

Mono- and di-nuclear 2,3-diazabutadiene and 2-azabutadiene complexes of Rhenium(I): Syntheses, luminescence spectra and X-ray structures

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ARTICLE INFO

Article history:

Received 29 March 2008

Accepted 21 May 2008

Available online 27 May 2008

Keywords:

2-Azabutadiene

2,3-Diazabutadiene

Azine

Thioether

Rhenium

Luminescence

ABSTRACT

Treatment of $[\text{Re}(\text{CO})_3(\text{THF})(\mu\text{-Br})_2]$ with 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene $[\text{Cl}_2\text{C}=\text{C}(\text{H})-\text{N}=\text{CPh}_2]$ (**1a**) yields the di-nuclear benzophenone azine-bridged compound $[(\text{OC})_3\text{Re}(\mu\text{-Ph}_2\text{C}=\text{N}=\text{N}=\text{CPh}_2)(\mu\text{-Br})_2\text{Re}(\text{CO})_3]$ (**2a**), albeit in low yield. Alternatively, compounds $[(\text{OC})_3\text{Re}(\mu\text{-Ph}_2\text{C}=\text{N}=\text{N}=\text{CPh}_2)(\mu\text{-X})_2\text{Re}(\text{CO})_3]$ (**2a,b**) ($\text{X} = \text{Br}, \text{Cl}$) are obtained in high yields by direct reaction of $[\text{Re}(\text{CO})_3(\text{THF})(\mu\text{-Br})_2]$ or $[\text{Re}(\text{CO})_5\text{Cl}]$ with benzophenone azine. Nucleophilic attack of NaSPh on **1a** affords the 2-azabutadiene derivative $[(\text{PhS})(\text{Cl})\text{C}=\text{C}(\text{H})-\text{N}=\text{CPh}_2]$ (**1b**), which upon reaction with $[\text{Re}(\text{CO})_3(\text{THF})(\mu\text{-Br})_2]$ forms the *S,N*-chelate complex *fac*- $[(\text{OC})_3\text{ReBr}(\text{PhS})(\text{Cl})\text{C}=\text{C}(\text{H})-\text{N}=\text{CPh}_2]$ (**3**). The crystal structures of **1b**, **2a** and **3** have been determined and the luminescence properties of **2** and **3** have been investigated.

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Apart from their application in homogenous catalysis [1–4], transition metal complexes chelated by 1,4-diazabutadiene (diimine) ligands are studied experimentally and theoretically by numerous research groups due to their interesting photophysical properties. In particular, the rich photophysics of Re(I) compounds have been the subject of many articles [5–12]. In continuation in our work on the organic and coordination chemistry of 2-azabutadiene compounds [13], we have recently exploited the reactivity of the vinyl-chlorine bonds of $[\text{Cl}_2\text{C}=\text{C}(\text{H})-\text{N}=\text{CPh}_2]$ (**1a**) for oxidative addition reactions across low-valent metal centers to synthesize σ -alkenyl complexes *trans*- $[\text{MCl}\{(\text{C}(\text{Cl})=\text{C}(\text{H})-\text{N}=\text{CPh}_2)\}(\text{PPh}_3)_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) possessing a π -conjugated organic array [13c]. Furthermore, the functionalisation of **1a** by two thioether groups gives rise to polydentate ligand systems, thus allowing the preparation of cyclometallated Pd and Pt *C,N,S*-pincer complexes [13d].

With the objective to synthesize some rhenium complexes ligated by these 2-azabutadiene ligands for luminescence studies, we reacted $[\text{Re}(\text{CO})_3(\text{THF})(\mu\text{-Br})_2]$ [14a,14b] with two equivalent of **1a**. Unfortunately, the outcome of the reaction was not straightforward and gave a mixture of several products. We succeeded to isolate by recrystallisation from CH_2Cl_2 /heptane in a low yield of just 16% yellow air-stable crystals of the di-nuclear azine-bridged compound $[(\text{OC})_3\text{Re}(\mu\text{-Ph}_2\text{C}=\text{N}=\text{N}=\text{CPh}_2)(\mu\text{-Br})_2\text{Re}(\text{CO})_3]$ (**2a**). We

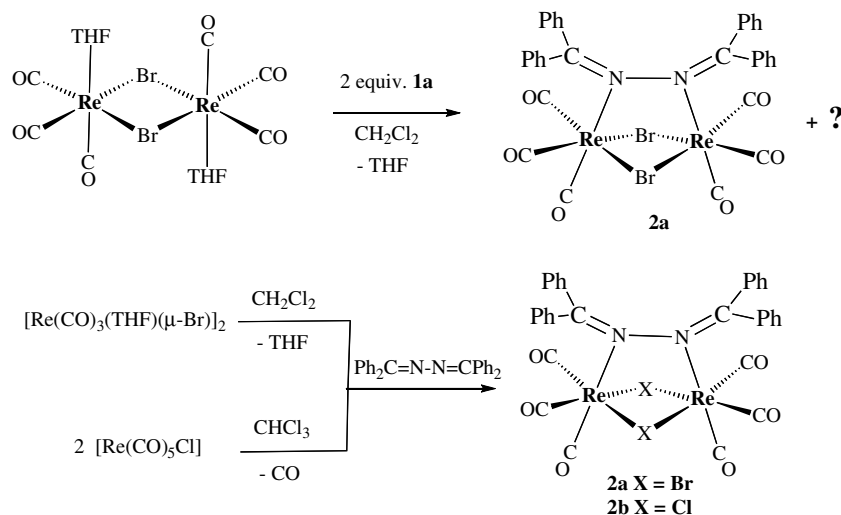
have not investigated in detail the mechanism of the scission of **1a**, and the nature of the other products formed in this reaction. We suppose that cleavage of **1a** may account for *in situ* formation of benzophenone azine, which then coordinates on $[\text{Re}(\text{CO})_3(\text{THF})(\mu\text{-Br})_2]$. Indeed, $[(\text{OC})_3\text{Re}(\mu\text{-Ph}_2\text{C}=\text{N}=\text{N}=\text{CPh}_2)(\mu\text{-Br})_2\text{Re}(\text{CO})_3]$ (**2a**) is also accessible in 81% yield by addition of independently prepared benzophenone azine to $[\text{Re}(\text{CO})_3(\text{THF})(\mu\text{-Br})_2]$ in a 1:1 ratio according Scheme 1.

As evidenced by an X-ray diffraction study, the di-nuclear bromide-bridged core motif of the precursor complex [14c] is also found in the solid-state structure of **2a** (Fig. 1).¹ The asymmetric unit of monoclinic lattice contains one di-nuclear complex molecule and one CH_2Cl_2 solvent molecule. The molecular structure of **2a** is quite similar to a series of complexes of the type $[(\text{OC})_3\text{Re}(\mu\text{-E-E})(\mu\text{-Br})_2\text{Re}(\text{CO})_3]$ ($\text{E} = \text{SPh}$ [15a], SMe [15b], SePh [15c], TePh [15d], PPh_2 [15e], SbPh_2 [15f]). The structure consists of two pseudo-octahedral Re(I) centers joined by a common $\text{Br} \cdots \text{Br}$ edge and a N–N azine bridge. Three last sites on each Re atom are occupied by terminal CO ligands in *fac*-geometry. The dihedral angle in the $\text{Re}(1)\text{--N}(1)\text{--N}(2)\text{--Re}(2)$ zigzag array amounts to $32.9(4)^\circ$. In the butterfly-like core

¹ Crystal data for **2a** (115(2) K) $\text{C}_{33}\text{H}_{22}\text{Br}_2\text{Cl}_2\text{N}_2\text{O}_6\text{Re}_2$: $M_r = 1145.65$, monoclinic, $P2_1/c$, $a = 17.5465(3) \text{ \AA}$, $b = 11.1189(2) \text{ \AA}$, $c = 18.9674(4) \text{ \AA}$, $\beta = 112.608(1)^\circ$, $V = 3416.1(1) \text{ \AA}^3$, $\mu = 9.623 \text{ mm}^{-1}$, $Z = 4$; $d = 2.228 \text{ g/cm}^3$, Mo $K\alpha = 0.71073 \text{ \AA}$, Nonius Kappa CCD; structure refined by full-matrix least-squares on F^2 to give final indices $R_1 = 0.0343$ and $wR_2 = 0.0760$; GOF = 1.046.

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Scheme 1.

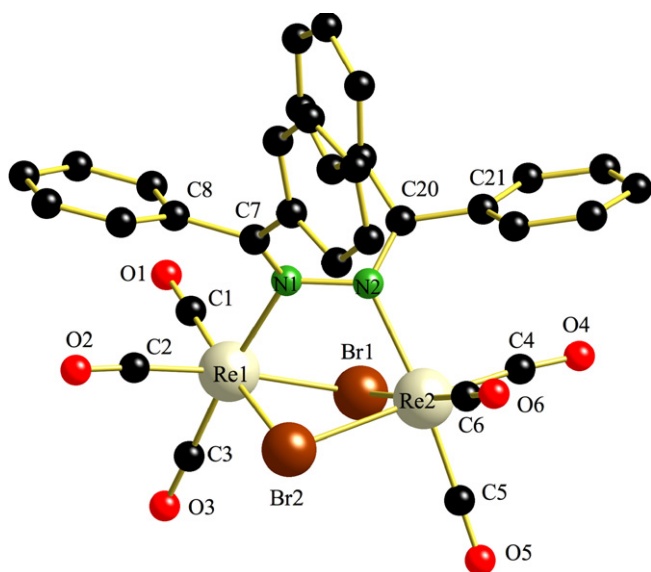
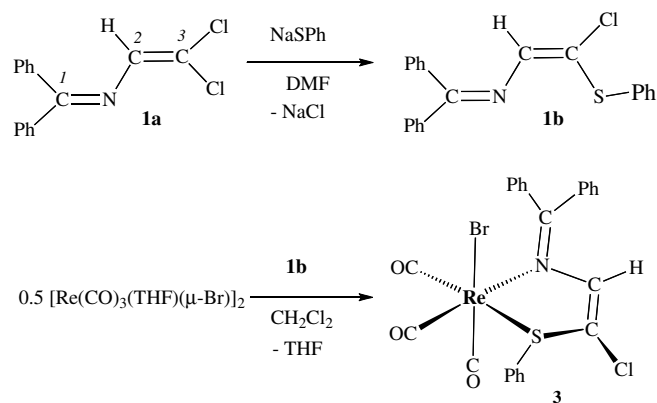


Fig. 1. View of the molecular structure of **2a**. Selected bond lengths [Å] and angles [°]: Re(1)–Re(2) 3.6958(3), Br(1)–Br(2) 3.4935(8), Re(1)–Br(1) 2.6090(6), Re(1)–Br(2) 2.6379(6), Re(2)–Br(1) 2.6351(6), Re(2)–Br(2) 2.6413(6), Re(1)–N(1) 2.253(4), Re(2)–N(2) 2.272(4), Re(1)–C(1) 1.900(6), Re(1)–C(2) 1.903(6), Re(1)–C(3) 1.908(6), Re(2)–C(4) 1.910(6), Re(2)–C(5) 1.921(6), Re(2)–C(6) 1.923(6), N(1)–N(2) 1.447(6), N(1)–C(7) 1.305(7), N(2)–C(20) 1.299(7); Re(1)–Br(1)–Re(2) 89.62(2), Re(1)–Br(2)–Re(2) 88.86(2), Br(1)–Re(1)–Br(2) 83.49(2), Br(1)–Re(2)–Br(2) 82.92(2), N(1)–Re(1)–Br(1) 85.9(1), N(1)–Re(1)–Br(2) 78.4(1), N(2)–Re(2)–Br(1) 77.6(1), N(2)–Re(2)–Br(2) 85.6(1), Re(1)–N(1)–N(2) 117.1(3), Re(2)–N(2)–N(1) 117.3(3).

formed by two equatorial $\text{ReBr}_2(\text{CO})_2$ seven-atom planes with shared Br1/Br2 edge the dihedral (*folding*) angle is equal to $37.0(1)^\circ$. When restricted to the four heavy atoms (Re, Br), this angle reaches $40.12(2)^\circ$. This is the largest folding angle observed in this di-nuclear family based on a $[(\text{OC})_3\text{Re}(\mu\text{-Br})_2\text{Re}(\text{CO})_3]$ core. On the other hand, the non-bonding Re...Re distance of $3.6958(3)$ Å is the shortest one reported for this family. In fact, both the folding angle and Re...Re distances depend on the E–E bond length, which is the shortest one [$1.447(6)$ Å] in azine-bridge of **2a**. The structural data show the following evolution of E–E and Re...Re separations (Å) and E–E folding angles (°): S_2Ph_2 2.140(9), 3.782(2), 33.0 [15a]; P_2Ph_4 2.308(6), 3.890(1), 23.4 [15e]; Te_2Ph_2 2.794(5), 3.945(2), 12.1 [15d]; Sb_2Ph_4 2.826(4), 3.970(2), 10.7 [15f]. Note that, apparently, this correlation



Scheme 2.

does not hold for $\mu\text{-Se}_2\text{Ph}_2$ complex, but the X-ray structure is of quite poor quality [15c]. Compared with the N–N bond distance of uncoordinated benzophenone azine, that of **2a** is somewhat elongated ($1.402(12)$ Å vs. $1.447(6)$ Å); in contrast, the C=N imine bonds ($1.287(9)$ Å vs. $1.302(7)$ Å) remain equal within the standard deviation [16].

The chloro-bridged derivative $[(\text{OC})_3\text{Re}(\mu\text{-Ph}_2\text{C=N-N=CPh}_2)(\mu\text{-Cl})_2\text{Re}(\text{CO})_3]$ (**2b**) was isolated as a yellowish crystalline solid after heating a CHCl_3 solution of $[\text{Re}(\text{CO})_5\text{Cl}]$ with benzophenone azine.² Note that reports on metal complexes with benzophenone azine as ligand are quite scarce [17]. One rare example is the complex $\text{cis-[Pt(C}_6\text{F}_5)_2(\eta^1\text{-Ph}_2\text{C=N-N=CPh}_2)(\text{CO})]$, with benzophenone azine acting as monodentate ligand [18]. This bonding mode has also been structurally evidenced for $[(\text{C}_6\text{F}_5)\text{Au}(\eta^1\text{-Ph}_2\text{C=N-N=CPh}_2)]$ [19].

Functionalization of azabutadiene **1a** by addition of 1.2 equivalent of sodium thiophenolate in dry DMF leads under mild conditions in a stereospecific manner to the thioether derivative $[(\text{PhS})(\text{Cl})\text{C=C(H)-N=CPh}_2]$ (**1b**) (Scheme 2) [13e,13f]. An X-ray diffraction analysis performed on this yellowish crystalline solid confirmed the conservation of the *transoid* conformation of the azabutadiene array found in precursor **1a** and the *cis*-disposition

² Selected data for **2b**: IR (CH_2Cl_2): 2044m, 2031s, 1936vs, 1913s cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_6\text{Re}_2$: C, 36.32; H, 1.94; N, 2.57. Found: C, 36.40%; H, 1.95%; N, 2.66%.

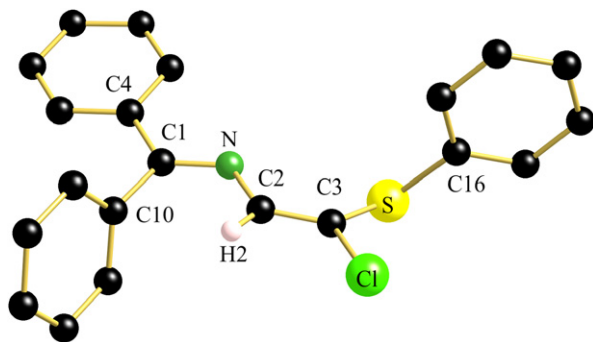


Fig. 2. View of the molecular structure of **1b**. The aromatic hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N–C(1) 1.297(3), N–C(2) 1.391(3), C(2)–C(3) 1.335(3), C(3)–Cl 1.747(3), C(3)–S 1.736(3), S–C(16) 1.773(3), C(1)–C(4) 1.479(4), C(1)–C(10) 1.497(3); S–C(3)–Cl 117.0(2), C(2)–C(3)–S 125.1(2), C(2)–C(3)–Cl 117.8(2), N–C(2)–C(3) 122.9(3), C(1)–N–C(2) 118.6(2), N–C(1)–C(4) 119.1(3), N–C(1)–C(10) 122.6(2), C(4)–C(1)–C(10) 118.4(2), C(3)–S–C(16) 102.1(1).

of the thioether and the imine group about the vinylic C=C bond (Fig. 2).³

Ligand **1b** is readily coordinated quantitatively within 1 h in a halide-bridge cleavage reaction on $[\text{Re}(\text{CO})_3(\text{THF})(\mu\text{-Br})_2]$ leading to the *S,N*-chelate complex *fac*- $[(\text{OC})_3\text{ReBr}\{(\text{PhS})(\text{Cl})\text{C}=\text{C}(\text{H})\text{-N}=\text{CPh}_2\}]$ (**3**), which was isolated in 84% yield in form of a red air-stable solid.⁴

The *fac*-arrangement of the three carbonyls and the *S,N*-chelation of the azabutadiene ligand is also corroborated by an X-ray diffraction analysis performed on a single crystal of complex **3** (Fig. 3).⁵ The octahedral coordination sphere around Re consists of a 5-membered *S,N*-bound organic chelate ring, a bromo ligand in *cis*-position relative to the imine-N atom and the sulphur atom, and three facially arranged carbonyl ligands. The Re–Br bond length compares with that of $[\text{ReBr}(\text{CO})_5]$ [2.6269(5) Å vs. 2.619(2) Å] [20]. The Re–N bond length of 2.266(3) Å lies in the same range as the mean Re–N value of **2a** [2.263(4) Å], the C=N bond distance of the chelating azabutadiene ligand is markedly longer than that of **1b** [1.335(5) Å vs. 1.299(3) Å]. Probably due to the rigidity of the chelate ring, the dative Re–S bond of 2.464(1) Å is somewhat shorter than the averaged Re–S distance of about 2.50 Å encountered in other Re(I) complexes ligated by PhS–thioether donors [21–23]. Probably for the same reason, some π -conjugation between one phenyl [C(4) through C(9)] and the azadiene chain C(1)–N–C(2)–C(3) observed in the ligand **1b** (dihedral angle = 12.5(2)°) is broken upon complexation in **3** [dihedral angle = 52.5(3)°]. The dihedral angle between the SPh-substituent and the azadiene chain remains with 87.4(2)° unchanged in both the structures of **1b** and **3**. Overall, the ligand arrangement of **3** is reminiscent to that reported for the *S,N*-chelate complex *fac*- $[(\text{OC})_3\text{ReBr}\{\text{bis}(\text{methylthio})\text{pyrrolo}[1,2\text{-}a]\text{benzimidzol-1-one}\}]$ [24].

The electronic absorption spectra of the di-nuclear complexes **2a** and **2b** display both one maximum at 267 nm with a shoulder

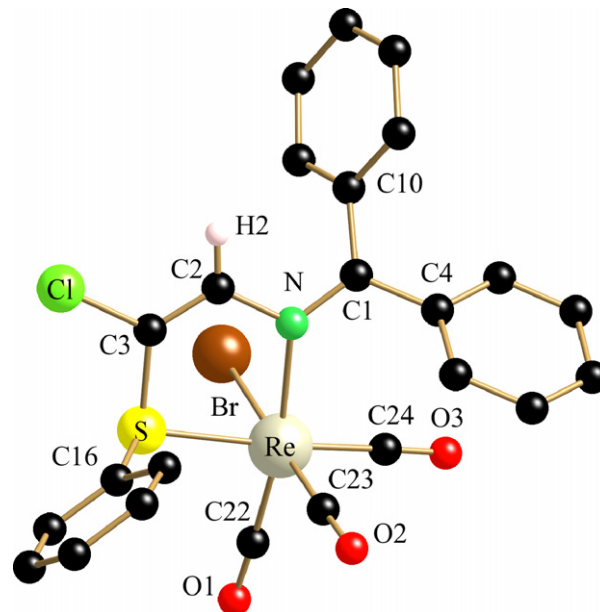


Fig. 3. View of the molecular structure of **3**. The aromatic hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re–Br 2.6269(5), Re–S 2.464(1), Re–N 2.266(3), Re–C(22) 1.919(4), Re–C(23) 1.900(5), Re–C(24) 1.924(5), C(3)–S 1.762(4), C(3)–Cl 1.739(4), C(2)–C(3) 1.323(6), N–C(2) 1.411(5), N–C(1) 1.335(5); N–Re–Br 80.83(9), N–Re–S 80.44(9), N–Re–C(22) 170.2(2), N–Re–C(23) 97.7(1), N–Re–C(24) 98.9(1), S–Re–C(24) 172.7(1), S–Re–C(23) 98.4(1), S–Re–C(22) 92.0(1), Br–Re–S 81.07(3), C(22)–Re–Br 91.8(1), C(23)–Re–Br 178.5(1), C(24)–Re–Br 91.6(1), N–C(2)–C(3) 121.7(4), C(1)–N–C(2) 117.4(3), S–C(3)–C(2) 123.8(3).

around 360 nm. Upon excitation at 460 nm, two similar broad, structureless emission maxima at 508 and 535 nm are observed. The emissions of **2a,b** depend slightly on the excitation wavelength and are comparable to those reported for other dimeric rhenium complexes of this kind [25]. The absorption spectrum of **3** exhibits two maxima at 270 and 344 nm. After excitation of **1b** and **3** at 360 and 450 nm, the emission maxima were observed at 450 and 617 nm, respectively (Fig. 4). Emissions in a similar spectral range have been observed in *fac*- $\text{XRe}(\text{CO})_3(\alpha\text{-diimine})$ compounds and were attributed to an emission from a MLCT excited state [6a,5].

In conclusion, it has been demonstrated for the first time that benzophenone azine may act as bridging ligand. The preparation of complexes $[(\text{OC})_3\text{Re}(\mu\text{-Ph}_2\text{C}=\text{N}=\text{N}=\text{CPh}_2)(\mu\text{-Hal})_2\text{Re}(\text{CO})_3]$ **2** completes the literature-known series of related di-nuclear complexes $[(\text{OC})_3\text{Re}(\mu\text{-Ph}_n\text{EPh}_n)(\mu\text{-Hal})_2\text{Re}(\text{CO})_3]$ (E = S, Se, Te, P, As, Sb). As shown in the case of the *S,N*-chelate complex **3**, ligand **1b** is prone to ligate to metal centers both via the soft thioether

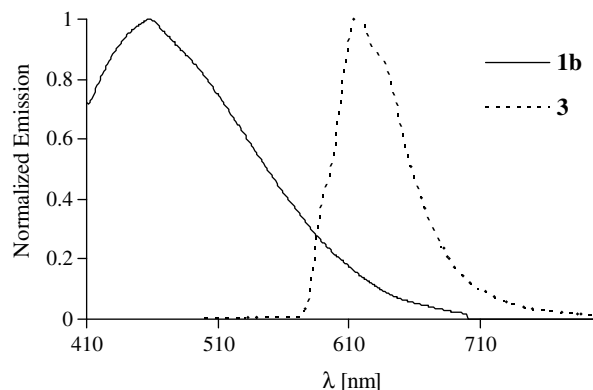


Fig. 4. Normalized emission spectra of **1b** and **3** in CH_2Cl_2 at room temperature.

³ Crystal data for **1b** (293(2) K) $\text{C}_{21}\text{H}_{16}\text{ClNS}$: $M_r = 349.86$, orthorhombic, $Pcab$, $a = 9.8697(2)$ Å, $b = 16.1390(4)$ Å, $c = 22.8024(6)$ Å, $V = 3632.1(1)$ Å³, $\mu = 0.326$ mm^{−1}, $Z = 8$; $d = 1.280$ g/cm³, Mo $K\alpha = 0.71073$ Å, Nonius Kappa CCD; structure refined by full-matrix least-squares on F^2 to give final indices $R_1 = 0.0469$ and $wR_2 = 0.0913$; GOF = 0.866.

⁴ Selected data for **3**: IR (CH_2Cl_2): 2036 vs., 1945 s, 1907 s cm^{−1}. ¹H NMR (CDCl_3): δ 7.18–7.94 (m, 16H, phenyl + H_{vinyl}). Anal. Calc. for $\text{C}_{24}\text{H}_{16}\text{BrNO}_3\text{ReS}$: C, 41.18; H, 2.30; N, 2.00. Found: C, 40.98%; H, 2.16%; N, 2.03%.

⁵ Crystal data for **3** (at 120(2) K) $\text{C}_{24}\text{H}_{16}\text{BrNO}_3\text{ReS}$: $M_r = 700.00$, monoclinic, $P2_1/n$, $a = 14.2621(3)$ Å, $b = 9.4314(2)$ Å, $c = 18.3687(3)$ Å, $\beta = 110.369(2)^\circ$, $V = 2316.30(8)$ Å³, $Z = 4$, $d = 2.007$ g/cm³; Nonius Kappa CCD, Mo $K\alpha = 0.71073$ Å, $\mu = 6.850$ mm^{−1}, structure refined by full-matrix least-squares on observed F^2 to give final indices $R_1 = 0.0365$ and $wR_2 = 0.0714$, GOF = 0.967.

function and the harder imine nitrogen. In order to investigate and to understand in more detail the photophysical properties of other *S,N*-chelate complexes, we are currently preparing a series of Mn(I), Re(I) and Ru(II) complexes ligated by various functionalized 2-azabutadiene ligands of type [(RS)₂C=C(H)–N=CAr₂].

Acknowledgement

Financial support from the Région of Franche-Comté for a Horiba JOBIN-YVON Fluorolog fluorescence spectrometer is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 682377, 682378 and 682379 contain the supplementary crystallographic data for **1b**, **2a** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.05.022.

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(f) Regioselective formation of the *cis*-isomer *Z*-[(PhS)(H)C=C(H)–Fc] is also observed upon attack of NaSPh on 2,2-dibromo-vinylferrocene-[Br₂C=C(H)–Fc] (see Ref. [23]).
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