Synthesis of the Dinuclear Halogeno-Bridged Complexes $[Re_2(\mu\text{-}X)_2(CO)_6(CH_3CN)_2]$, (X = Cl, Br)

Rosa Carballo, Emilia García-Martínez, Gumersindo Pereiras-Gabián, and Ezequiel M. Vázquez-López

Universidade de Vigo, Departamento de Química Inorgánica, Facultade de Ciencias, E-36200 Vigo, Galicia/Spain

Reprint requests to Prof. E. M. Vázquez-López. Fax: +34 986 812556. E-mail: ezequiel@uvigo.es

Z. Naturforsch. **58b,** 1021 – 1023 (2003); received June 12, 2003

Complexes $[Re_2(\mu\text{-}X)_2(CO)_6(NCCH_3)_2]$ (X = Cl, Br) have been easily prepared in high yield by refluxing of *fac*-$[ReX(CO)_3(NCCH_3)_2]$ in toluene. The crystal and molecular structure of the bromine derivative have been determined by X-ray analysis. The molecule consists of two *fac*-$Re(CO)_3$ fragments bridged by two bromine atoms. The acetonitrile molecules reside above and below the Re_2Br_2 plane.

Key words: Rhenium, Carbonyls, Crystal Structure, Acetonitrile Complexes

The dinuclear tetracarbonyl rhenium halides, $[Re_2(\mu\text{-}X)_2(CO)_8]$ (X = Cl, Br, I), are colourless or yellow solids stable to air, as obtained by refluxing of the corresponding pentacarbonyl halides in an inert solvent [1]. The existence of halogen bridges is indicated by the infrared spectra [2]. Although the compounds undergo substitution reactions in a similar fashion as the pentacarbonyl halides, the rate of reaction is much greater [1]. Specifically, they react with tetrahydrofuran (THF) under an inert atmosphere to form the derivatives $[Re_2(\mu\text{-}X)_2(CO)_6(THF)_2]$ [3]. These solvent complexes have been successfully used in the synthesis of heterobimetallic halogeno bridged complexes by Severin *et al.* [4] due to their enhanced reactivity under mild conditions.

We have used the acetonitrile derivatives *fac*-$[ReX(CO)_3(NCCH_3)_2]$ (**1**) (X = Cl, Br) as sources of the fragment "$Re(CO)_3$" under mild conditions [5]. This synthesis is easy and gives high yields, and the compounds are air stable and soluble in most common apolar solvents [6]. However, we have isolated by-products in the course of some reactions in inert solvents whose elemental analysis and spectroscopic properties suggested the formation of $[Re_2(\mu\text{-}X)_2(CO)_6(NCCH_3)_2]$ (**2**). Compounds **2** have, to our knowledge, no literature precedent (although the formation of a manganese derivative has been reported [6]) and, consequently, we have designed a route for their synthesis which turned out to be particularly facile and appears to be quite general.

$$2\ \textit{fac}\text{-}\underset{\mathbf{1}}{[ReX(CO)_3(NCCH_3)_2]}\ (X = Cl, Br) \rightarrow \underset{\mathbf{2}}{[Re_2(\mu\text{-}X)_2(CO)_6(NCCH_3)_2]} + 2\ CH_3CN$$

Scheme 1.

Compounds **2** were obtained in high yield by refluxing the corresponding compound **1** in dry toluene as air stable colourless solids that are soluble in acetone but very poorly soluble in toluene. Table 1 gives IR data obtained for compounds **1** and **2** for comparative purpose. The spectra of **2** show two weak bands due to the CN acetonitrile ligand around 2000 cm^{-1} and three strong CO bands between 2050 – 1900 cm^{-1} due to *fac* carbonyl ligands. While the CN bands are hardly shifted with respect to precursor **1** (Table 1) the ν(CO) bands are shifted significantly to higher wave numbers. This is likely due to the poor donor character of the μ-X ligand *versus* the acetonitrile ligand.

Both compounds **1** show a band of medium intensity between 300 – 200 cm^{-1} due to ν(Re-X). The ratio ν(Re-Br) / ν(Re-Cl) of 0.74 confirms the assignments according to Clark & Williams [7]. The band is shifted to lower energy (6 cm^{-1}) as the chlorine atom appears in bridged connections [8]. The expected position of this band for **2b** close to the low spectral limit of our IR spectrophotometer (200 cm^{-1}), prevents its assignment. Fortunately, this compound crystallized from the filtered toluene solution and its structure was determined by X-ray diffraction. Fig. 1 shows a representation of its molecular structure and the atomic numbering scheme employed. The crystals comprise discrete molecules with no intermolecular distances short enough to suggest bonding.

The molecular structure of **2b** has C_i symmetry and consists of a planar Re_2Br_2 ring with the centroid at origin, bearing six terminal carbonyl groups and two terminal acetonitrile molecules. The two solvent ligands are bound on opposite sides of the Re_2Br_2

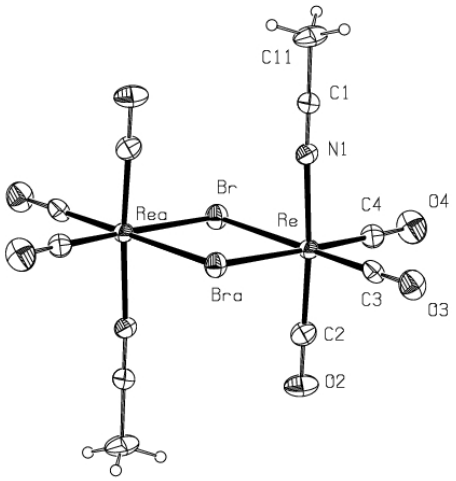

Fig. 1. Molecular structure of compound **2b** showing the numbering scheme. (Thermal ellipsoids are drawn at the 30% probability level).

Table 1. Selected spectroscopic data for the complexes.

	ν(CN)	ν(CO)	ν(Re-X)
1a (X=Cl)	2320w, 2300w	2030s, 1904s, 1885s	291m
	2307w, 2283w[b]	*2025s, 1932s, 1895s*[b]	
1b (X= Br)	2324w, 2296w	2034s, 1914s, 1893s	216m
	2309w,2283w[b]	*2039s, 1916s, 1896s*[b]	
2a (X= Cl)	2326w, 2299w	2054s, 1921s,b	285m
2b (X= Br)	2325w, 2298w	2050s, 1923s,b	–

[a] ν in cm^{-1}, b = broad, m = medium, s = strong, w = weak;
[b] data obtained from reference [6].

plane. The bromine ligands form slightly asymmetric bridges between the rhenium atoms (Table 2), resulting in a Re-Re distance that implies the absence of any metal-metal interaction. The Re-Br distances are longer than those usually observed for terminal ligands [see for instance reference 9] and in the binuclear diorganodisulphide complexes $[Re_2(\mu\text{-}Br)_2(CO)_6(\mu\text{-}S_2R_2)]$ (R=Me, Ph; 2.583(5)–2.616(4) and 2.607(3) Å, respectively) [10] and the anionic $[Re_2Br_3(CO)_6]^-$ complex (2.645(1) Å) [4]. The angle of the bent bridge Re-Br-Re[a] falls well in the range seen in other μ-Br complexes (70–100°).

The acetonitrile molecules are coordinated in an essentially linear way (Re-N-C= 176.6(8)°) and the Re-N bond length is similar to those found in the mononuclear anionic complex $[Et_4N][ReBr_2(CO)_3(NCCH_3)]$ (2.150(6) Å) [11] and the cationic complexes $[Re(CO)_3(NCCH_3)_3][BF_4]$ (2.125(18)–2.134(16) Å) [12] and $[Re(CO)_3(NCCH_3)_3][BrI_2]$ (2.12(1)–2.16(2) Å) [13].

Table 2. Interatomic distances [Å] and angles [°] for **2b**.

Re-N(1)	2.134(8)	Re-C(3)	1.919(10)
Re-Br	2.6588(10)	C(2)-O(2)	1.164(12)
Re-Br[a]	2.6626(11)	C(3)-O(3)	1.138(12)
Re-Re[a]	3.9849(9)	C(4)-O(4)	1.159(11)
Re-C(4)	1.891(10)	N(1)-C(1)	1.141(11)
Re-C(2)	1.901(11)	C(1)-C(11)	1.478(14)
C(4)-Re-C(3)	87.6(4)	C(4)-Re-Br	94.4(3)
C(2)-Re-C(3)	89.6(4)	C(2)-Re-Br	91.4(3)
C(4)-Re-N(1)	94.1(4)	C(3)-Re-Br	177.8(3)
C(2)-Re-N(1)	175.5(4)	N(1)-Re-Br	85.1(2)
C(3)-Re-N(1)	93.8(4)	C(4)-Re-Br[a]	177.4(3)
C(3)-Re-Br[a]	95.0(3)	C(2)-Re-Br[a]	91.5(3)
N(1)-Re-Br[a]	85.2(2)	Br-Re-Br[a]	83.02(3)

Symmetry transformations used to generate equivalent atoms:
[a] $-x+2, -y, -z$.

The main distortions from an ideal octahedron around rhenium atom concern the Br-Re-Br[a] and N-Re-Br angles.

Experimental Section

$[ReX(CO)_5]$ and *fac*-$[ReX(CO)_3(CH_3CN)_2]$ (X=Cl, Br) were synthesized by the published methods [14, 6]. Melting points and mass, IR and NMR spectra were obtained in the same way as reported previously [15].

Synthesis of $[Re_2(\mu\text{-}X)_2(CO)_6(CH_3CN)_2]$ (X=Cl, **2a***; Br;* **2b***)*

The two complexes were obtained as follows: A suspension of 200 mg of *fac*-$[ReX(CO)_3(CH_3CN)_2]$ (0.46 mmol of **1a** or 0.52 mmol of **1b**) in 5 ml of freshly distilled toluene was refluxed for 7.5 h under an argon atmosphere. The solids formed were filtered, washed with chloroform and dried in a vacuum.

Data for 2a. Yield: 163 mg (91%). M.p. 280 °C (dec.). – MS(FAB, NBA): *m/z*(%) = 692(2) $[M^+]$. – $C_5H_3O_3NClRe$ (346.74): calcd. C 17.32, H 0.87, N 4.04; found C 17.47, H 0.86, N 4.07.

Data for 2b. Yield: 150 mg (83%). M.p.: 280 °C (dec.). – $C_5H_3O_3NBrRe$ (391.19): calcd. C 15.35, H 0.77, N 3.58; found C 15.45, H 0.75, N 3.57.

X-ray data collection, structure solution and refinement. Bruker Smart CCD diffractometer, Mo-K_α radiation (λ = 0.71073 Å), T = 293(2) K. Crystal size: 0.06 × 0.06 × 0.12 mm^3, colourless prism, space group $P2_1/c$, monoclinic, a = 7.4198(10), b = 12.3864(17), c = 9.2350(13) Å, β = 99.561(3) Å, V = 836.9(2) $Å^3$, Z = 2, ρ_{cal} = 3.105 g/cm^3. Θ range = 2.78–28.03°, 4885 reflections collected, 1914 of which were independent (R_{int} = 0.0707), multiscan absorption correction (SADABS [16], T_{min} = 0.6921, T_{max} = 1.0000), 100 refined parameters, final R indices R = 0.0707, wR_2 = 0.0725; for $[I > 2\sigma(I)]R$ = 0.0378, wR_2 = 0.0662.

Structure solution: direct methods (SHELXS97 [17]), refinement on F^2 (SHELXL97 [17]). H atoms were calculated and refined as riding model. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications CCDC-212413. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. Code + 44(1223)336-033; E-mail: fileserv@ccdc.cam.ac.uk.

Acknowledgements

We thank the Directorates General for Regional Policies (E.U.) and for Research of the Spanish Ministry of Science and Technology for financial support (ERDF programs) under project BQU2002-03543.

[1] E. W. Abel, G. B. Hargreaves, G. Wilkinson, J. Chem. Soc. 3149 (1958).
[2] J. C. Hileman, D. K. Huggins, H. D. Kaesz, Inorg. Chem. **1**, 933 (1962).
[3] F. Vitali, D. Calderazzo, Gazz. Chim. Ital. **102**, 587 (1972).
[4] A. C. Silva, H. Piotrwski, P. Mayer, K. Polborn, K. Severin, J. Chem. Soc., Dalton Trans. 2960 (2000).
[5] R. Carballo, J. S. Casas, E. García-Martínez, G. Pereiras-Gabián, A. Sánchez, J. Sordo, E. M. Vázquez-López, Inorg. Chem., DOI URL: http://dx.doi.org/10.1021/ic030154q.
[6] M. F. Farona, K. F. Kraus, Inorg. Chem. **9**, 1700 (1970).
[7] R. J. H. Clark, C. S. Williams, Inorg. Chem. **4**, 350 (1965).
[8] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, part B, p. 184, John Wiley and Sons, Inc., New York (1997).
[9] R. Carballo, A. Castiñeiras, S. García-Fontán, P. Losada-González, U. Abram, E. M. Vázquez-López, Polyhedron **20**, 2371 (2001).
[10] I. Bernal, J. L. Atwood, F. Calderazzo, D. Vitali, Gazz. Chim. Ital. **106**, 971 (1976).
[11] U. Abram, S. Abram, R. Schibili, R. Alberto, J. R. Dilworth, Polyhedron, **17**, 1303 (1998).
[12] L. Y. Y. Chan, E. E. Isaacs, W. A. G. Graham, Can. J. Chem. **55**, 111 (1977). P. K. Baker, M. G. B. Drew, M. M. Meehan, Inorg. Chem. Commun. **3**, 393 (2000).
[13] S. P. Schmidt, W. C. Trogler, F. Basolo, Inorg. Synth. **28**, 160 (1990).
[14] R. Carballo, P. Losada-González, E. M. Vázquez-López, Z. Anorg. Allg. Chem. **629**, 249 (2003).
[15] G. M. Sheldrick SADABS, University of Göttingen, Germany (1996).
[16] G. M. Sheldrick SHELX-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany (1997).