\underline{C}Cl_3$), 109.6 ($\underline{C\text{-}5}$), 115.8 (s. $\underline{C\text{-}2}$), 125.0-131.0 (10 $\underline{C}$Har), 135.8 ($\underline{C}$ar) , 137.6 ($\underline{C}$ar), 155.5 ($\underline{C}$=O).

1.7. 4.4-dichloro-1.1-diphenyl-2-azabuta-1.3-diene (7):

Yield= 70%; MP: 127±1 C; IR-TF(ATR): υ(cm^{-1}) = 1031(m), 1076(m), 1119(m), 1190(m), 1280(m), 1296(s), 1323(s), 1446(s), 1491(m), 1549(C=N), 1587(C=C),2998(m); ^{1}H NMR ($CDCl_3$): δ(ppm) = 7.05(s, CH), 7.21-7.77(m, 10H, Ph); ^{13}C NMR {^{1}H} ($CDCl_3$): δ(ppm) = 123.5 (C. C-Cl). 128.3-133.6 (8C. Ar), 138.7 (C. CH), 168.5(C=N).

1.8. 4.4-di*para*-*t*butylbenzenethio-1.1-diphenyl-2-azabuta-1.3-diene (8)

Yield= 62%; IR-TF(ATR) : υ(cm^{-1}) = 1014(m), 1118(m), 1268(m), 1363(m), 1398(m), 1445(m), 1461(m). 1489(s), 1553(C=N), 1597(C=C), 2867 (s), 2903(s), 2961(s), 3059(m); ^{1}H NMR ($CDCl_3$): δ(ppm) = 1.31(s, 9H. $C(CH_3)_3$), 1.32(s, 9H. C $(CH_3)_3$), 7.01-7.21(m, 8H), 7.27-7.76(m, 11H); ^{13}C NMR {^{1}H} ($CDCl_3$): δ(ppm) = 31.3 (-CH_3, *t*-Bu), 34.5 (C, *t*-Bu), 125.1-133.7 (15C, Ar + C-S), 139.8 (C, CH), 150.3 and 150.7 (2C. Ar), 165.43(C=N).

1.9. 1.2-bis(4-tert-butylphenyl)disulfane (9)

Yield= 15%; IR-TF(ATR): υ(cm^{-1}) = 1117 (m),1250(m), 1398(m), 1489(m), 1558(m). ^{1}H NMR ($CDCl_3$): δ(ppm) = 1.34(s, 18H, $(CH_3)_6$), 7.01-7.21(m, 8H).

1.10. [$RuCl(CO)_3L$=8] : (10)

Yield= 40%; PD: 250±1°C. IR-TF(ATR): υ(cm^{-1}) = 2065(s) (CO),2085(s) (CO), 2144(s) (CO); ^{1}H NMR ($CDCl_3$): δ(ppm) = 1.30(s, 9H, $C(CH_3)_3$), 1.31(s, 9H, $C(CH_3)_3$), 7.18(s, 1H), 7.30-8.08(m, 18H).

1.11. [$ReBr(CO)_3L$=8] : (11)

Yield= 60%; IR-TF(ATR): υ(cm^{-1}) = 1910(w) (CO), 1941(w) (CO), 2034(w) (CO); ^{1}H NMR ($CDCl_3$): δ(ppm) = 1.31(s, 9H, $C(CH_3)_3$), 1.33(s, 9H, $C(CH_3)_3$), 7.27-7.39(m. 5H), 7.41-7.51(m, 8H), 7.57-7.67(m. 4H). 7.80-7.83(d,^{3}J = 7.8 Hz, 2H); ^{13}C NMR {^{1}H} ($CDCl_3$): δ(ppm) = 30.6 (-CH_3, *t*-Bu), 30.6 (C, *t*-Bu), 125.5-136.9 (19C, Ar + C-S), 142.1 (C, CH), 149.8 – 153.3 (3C, Ar), 177.20(C=N), 189.3-192.24 (3C, *C*≡O).

2. Infrared spectral study

Progression reactions was controlled by IR spectroscopy, in fact, the disappearance of vibration bands ν(CO) associated to initial complex $ReBr(CO)_5$ and the appearance of three intense new bands proves the reaction evolution, and the formation of complexes *fac*- [ReBr $(CO)_3$L] (11). Indeed, the three new bands assigned to the complex (11) are ν(CO) (2034; 1941 et 1910cm^{-1}) and two bands of the precursor $ReBr(CO)_5$ in ν (CO) (1990 et 2048 cm^{-1}).

3. Electronic properties

3.1. UV-visible absorption and emission ligand Spectrums

UV-visible absorption and emission normalized spectra of ligand **8** measured in dichloromethane at room temperature was reported in figure 1. The substitution of both chlorine atoms by (-S-4-tBuPh) group (**8**) is revealed by the appearance of a new band around 384 nm.

Table I: Values of absorption maxima and their coefficients of extinction molars partners, as well as the wavelengths of excitation and emission

Ligands	**Absorption UV-visible** **λ_{max} nm (ε $M^{-1}cm^{-1}$)^a**	**Emission** **λ_{excit}^{b} (λ_{em})^c nm**	**ϕ (%)^d**
8 (CH_2Cl_2)	255 (38000). 384 (23040)	330(427)	1.1

a) Values of the maxima of absorption and their coefficients of extinction molars partners; b) Wavelength of excitement (nm); c) Wavelength of emission (nm); d) Yield on fluorescence calculated with regard to $[Ru(bipy)_3]^{2+}$ in the dichloromethane at room temperature.

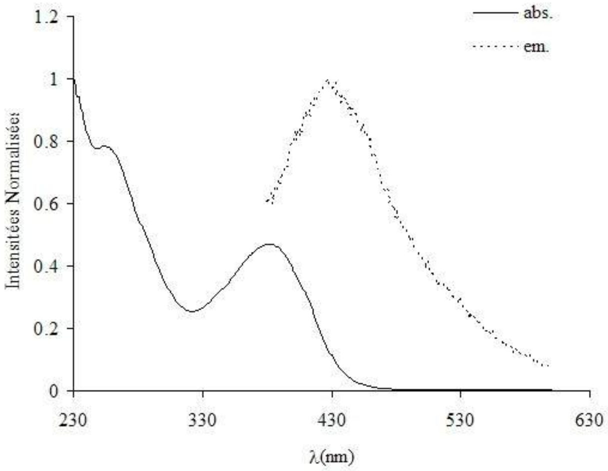


Fig. 1: Superposition of absorption and emission normalized spectra of ligand **8** measured in the CH_2Cl_2 at room temperature.

The excitation of ligand **8** in solution in CH_2Cl_2 with wavelengths going of 330 nm, leads to an emission with a maxima near 427 nm. This transmitting band observed for the ligand can be attributed without ambiguity to a radioactive deactivation of the singlet state S1. Quantum luminescence yields are relatively low for ligand **8**.

3.2. Complex UV-visible absorption and emission study

For the complex of ruthenium **10**, the excitation in 270 nm is translated by a transmitting band with one maxima respectively in 373 nm. This emission is independent from the wavelength of excitement indicating the presence of a single issuing energy level. The transmitting band of complex **10** is centered on the ligand.

For the complex of rhenium **11**, the excitement from (11) to 364 nm, is translated by a transmitting

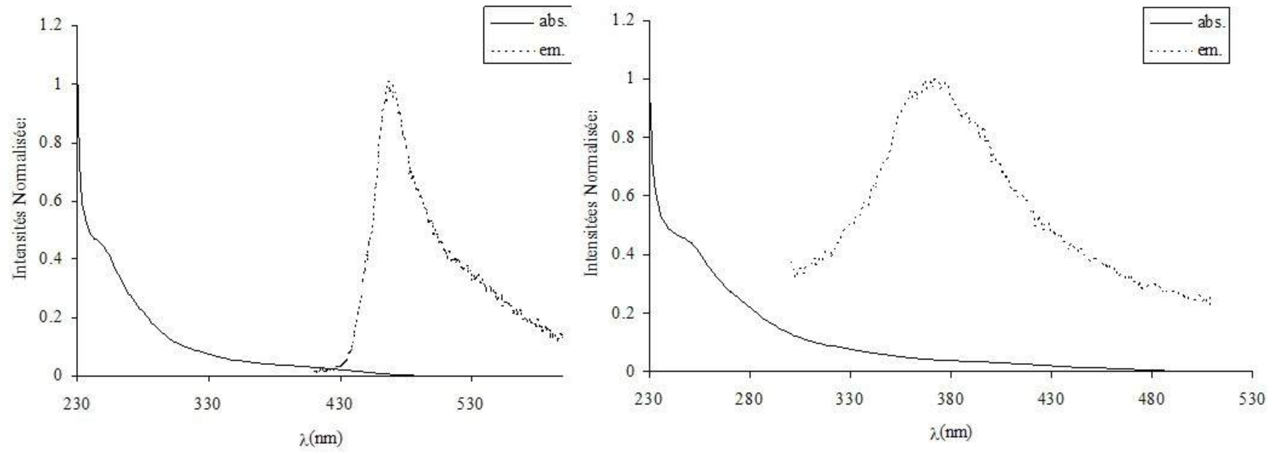


Fig. 2: Normalized UV-visible absorption and emission Spectra of complex **10** (to the right) and the complex **11** (to the left) measured in CH_2Cl_2 at room temperature.

band with one maxima in 470. The emission of this complex is characteristic of charge transfer bands from ligand towards Rhenium.

CONCLUSION

The objective of this work was the synthesis of a new 2-azabutadienes, and their functionalization by a thiolates group *via* a substitution-elimination reaction. The obtained results allowed us to conclude that the formation of 2-azabutadienes Ph_2C=N-CH=C $(SR)_2$ containing two thiol functions on the same carbon can be considered as an exceptional case. The capacity of these dithioether as S, N chelatant ligands through thioether and imine functions was the object of a study coordination with metals carbonyls complexes of Re (I) and Ru (II). The analyses of fluorescence spectra show that the emission Ru(II) complexes is essentially centered on ligand. Whereas, in the case of Re(I) complex is due to a bands of load transfer from ligand towards metal.

REFERENCES

[1] R. Kinghat, A. Khatyr, G. Schmitt, M. Knorr, M. M. Kubicki, E. Vigier, F. Villafañe, *Inorg. Chem. Commun*. **2008**. 1060.
[2] A. Padwa Ed.. *J. Wiley and Sons. Interscience.* 1.3-Dipolar Cycloaddition Chemistry. **1984**, 1 and 2.
[3] R. Huisgen. *Angew. Chem. Inter. Ed.* **1963**, *2*, 565.
[4] K. Mashima, Y. Matsuo, S. Nakahara. *J. of Organometallic Chem*., **2000**, *96*, 593.
[5] R. Siebenlist, H. W. Frühauf, K. Vrieze. *J of Inor. Chem*., **2000**, 2000, 907.
[6] a) L.F. Tietze, G. Kettschau. *Top. Curr. Chem.* **1997**, *1*, 189.
b) L. Ghosez. In Stereocontrolled organic synthesis; Backwell: Oxford. **1994**. 193.
c) J. Barluenga, M. Thomas, *Adv. Heterocyclic. Chem*. **1993**, *1*, 57.
[7] V. Lloveras, A. Carballero, A. Tarraga, M. Desamparados Velasco, A. Espinosa, K. Wurst, D.J. Evans, J. Vidal-Gancedo, C. Rovira, P. Molina, J. Vecina, *Eur. J. Inorg. Chem.* **2005**. 2436.
[8] a) T. Hirao. *Coord. Chem. Rev*. **2002**, 226, 81.
b) W. Y. Wong. *Coord. Chem. Rev*. **2005**. 249.
[9] a) F. Guyon, M.N. Jayaswal, H.N. Peindy, M. Knorr, N. Avarvari, *Synth. Met*. **2005,** *151*, 186.
b) M.N. Javaswal, H.N. Peindy, M. Knorr, N. Avarvari, M. Fourmigué, *Eur. J. Inorg. Chem.* **2004**. 2646.
[10] a) K. R. J. Thomas, J.T. Lin, K.J. Lin, *Organometallics.* **1999**, *18*, 5285.
b) M. Landman, M.V. Staden, H. Görls, S. Lotz, *Inorg. Chim. Acta*. **2005**, *358*, 2602.
[11] D. J. Temple, L. K. Johnson, R. L. Huff, P. S. White, M. Brook-hart, *J. Am. Chem. Soc.* **2000**, *122*, 6686.
[12] I. E. Buys, S. Elgafi,L.D. Field, T.W. Hambley, B.A. Messerle, *Inorg. Chem*. **1994**, *33*, 1539.
[13] R. Mosscheles. *Chem. Ber*. **1891**, 24, 1803.
[14] F. Feist. *Chem. Ber.* **1912**, *45*, 945
[15] H. Ulrich. B. Tucker and A.A.R. Sayigh. *J. Org. Chem.* **1968**, *33*, 2887.
[16] H. H. Szmant, C.McGinnis, *J. Am. Chem. Soc.* **1950**, 72, 2890.
[17] B. P. Giri, G. Prasad, K.N. Mehrotra Can. *J. Chem.* **1979**, *57*, 1157.
[18] W. Schroeder. L. Katz. *J. Org. Chem.* **1954**, *19*, 718.
[19] S. Jacquot-Rousseau, G. Schmitt, A Kathyr, M. Knorr, M.M. Kubicki, E. Vigier, O. Blacque. *Eur. J. Org. Chem*. **2006**. 1555.
[20] a) Progress in Inorganic chemistry.
b) Murray *Chem. Rev*. 81. **1981**. 365.
[21] G. Wu, D.R. Glass, D. May, W.H. Watson, D. Wiedenfeld, M.G. Richmond, *J. Organomet. Chem*. **2005**, *690*, 4993.