A New Dichroic, Nitroso-Bridged Complex of Rhenium: Di-μ_2-chloro[μ_2-(η^2-*N*,*O*)-*N*,*N*-dimethyl-4-nitrosoaniline]bis[tricarbonylrhenium(I)]

Roland Wilberger,[a] Christoph Krinninger,[a] Holger Piotrowski,[a] Peter Mayer,[a] and Ingo-Peter Lorenz*[a]

Keywords: Rhenium / C,N ligand / N,O bridge / Dichroism

The dimeric μ_2-amino-phenoxy complexes of rhenium $[(CO)_3Re(\mu_2\text{-}O^{\cap}NH_2)]_2$ (**1**) do not react with the *C*-nitroso compounds $R{-}C_6H_4NO$ [R = NMe_2 (**2**), H (**2′**)] in the presence of $AlCl_3$ by a condensation reaction to give the desired azo dye complexes $[(CO)_3Re(\mu_2\text{-}O^{\cap}N{=}NC_6H_4R)]_2$. Instead, they react to give the novel neutral η^2-*N*,*O*-bridged *C*-nitroso complexes $[\{CO)_3ReCl\}_2ONC_6H_4R]$ (**3**, **3′**) by means of a substitution reaction. Both complexes yield golden gleaming crystals, and their solutions are deeply blue (**3**) or violet (**3′**) due to the broad UV/Vis absorption at λ = 617 (**3**) and 505 nm (**3′**). Single crystals of **3**, **3′** show nonlinear optical properties, they are dichroic and have a red and blue (**3**) or violet and green (**3′**) side. The molecular structures of **3**, **3′** have been determined by single-crystal X-ray analyses. Both compounds contain two face-joined octahedra, with two chloro and the NO ligands as bridges. The *C*-nitroso groups together with the NC_2 moiety of NMe_2 (**3**) lie almost exactly within the symmetry plane of the molecules. Both the N atoms of **3** have a trigonal-planar geometry. **3** and **3′** are the first single, neutral and dinuclear *C*-nitroso complexes with the rare non-assisted μ-(η^2-*N*,*O*) bridge and only single atoms as additional bridges.

Introduction

Recently we reported on the syntheses and structures of several dimeric μ_2-O amino-phenoxy complexes of rhenium of the type $[(CO)_3Re(\mu_2\text{-}O^{\cap}NH_2)]_2$ as well as on their condensation reactions with acetone to give the corresponding Schiff base products $[(CO)_3Re(\mu_2\text{-}O^{\cap}N{=}CMe_2)]_2$ in almost quantitative yields.[1] Because of the high reactivity and good selectivity of the complexes $[(CO)_3Re(\mu_2\text{-}O^{\cap}NH_2)_2]$ towards organic carbonyl compounds, the analogous condensation reaction with *C*-nitroso compounds should also be possible and should yield an N=N bond and hence the directed synthesis of azo dyes in the coordination sphere of a transition metal atom. The starting materials, however, did not react, and refluxing them for more than 2 h led to their decomposition. Attempts to catalyze the desired reaction by addition of some $AlCl_3$ for activating the nitroso compound immediately changed the situation. After a few minutes, the solution turned deep blue, and finally an almost black solid was separated, though in bad yield. Its characterization proved it to be the novel, neutral η^2-*N*,*O*-bridged nitroso complex $\{(CO)_3ReCl\}_2ONC_6H_4N(CH_3)_2$ (**3**).

There are three types of R_xNO-containing complexes ($x = 0, 1$). The first one ($x = 0$) is the large and well-known group of nitrosyl complexes.[2,3] They show the terminal linear (η^1-NO, 3e-donor), bent (η^1-NO, 1e-donor) or bridging μ_n-NO ligand function ($n = 2-4$). Even in the NO-containing triply bridged rhenium dimer, which is similar to **3**, the NO ligand is to be found in the terminal position.[4] Recently, metastable states of $[(CN)_5FeNO]^{2-}$ were detected with side-on-bound NO (η^2-NO) and η^1-ON ligands (isonitrosyl).[5]

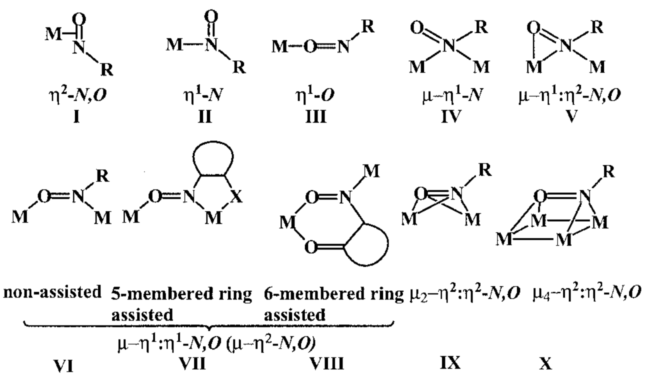
The next family are RNO$^{\cdot}$ nitroxyl radicals, which normally coordinate through the oxygen atom.[6] Jaitner et al., however, reported on the η^2-*N*,*O* coordination of the special 2,2,6,6-tetramethylpiperidine-1-oxyl (= TEMPO).[7]

The coordination chemistry of organic RNO nitroso compounds has also been investigated,[8] their different ligand functions are summarized in Scheme 1. The terminal η^2-*N*,*O* ligand function (**I**) dominates,[9] the η^1-*N*,*O* linkage through the nitrogen atom (**II**) has also been well documented,[10,11] whereas that through the oxygen atom (**III**) has rarely been found.[12] The *C*-nitroso group may also bridge two metal centers in an η^1-*N* (**IV**),[11] an η^1- and η^2-fashion [μ-(η^1:η^2-*N*,*O*), **V**][13] or as an η^2-*N*,*O* moiety [μ-(η^1:η^1-*N*,*O*), **VI**]. The latter simply as a bridging ligand is less common;[11,14,15] most examples are known with supporting second coordination by a further donor system forming in addition a five- (**VII**)[16] or six-membered ring (**VIII**).[17] Only a few examples are known for bridging two metal atoms [μ_2-(η^2:η^2-*N*,*O*), **IX**][18] or four metal atoms

---

[a] Ludwig-Maximilians Universität München, Department of Chemistry,
Butenandtstraße 5−13, 81377 München, Germany
Fax: (internat.) + 49-(0)89-2180-77867
E-mail: ipl@cup.uni-muenchen.de

DOI: 10.1002/ejic.200300928

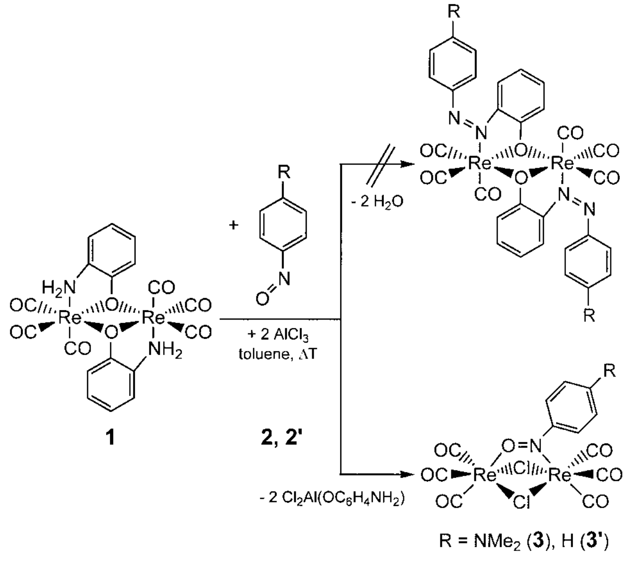


Scheme 1. Coordination modes of *C*-nitroso ligands

[μ_4-(η^2:η^2-*N*,*O*), **X**].[19] To the best of our knowledge type **VI** is only realized, besides a special case[11] in cationic dimers, with two further μ_2-thiolato bridges.[14]

Results and Discussion

The bad yield mentioned above and the chloro bridges of **3** led us to repeat the reaction not catalytically, but stoichiometrically. The reaction of **1**, **2** and $AlCl_3$ in the molar ratio 1:1:2 in boiling toluene for 5−10 min resulted in the formation of neutral di-μ_2-chloro[μ_2-(η^2-*N*,*O*)-*N*,*N*-dimethyl-4-nitrosoaniline]bis[tricarbonylrhenium(I)] (**3**; Scheme 2), and, indeed, the yield rose to about 70%. The same reaction was repeated with **1**, **2′** (nitrosobenzene) and $AlCl_3$, and the analogous nitroso complex **3′** was obtained. Many nitroso complexes have been synthesized by reduction of organic nitro compounds, which may proceed through an intermediate nitroso compound,[8] or by a nitrosyl migration reaction.[8]



Scheme 2. Synthesis of **3**, **3′**

Compounds **3** and **3′** are obtained as golden gleaming crystals, which are stable towards air. They are soluble in THF, toluene, ketones and CH_2Cl_2 and even in pentane (**3′**). Compound **3** is not soluble in pentane. Solutions of **3** and **3′** in $CHCl_3$, CH_2Cl_2, THF or toluene are deep blue or violet, respectively. In the UV/Vis spectrum ($CHCl_3$) one very broad absorption at $\lambda = 617$ (**3**) and 505 nm (**3′**) due to a ligand-to-metal CT band [NO−Re(I)] is observed, which is shifted to lower frequency than the corresponding electronic transition ($\pi-\pi^*$ NO) of the ligands **2** (λ = 419 nm) and **2′** (λ = 306 nm). Single crystals of **3** and **3′** show non-linear optical properties; they are dichroic and viewed by transmitted light; they have a red and a blue (**3**) or violet and green side (**3′**), respectively. The absorption maxima of **3** are found at λ = 495 and 575 nm, those of **3′** have not yet been measured because of technical problems.

The IR spectra of **3**, **3′** in CH_2Cl_2 show four ν(CO) absorptions. As the NO group coordinates to one rhenium center with the nitrogen atom and to the other with the oxygen atom, the electronic situation at both rhenium centers is different. Therefore, there are two different $Re(CO)_3$ fragments, each with C_{3v} local symmetry, and we observe two separated patterns of ν(CO) (A_1 + E). Resulting from electronic reasons, the two absorptions at higher wavenumbers are assigned to the $\{(CO)_3Re-N\}$ fragment [$\tilde{\nu}$ = 2041 (A_1), 1946 (E) cm^{-1}], whereas the two at $\tilde{\nu}$ = 2024 (A_1) and 1917 (E) cm^{-1} belong to the $\{(CO)_3Re-O\}$ fragment as in **3**. The ν(NO) of **3** absorbs significantly lower at $\tilde{\nu}$ = 1605 cm^{-1}.

The ^1H NMR spectrum of **3** (in [D_8]THF) shows two singlets at δ = 3.54 and 3.55 ppm for the *N*-methyl protons, and the four double-doublets for the different pairs of *o*- and *m*-phenyl protons (see Exp. Sect.), that of **3′** (in CD_2Cl_2) exhibits only the multiplet at δ = 7.34−7.65 ppm for the phenyl protons. In the $^{13}C\{^1H\}$ NMR spectrum of **3** (in [D_8]THF) each carbon atom of the NMe_2 group and of the phenyl ring is found by separated signals between δ = 30 and 160 ppm; the signals of the CO ligands appear at δ = 190−200 ppm. The signals of the carbon atoms of **3′** are observed at δ = 129.1−131.3 ppm (phenyl) and δ = 188 ppm (CO) (in $CDCl_2$).

In the mass spectra of **3**, the parent peak as well as all signals of fragments resulting from the loss of up to six carbonyl groups are observed.

The composition and structure of complex **3** was confirmed by X-ray structure analysis; single crystals were obtained by diffusion of pentane into a solution of **3** in $CHCl_3$. The molecular structure and selected bond lengths and angles are given in Figure 1,[20] which shows two face-joined octahedra with two chloro and the NO ligands as bridges. The distance N(1)−O(1) is 1.319(8) Å and clearly longer than the N−O distance in the free *N*,*N*-dimethyl-4-nitrosoaniline (1.212 Å[21]). The bond Re(1)−O(1) [2.131(6)] is shorter than the Re(2)−N(1) [2.208(7)], whereas all Re−Cl bonds in the bridge are exactly the same [Re(1)−Cl*n* = 2.49 Å, Re(2)−Cl*n* = 2.49 Å). The dihedral angles Re(1)−O(1)−N(1)−Re(2) and O(1)−N(1)−C(1)−C(6) are 6.54° or 12.00°, respectively; that is, the NO group

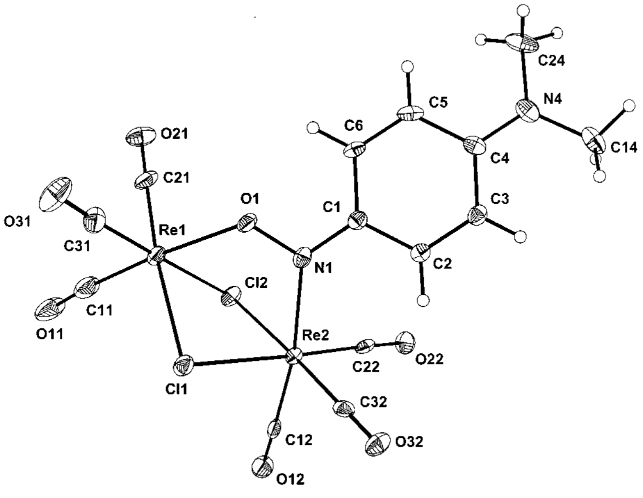


Figure 1. Molecular structure of **3**; selected bond lengths [Å] and angles [°]: Re(1)−C(11) 1.882(11), Re(1)−C(21) 1.887(10), Re(1)−C(31) 1.913(11), Re(1)−O(1) 2.131(6), Re(1)−Cl(2) 2.492(2), Re(1)−Cl(1) 2.497(2), C(11)−O(11) 1.175(13), C(21)−O(21) 1.161(11), C(31)−O(31) 1.132(11), Re(2)−C(22) 1.889(9), Re(2)−C(32) 1.891(9), Re(2)−C(12) 1.922(10), Re(2)−N(1) 2.208(7), Re(2)−Cl(2) 2.490(2), Re(2)−Cl(1) 2.493(2), C(12)−O(12) 1.145(10), C(22)−O(22) 1.170(10), C(32)−O(32) 1.169(10), O(1)−N(1) 1.319(8); C(21)−Re(1)−Cl(2) 95.6(3), Cl(2)−Re(1)−Cl(1) 80.69(7), O(1)−N(1)−C(1) 113.4(7), Re(2)−Cl(1)−Re(1) 90.36(7), Re(2)−Cl(2)−Re(1) 90.53(6)

lies almost within the symmetry plane of the molecule, whereas the phenyl ring is larger and turned out of this plane. It is noteworthy that both the nitrogen atoms are exactly trigonal planar in geometry [sum of angles for N(1) = 359°, for N(4) = 360°], consistent with their sp^2 nature. The analogous molecular structure was also found for **3′**, and is given in Figure 2.[20] In both compounds there is no Re−Re interaction [Re(1)−Re(2) 3.540 Å (**3**), 3.463 Å (**3′**)].

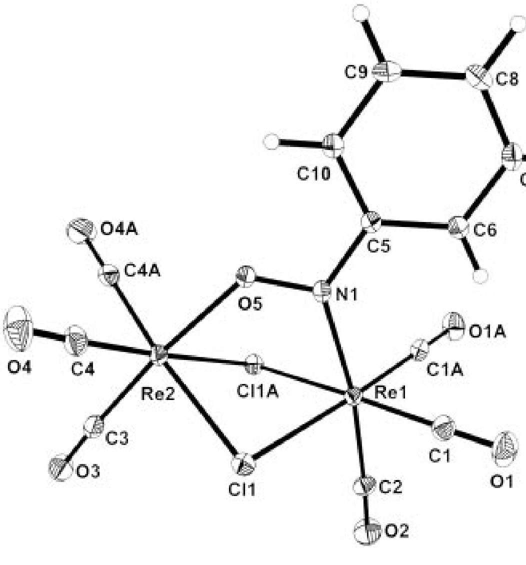


Figure 2. Molecular structure of **3′**; selected bond lengths [Å] and angles [°]: Re(1)−C(1) 1.906 (5), Re(1)−C(2) 1.976 (6), Re(1)−Cl(1) 2.4829 (12), Re(1)−N(1) 2.092 (5), Re(2)−C(3) 1.930 (8), Re(2)−C(4) 1.904 (6), Re(2)−Cl(1) 2.4829 (12), Re(2)−O(5) 2.106 (4), O(5)−N(1) 1.282 (7), N(1)−C(5) 1.440 (8), C(1)−O(1) 1.145 (6), C(2)−O(2) 1.124 (8), C(3)−O(3) 1.151 (9), C(4)−O(4) 1.144 (7); C(1)−Re(1)−Cl(1) 94.92 (14), O(5)−N(1)−C(5) 110.5 (5), Re(1)−Cl(1)−Re(2) 88.41 (4).

Compounds **3** and **3′** are the first simple, neutral and dinuclear *C*-nitroso complexes which have the very rare non-assisted μ-(η^2-*N*,*O*) bridge (**VI**) and only single atoms as additional bridges, and which have been synthesized directly by means of nitroso compounds as starting materials. Their observed dichroism may be derived from the special ligand function of the nitroso compound and of its placement exactly in the plane of symmetry of **3** and **3′**. In a recent paper[22] a very similar structure of dialkylnitrosoamine complexes (*N*-nitroso ligand) of Cu^{II} with the same μ-(η^2-*N*,*O*) coordination and with the NO group roughly parallel to the Cu−Cu direction. Their single crystals, however, do not exhibit the dichroic effect.

First attempts using AlX_3 (X = Br, I) instead of $AlCl_3$ resulted in the formation of the corresponding bromo- and iodo-bridged dinuclear complexes. The μ_2-*O*-bridged precursor **1** apparently serves as a source for $Re(CO)_3$ fragments. Therefore, it might be assumed that $[Re(CO)_5Cl]$ can be used instead of **1**. First attempts with $[Re(CO)_5Cl]$ and **2** show that **3** is indeed formed.

Experimental Section

General: To remove oxygen, all operations were carried out under Ar in dry and Ar-saturated solvents.[23] $[(CO)_3Re(\mu_2\text{-}O{\cap}NH_2)]_2$ (**1**) was prepared according to a literature procedure.[1] *N*,*N*-Dimethyl-4-nitrosoaniline (**2**), nitrosobenzene (**2′**) and $AlCl_3$ were used as purchased. NMR spectra were recorded with a Jeol EX 400 spectrometer (^{1}H: 399.78 MHz; ^{13}C: 100.54 MHz) in [D$_8$]THF or CD_2Cl_2. Mass spectra were obtained with a Jeol MStation JMS 700. IR and UV/Vis spectra were measured with a Perkin−Elmer Spectrum One FT-IR or Perkin−Elmer UV Lambda 16 spectrometer, respectively. Elemental analyses were performed with a Heraeus Elementar Vario EL.

3: **1** (388.2 mg, 0.513 mmol), **2** (118.2 mg, 0.787 mmol) and $AlCl_3$ (173.2 mg, 1.035 mmol) were dissolved in toluene (100 mL) and refluxed for 10 min, whereby the solution turned deep blue. The solvent was evaporated, the shiny blue, almost black, residue was dissolved in CH_2Cl_2 and the compound purified by column chromatography. Yield: 258 mg (0.338 mmol, 66%), blue-red dichroic crystals; m.p. 189−191 °C (dec.). ^{1}H NMR (399.78 MHz, [D$_8$]THF): δ = 3.54 [s, 3 H, N(C*H*$_3$)$_2$], 3.55 [s, 3 H, N(C*H*$_3$)$_2$], 7.24 (dd, ^3J = 10.16, ^4J = 2.64 Hz, 1 H, *o*-Ar-*H*), 7.41 (dd, ^3J = 10.27, ^4J = 2.75 Hz, 1 H, *o*-Ar-*H*), 8.02 (dd, ^3J = 10.22, ^4J = 2.64 Hz, 1 H, *m*-Ar-*H*), 8.51 (dd, ^3J = 10.22, ^4J = 2.64 Hz, 1 H, *m*-Ar-*H*) ppm. ^{13}C{^{1}H} NMR (100.53 MHz, [D$_8$]THF): δ = 30.6 (*C*H$_3$NCH$_3$), 43.1 (CH$_3$N*C*H$_3$), 118.0 (*o*-Ar-*C*), 119.2 (*o*-Ar-*C*), 128.2 (*m*-Ar-*C*), 139.4 (*m*-Ar-*C*), 160.9 (Me$_2$NAr-*C*$_q$), 161.6 (ONAr-*C*$_q$), 191.8 (*C*O), 192.0 (*C*O), 195.3 (*C*O), 198.4 (*C*O) ppm. IR (KBr): $\tilde{\nu}$ = 3099.1 w [ν(Ar−H)], 2938.0 w [ν(CH$_2$)], 2857.4 w [ν(CH$_2$)], 2732.9 w, 2039.8 vs [ν(CO), A$_1$], 2021.4 vs [ν(CO), A$_1$], 1904.3 vs [ν(CO), E], 1604.4 s [ν(NO)], 1393.5 s [δ(CH$_3$)], 1331.1 s, 1170.7 vs, 1129.8 m, 930.9 w, 879.3 w, 833.7 m [γ(Ar)], 741.3 s, 644.3 w, 565.7 w, 518.2 w, 493.5 w, 465.8 w, 398.5 w cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2041.4 s [ν(CO), A$_1$], 2024.0 vs [ν(CO), A$_1$], 1946.0 m [ν(CO), E], 1916.9 s [ν(CO), E], 1605.1 m [ν(NO)] cm^{-1}. UV/Vis ($CHCl_3$): λ (*A*) = 265 (0.3234), 364 (0.1048), 617 (0.9901) nm. $C_{14}H_{10}Cl_2N_2O_7Re_2$ (761.54): calcd. C 22.08, H 1.32, N 3.68; found

Table 1. X-ray structure analysis of **3**[20]

	3	**3′**
Empirical formula	$C_{14}H_{10}Cl_2N_2O_7Re_2$	$C_{12}H_5Cl_2NO_7Re_2$
Formula mass [g mol^{-1}]	761.54	718.49
Crystal size [mm]	0.10 × 0.05 × 0.004	0.16 × 0.24 × 0.30
Crystal colour, habit	red platelet	black block
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/m$
a [Å]	6.4246(2)	19.0607(7)
b [Å]	9.5409(3)	7.1842(3)
c [Å]	16.6048(4)	13.0451(4)
α [°]	83.7500(13)	90
β [°]	83.0888(13)	112.005(2)
γ [°]	70.9047(12)	90
Volume [Å^3]	952.20(5)	1656.21(11)
Z	2	4
Density calcd. [g cm^{-3}]	2.65620(14)	2.88151(17)
Absorption coefficient [mm^{-1}]	13.020	14.960
$F(000)$	696	1296
Index ranges	$-7 \leq h \leq 7$	$-24 \leq h \leq 24$
	$-11 \leq k \leq 11$	$-9 \leq k \leq 9$
	$-19 \leq l \leq 19$	$-16 \leq l \leq 16$
θ range [°]	3.41−25.00	3.28−27.48
Reflections collected	14429	9317
Independent reflections	3364	2026
Observed reflections	2737	1864
Parameter/restrains	246/0	130/0
$R1/wR2$ (all data)	0.0471/0.0731	0.0292/0.0560
$R1/wR2$ (final)	0.0331/0.0694	0.0242/0.0547
Goodness of fit	1.112	1.137
Min./max. ρ_e [e Å^3]	−1.125/1.321	−1.279/0.876
Temperature [K]	200(2)	200(2)
Diffractometer used	Nonius Kappa CCD	Nonius Kappa CCD
Scan type	area detection	area detection
Solution	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97

C 22.85, H 1.49, N 3.63. MS (DEI): *m*/*z* (%) = 762.5 (56) [M$^+$], 678.4 (9) [M$^+$ − 3 CO], 650.4 (62) [M$^+$ − 4 CO], 622.4 (35) [M$^+$ − 5 CO], 594.4 (29) [M$^+$ − 6 CO].

3′: Analogous procedure as for **3**, with **1** (83.9 mg, 0.111 mmol), **2′** (23.7 mg) and $AlCl_3$ (29.6 mg, 0.222 mmol) in toluene (20 mL), and stirring for 16 h, yield: 56.6 mg (0.079 mmol, 71%), violet-green dichroic crystals; m.p. 175−181 °C (dec.). ^{1}H NMR (399.78 MHz, CD_2Cl_2): δ = 7.34−7.65 (m, 5 H, Ar-*H*) ppm. $^{13}C\{^1H\}$ NMR (100.53 MHz, CD_2Cl_2): δ = 129.1 (Ar-*C*), 129.4 (Ar-*C*), 129.9 (Ar-*C*), 131.3 (Ar-*C*), 188.0 (*C*O). IR (KBr): $\tilde{\nu}$ = 2062.8 vs [ν(CO), A_1], 2029.1 vs [ν(CO), A_1], 1992.7 vs [ν(CO), E], 1916.2 vs [ν(CO), E], 1579.9 m [ν(NO)], 1262.3 s, 1190.7 w, 1141.1 s, 1099.3 s, 1023.4 s, 955.1 w, 887.6 w, 802.9 s, 703.4 w, 666.0 m, 628.1 w, 640.7 w, 490.8 w, 455.5 w, 437.4 w, 408.2 w cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2066.8 m [ν(CO), A_1], 2023.8 vs [ν(CO), A_1], 1987.8 m [ν(CO), E], 1944.6 s [ν(CO), E] cm^{-1}. UV/Vis ($CHCl_3$): λ (*A*) = 255 (0.670), 322 (0.275), 505 (0.623), 709 (0.267) nm. $C_{12}H_5Cl_2NO_7Re_2$ (718.49): calcd. C 20.06, H 0.70, N 1.95; found C 20.18; H 0.65, N 1.91. MS (DEI): *m*/*z* (%) = 718.7 (75) [M$^+$], 634.8 (97) [M$^+$ − 3 CO], 578.8 (63) [M$^+$ − 5 CO], 550.8 (100) [M$^+$ − 6 CO].

Acknowledgments

We thank Sabine Otto and Christiane Kofink for their experimental support and Dr. Gregor Jung for his UV/Vis spectroscopic measurements.

---

[1] R. Wilberger, H. Piotrowski, P. Mayer, I..-P. Lorenz, *Inorg. Chem. Commun.* **2002**, *5*, 897−902.

[2] [2a] D. M. P. Mingos, D. J. Sherman, *Adv. Inorg. Chem.* **1989**, *34*, 293−377. [2b] B. F. G. Johnson, B. L. Haymore, J. R. Dilworth, *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, **1987**, vol. 2, p. 99−118. [2c]J. H. Enemark, R. D. Feltham, *Coord. Chem. Rev.* **1974**, *13*, 339−406. [2d] K. G. Caulton, *Coord. Chem. Rev.* **1975**, *14*, 317−355.

[3] [3a] A. K. Patra, R. Afshar, M. N. Olmstead, P. K. Mascharek, *Angew. Chem.* **2002**, *114*, 2622−2625; *Angew. Chem. Int. Ed.* **2002**, *41*, 2512−2515. [3b] D. Gusev, A. Llamazares, G. Artus, H. Jacobsen, H. Berke, *Organometallics* **1999**, *18*, 75−89. [3c] M. Schweiger, W. Beck, *Z. Anorg. Allg. Chem.* **1991**, *595*, 203−210. [3d] D. Veghini, S. E. Nefedov, H. Schmalle, H. Berke, *J. Organomet. Chem.* **1996**, *526*, 117−134.

[4] J. R. Norton, G. Dolcetti, *Inorg. Chem.* **1973**, *12*, 485−487.

[5] H. Paulsen, V. Rusanov, R. Benda, C. Herta, V. Scheinemann, C. Janiak, T. Dorn, A. I. Churmakov, H. Winkler, A. X. Trautwein, *J. Am. Chem. Soc.* **2002**, *124*, 3007−3011.

[6] [6a] N. Soh, T. Imato, K. Kawamura, M. Maeda, Y. Katayama, *Chem. Commun.* **2002**, 2650−2651. [6b] J. J. Watkins, A. L. Balch, *Inorg. Chem.* **1975**, *14*, 2720−2723.

[7] [7a] P. Jaitner, J. Veciana, C. Sporer, H. Kopacka, K. Wurst, D. Ruiz-Molina, *Organometallics* **2001**, *20*, 568−571. [7b] P. Jaitner, K. Jäger, A. Dorfer, K.-E. Schwarzhans, *J. Organomet. Chem.* **2001**, *621*, 173−176.

[8] M. Cameron, B. G. Gowenlock, G. Vasapollo, *Chem. Soc. Rev.* **1990**, *19*, 355−379.

[9] [9a] S. Otsuka, Y. Aotani, Y. Tatsuno, T. Yoshida, *Inorg. Chem.*

1976, *15*, 656–660. [9b] L. S. Liebeskind, K. B. Sharpless, R. D. Wilson, J. A. Ibers, *J. Am. Chem. Soc.* **1978**, *100*, 7061–7063. [9c] D. A. Muccigrosso, S. E. Jacobson, P. A. Apgar, F. Mares, *J. Am. Chem. Soc.* **1978**, *100*, 7063–7065. [9d] C. J. Jones, J. A. McCleverty, A. S. Rothin, *J. Chem. Soc., Dalton Trans.* **1985**, 401–403. [9e] M. Pizzotti, F. Porta, S. Cenini, F. Demartin, N. Masciocchi, *J. Organomet. Chem.* **1987**, *330*, 265–278. [9f] C. Crotti, C. Sishta, A. Pacheco, B. R. James, *Inorg. Chim. Acta* **1988**, *141*, 13–15. [9g] M. Herberhold, A. F. Hill, *J. Organomet. Chem.* **1989**, *363*, 371–376. [9h] S. J. Skoog, J. P. Campbell, W. L. Gladfelter, *Organometallics* **1994**, *13*, 4137–4139. [9i] S. J. Skoog, W. L. Gladfelter, *J. Am. Chem. Soc.* **1997**, *119*, 11049–11060.

[10] [10a] R. G. Little, R. J. Doedens, *Inorg. Chem.* **1973**, *12*, 537–540. [10b] W. L. Bowden, W. F. Little, T. J. Meyer, *J. Am. Chem. Soc.* **1974**, *96*, 5605–5609. [10c] W. L. Bowden, W. F. Little, T. J. Meyer, *J. Am. Chem. Soc.* **1976**, *98*, 444–448. [10d] D. Mansuy, M. Dreme, J.-C. Chottard, J. Guilhem, *J. Organomet. Chem.* **1978**, *161*, 207–220. [10e] D. Mansuy, P. Battioni, J.-C. Chottard, C. Riche, A. Chiaroni, *J. Am. Chem. Soc.* **1983**, *105*, 455–463. [10f] C. J. Jones, J. A. McCleverty, A. S. Rothin, *J. Chem. Soc., Dalton Trans.* **1985**, 401–403. [10g] C. Crotti, C. Sishta, A. Pacheco, B. R. James, *Inorg. Chim. Acta* **1988**, *141*, 13–15. [10h] J. Chang, M. D. Seidler, R. G. Bergman, *J. Am. Chem. Soc.* **1989**, *111*, 3258–3271. [10i] R. S. Pilato, C. McGettigan, G. L. Geoffro, A. L. Rheingold, S. J. Geib, *Organometallics* **1990**, *9*, 312–317. [10j] W. H. Chin, K.-K. Cheung, C.-M. Che, *J. Chem. Soc., Chem. Commun.* **1995**, 441–442. [10k] J.-L. Liang, J.-S. Huang, Z.-Y. Zhon, K.-K. Cheung, C.-M. Che, *Chem. Eur. J.* **2001**, *7*, 2306–2317.

[11] D. L. Packett, W. C. Trogler, A. L. Rheingold, *Inorg. Chem.* **1987**, *26*, 4308–4309.

[12] [12a] G. Matsubayashi, K. Nakatsu, *Inorg. Chim. Acta* **1982**, *64*, L163–L164. [12b] S. Hu, D. M. Thompson, P. Ikekwere, R. J. Barton, K. E. Johnson, B. E. Robertson, *Inorg. Chem.* **1989**, *28*, 4552–4554.

[13] [13a] M. Calligaris, T. Yoshida, S. Otsuka, *Inorg. Chim. Acta* **1974**, *11*, L15–L16. [13b] P. R. Sharp, D. W. Hoard, C. L. Barnes, *J. Am. Chem. Soc.* **1990**, *112*, 2024–2026. [13c] D. W. Hoard, P.-R. Sharp, *Inorg. Chem.* **1993**, *32*, 612–620. [13d] H. G. Ang, W. L. Kwik, K. K. Ong, *J. Fluorine Chem.* **1993**, *60*, 43–48.

[14] T. Iwasa, H. Shimada, A. Takami, H. Matsuzaka, Y. Ishii, M. Hidai, *Inorg. Chem.* **1999**, *38*, 2851–2859.

[15] The recently reported Pt–Ge complex $(Et_3P)_2PtN(Ph)OGe\{N(SiMe_3)_2\}_2(Pt-Ge)$ must be viewed as a special case obtained by cycloaddition of the corresponding germylene complex and nitrosobenzene, and having, therefore, a very long N–O bond: K. E. Litz, J. W. Kampf, M. M. B. Holl, *J. Am. Chem. Soc.* **1998**, *120*, 7484–7492.

[16] [16a] E. Colacio, J. M. Dominguez-Vera, A. Escuer, R. Kivekas, A. Romerosa, *Inorg. Chem.* **1994**, *33*, 3914–3924. [16b] E. Colacio, J. M. Dominguez-Vera, E. Escuer, M. Klinga, R. Kivekas, A. Romerosa, *J. Chem. Soc., Dalton Trans.* **1995**, 343–348. [16c] E. Colacio, J. M. Dominguez-Vera, A. Escuer, R. Kivekas, M. Klinga, J.-M. Moreno, A. Romerosa, *J. Chem. Soc., Dalton Trans.* **1997**, 1685–1689. [16d] K. K.-H. Lee, W.-T. Wong, *J. Chem. Soc., Dalton Trans.* **1997**, 2987–2995.

[17] [17a] E. Colacio, J. M. Dominguez-Vera, A. Romerosa, R. Kivekas, M. Klinga, A. Escuer, *Inorg. Chim. Acta* **1995**, *234*, 61–65. [17b] E. Colacio, C. Lopez-Magana, V. McKee, A. Romerosa, *J. Chem. Soc., Dalton Trans.* **1999**, 2923–2926.

[18] M. J. Scott, S. J. Lippard, *Organometallics* **1998**, *17*, 466–474.

[19] G. Gervasio, R. Rossetti, P. L. Stanghellini, *Chem. Commun.* **1997**, 387–388.

[20] CCDC-229256 (**3**) and -229255 (**3′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

[21] C. Romming, H. J. Talberg, *Acta Chem. Scand.* **1973**, *27*, 2246–2248.

[22] A. Schmidpeter, H. Nöth, *Inorg. Chim. Acta* **1998**, *269*, 7–12.

[23] *Trocknen im Labor*, brochure from the series "Reagenzien", Merck, Darmstadt.

Received December 9, 2003
Early View Article