

Formation of a Six-Coordinate *fac*-[Re(CO)₃]⁺ Complex by the N-C Bond Cleavage of a Potentially Tetradentate Ligand

I. Booyesen^a, T.I.A. Gerber^{a,*}, E. Hosten^a and P. Mayer^b

^aDepartment of Chemistry, Nelson Mandela Metropolitan University, 6031 Port Elizabeth, South Africa

^bDepartment of Chemistry, Ludwig-Maximilians University, D-81377 Munich, Germany

(Received 13 December 2007, Accepted 11 February 2008)

The rhenium(I) compound *fac*-[Re(CO)₃(daa)].Hpab.H₂O (Hpab = N,N'-(1,2-phenylene)bis(2'-aminobenzamide); Hdaa = 2-amino-N-(2-aminophenyl)benzamide) was synthesized from the reaction of [Re(CO)₅Br] with two equivalent of Hpab in toluene. The monoanionic tridentate ligand daa was formed by the rhenium-mediated cleavage of an amido N-C bond of the potentially tetradentate ligand Hpab. The compound was characterized by IR spectroscopy and X-ray crystallography, and daa is coordinated as a diaminoamide *via* three nitrogen-donor atoms.

Keywords: Rhenium(I), Cleavage of N-C bond, Diaminoamide, Crystal structure

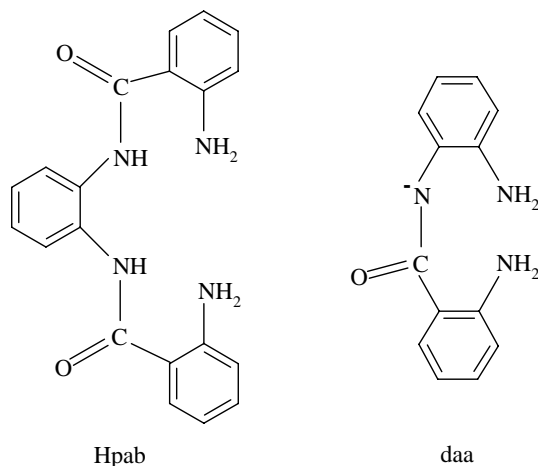
INTRODUCTION

The favorable nuclear properties of the isotopes ^{99m}Tc and ^{186/188}Re have made them the radionuclides of choice for the development of target-specific radiopharmaceuticals [1]. The initial success in this field was achieved by agents containing the [Tc^{VO}]³⁺ core for imaging of the brain (CereteTM) [2], heart (MyoviewTM) [3] and kidneys [4]. However, since the discovery of the cardiac imaging agent [^{99m}Tc^I(MIBI)₆]⁺ (MIBI = 2-methoxy-2-methylpropylisocyanide) [5], much of the research focus has shifted to M(I) (M = Tc, Re) compounds. A great impetus in this oxidation state was provided by the work of Alberto and co-workers, who substantially developed the coordination chemistry of the M(I) tricarbonyl complexes containing the *fac*-[M(CO)₃]⁺ core [6]. Their easy syntheses of the species [M(CO)₃(H₂O)₃]⁺ and [M(CO)₃X₃]²⁻ (X = Cl⁻, Br⁻) provided efficient synthons for the production of a large variety of complexes containing the *fac*-

[M(CO)₃]⁺ core, since the aqua and halide ligands can be substituted quite easily by a variety of functional groups like phosphines, amines and thiols [7].

We have recently reported a series of rhenium(V) complexes containing multidentate aromatic nitrogen-donor ligands [8], and are in the process to extend this work to rhenium(I). Here we report on the product of the reaction of [Re(CO)₅Br] with the potentially tetradentate N₄-donor ligand N,N'-(1,2-phenylene)bis(2'-aminobenzamide) (Hpab). In toluene as solvent, *fac*-[Re(CO)₃(daa)] was isolated as the only product, where the monoanionic tridentate ligand daa (Hdaa = 2-amino-N-(2-aminophenyl)benzamide) was formed by the N-C cleavage of one of the amide bonds of Hpab. Rhenium-induced cleavage of a N-C bond has been observed before [9], and parallels the known cleavage of tertiary amines by transition metals [10]. Tridentate ligands of the N₃-donor atom type like *bis*-(imidazol-2-yl-methyl)amine and *bis*-quinolin-2-ylmethylamine (L³) have previously been used to give six-coordinate cationic species of the type *fac*-[Re(CO)₃L³]Br [11].

*Corresponding author. E-mail: thomas.gerber@nmmu.ac.za



EXPERIMENTAL

Reactants and Methods

[Re(CO)₅Br] was obtained commercially (Aldrich), and Hpab was synthesized by a literature method [12]. Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. All manipulations were done under nitrogen using standard Schlenk and Cannula techniques. Infrared spectra were recorded in KBr pellets on a Nicolet 20 DXC FTIR spectrophotometer, and ¹H NMR spectra (300 MHz) were run in *d*₆-DMSO on a Bruker AMX-300 spectrometer at room temperature. Elemental analyses were carried out as reported earlier [13].

Synthesis

***fac*-[Re(CO)₃(daa)].Hpab.H₂O (1).** Hpab (170 mg, 491 μmol) was added to a solution of [Re(CO)₅Br] (100 mg, 246 μmol) in 20 ml toluene and the mixture was heated under reflux for 1 h under a nitrogen atmosphere. After cooling to room temperature, a cream precipitate was removed by filtration and was washed with toluene, ethanol and acetone.

Recrystallization from a 2:1 v/v mixture of dichloromethane: ethanol gave colourless crystals suitable for X-ray crystallographic analysis. Yield = 146 mg (69% based on Re); m.p.: 146 °C. Anal. Calcd. (%): C, 50.23; H, 3.75; N, 11.39. Found: C, 50.57; H, 3.86; N, 11.51. IR (cm⁻¹): ν(NH₂) 3182, 3234, 3384; ν(CO)_{fac} 1905, 2027; ν(Re-N) 492, 515.

Crystallography

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured at 200 K on a Nonius Kappa CCD single-crystal diffractometer, using Mo-Kα radiation and operating in the ω-2θ mode empirical absorption correction (ψ-scans). Data reduction was done with WINGX [14]. The structure was solved by direct methods with SIR97 [15] and refined by full-matrix least-squares analysis with SHELXL-97 [16]. Non-hydrogen atoms were refined with anisotropic thermal parameters, and the H-atoms were placed in idealized positions and allowed to ride on the parent atom. A summary of the crystal data and refinement details are given in Table 1.

RESULTS AND DISCUSSION

The rhenium(I) complex [Re(CO)₃(daa)] was prepared by the reaction of [Re(CO)₅Br] with two equivalents of Hpab in refluxing toluene as solvent. The formation and coordination of the tridentate ligand daa instead of the original tetradentate Hpab was unexpected. The assumption that Hdaa is possibly a byproduct in the synthesis of Hpab and may preferentially react with [Re(CO)₅Br] to give **1** as product can be excluded. No mention was made of a byproduct in the original published synthetic procedure of Hpab [12]. Hpab was recrystallized as yellow needles with a sharp melting point of 259 °C, and excellent microanalysis and a clear ¹H NMR spectrum, containing no impurities, were obtained [17]. It would also be unlikely that Hpab would contain a 50% impurity of Hdaa before the reaction, as is shown in the crystal structure of the compound [Re(CO)₃(daa)].Hpab.H₂O (**1**). Hpab was also heated under reflux for an hour in toluene in the absence of the rhenium precursor, and only pure Hpab was isolated (established by ¹H NMR). The formation of daa is therefore interpreted as a rhenium-induced ligand conversion.

The IR spectrum of **1** exhibits a sharp, strong band at 2027 cm⁻¹ and a broad, intense absorption at 1905 cm⁻¹, attributed to ν(C-O) of the *fac*-[Re(CO)₃]⁺ unit [18]. Two medium intensity peaks at 492 and 515 cm⁻¹ are assigned to ν(Re-NH₂) and ν(Re-N(2)), respectively. Due to the presence of the free ligand Hpab in **1**, no meaningful information could be obtained from its ¹H NMR spectrum.

Formation of a Six-Coordinate *fac*-[Re(CO)₃]⁺ Complex

Table 1. Crystal and Structure Refinement Data for **1**

Chemical formula	C ₃₆ H ₃₂ N ₇ O ₇ Re
Formula weight	860.89
Crystal system	Triclinic
Unit cell dimensions (Å, °)	
<i>a</i>	10.3179(2)
<i>b</i>	11.2813(2)
<i>c</i>	15.5353(3)
α	107.385(1)
β	93.313(1)
γ	93.714(1)
Volume (Å ³)	1716.41(6)
<i>Z</i>	2
Density (Calcd.) (mg m ⁻³)	1.662
Absorption coefficient (mm ⁻¹)	3.600
<i>F</i> (000)	852
Crystal size (mm)	0.03 × 0.03 × 0.11
θ Range for data collection (°)	3.3-27.6
Index ranges	-13 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -20 ≤ <i>l</i> ≤ 20
Reflections measured	38005
Independent/observed reflections	7866/6616
Data/parameters	7866/460
Goodness-of-fit on <i>F</i> ²	1.05
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0320 (<i>wR</i> ₂ = 0.0764)
Largest diff. peak/hole (e Å ⁻³)	1.27, -1.15

A perspective view of the asymmetric unit of **1** is shown in Fig. 1. It contains a molecule of [Re(CO)₃(daa)], an uncoordinated molecule of Hpab and a water of crystallization. The X-ray results show that the rhenium(I) complex contains the chemically robust *fac*-[Re(CO)₃]⁺ core and a distorted octahedral geometry. The rhenium(I) is coordinated to three carbonyl donors in a *facial* orientation, to the two amino nitrogens N(1) and N(3), and to the amido nitrogen N(2). The Re-CO bond distances [average of 1.916(5) Å; Table 2] fall in the range observed [1.900(2)-1.928(2) Å] for similar complexes [11,19]. The two Re-NH₂ bonds [Re-N(1) = 2.224(3) Å, Re-N(3) = 2.230(3) Å] are practically identical, and is typical for Re-N(amino) bonds [20]. The Re-N(2) bond is considerably shorter at 2.173(3) Å, and is similar to other Re-N(amide) bonds [20,21]. The distortion from

octahedral ideality in the complex is mainly the result of the *trans* angles, which fall in the range 169.5(2)-173.6(2)°. These distortions are the result of the constraints imposed by the tridentate ligand daa, which forms a five-membered [N(2)-Re-N(3) = 73.0(1)°] and six-membered metalloring [N(1)-Re-N(2) = 77.3(1)°] with the rhenium center. The N(1)-Re-N(3) angle [89.2(1)°] is remarkably close to orthogonality. The daa ligand was formed by the fission of either the N(5)-C(23) or N(6)-C(30) bonds of Hpab (Fig. 1), and small differences in intraligand bond lengths and angles of daa and the daa fraction of Hpab are to be expected. The two C-NH₂ bonds [1.450(5) Å average] in daa are longer than these two bonds in the uncoordinated Hpab [1.370(6) Å average], illustrating the effect of coordination to rhenium(I), which is also evident in the bond angles around N(2) [C(10)-N(2)-C(11) = 119.3(3)°]

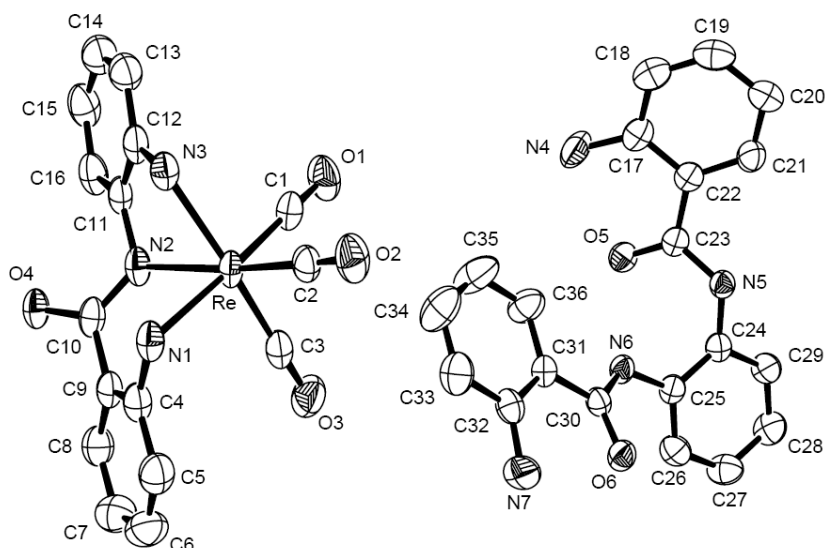


Fig. 1. An ORTEP of $[\text{Re}(\text{CO})_3(\text{daa})]\cdot\text{Hpab}$, showing the atom labelling scheme and thermal ellipsoids at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Re-N(1)	2.224(3)	Re-C(1)	1.916(5)
Re-N(2)	2.173(3)	Re-C(2)	1.933(4)
N(2)-C(11)	1.435(5)	Re-C(3)	1.898(4)
Re-N(3)	2.230(3)	N(4)-C(17)	1.374(6)
N(1)-C(4)	1.439(5)	N(7)-C(32)	1.365(6)
N(3)-C(12)	1.460(5)	O(5)-C(23)	1.247(4)
O(4)-C(10)	1.267(4)	O(6)-C(30)	1.241(5)
C(1)-O(1)	1.148(6)	N(5)-C(23)	1.357(5)
N(2)-C(10)	1.323(5)	N(5)-C(24)	1.427(5)
Re-C(1)-O(1)	179.0(4)	C(1)-Re-N(1)	173.6(2)
Re-C(2)-O(2)	178.1(4)	C(2)-Re-N(2)	169.5(2)
Re-C(3)-O(3)	178.3(4)	C(3)-Re-N(3)	173.0(2)
C(1)-Re-N(2)	96.4(2)	C(1)-Re-N(3)	90.3(2)
C(2)-Re-N(1)	97.5(1)	C(2)-Re-N(3)	98.1(1)
C(3)-Re-N(1)	91.7(2)	C(3)-Re-N(2)	100.4(2)
C(10)-N(2)-C(11)	119.3(3)	C(23)-N(5)-C(24)	126.1(3)
Re-N(2)-C(11)	110.3(2)	C(25)-N(6)-C(30)	125.2(3)
Re-N(1)-C(4)	107.3(2)	N(4)-C(17)-C(22)	123.6(4)
Re-N(3)-C(12)	106.4(2)	N(5)-C(23)-O(5)	120.0(4)
N(2)-C(10)-O(4)	125.1(4)	N(6)-C(30)-O(6)	121.0(4)
N(1)-Re-N(2)	77.3(1)	N(7)-C(32)-C(31)	123.4(4)
N(2)-Re-N(3)	73.0(1)	N(1)-Re-N(3)	89.2(1)

and N(5) and N(6) [125.6(3)° average].

SUPPLEMENTARY MATERIAL

CCDC-667999 contains the crystallographic data for **1**. These data can be obtained at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 (0) 1223-336033; Email: deposit@ccdc.cam.ac.uk.

REFERENCES

- [1] a) S.S. Jurisson, J.D. Lydon, *Chem. Rev.* 99 (1999) 2205; b) W.A. Volkert, T.J. Hoffman, *Chem. Rev.* 99 (1999) 2269; c) E.D. Yorke, P. Beaumier, B. Wessels, A. Fritzberg, A. Morgan, *Nucl. Med. Biol.* 18 (1991) 827.
- [2] J.P. Leonard, D.P. Novotnik, R.D. Neirinckx, *J. Nucl. Med.* 27 (1986) 1819.
- [3] D. Piwnica-Worms, B.L. Holman, *J. Nucl. Med.* 31 (1990) 1166.
- [4] A.R. Fritzberg, S. Kasina, D. Eshima, D.L. Johnson, *J. Nucl. Med.* 27 (1986) 111.
- [5] B.L. Holman, A.G. Jones, J. Lister-James, A. Davison, M.J. Abrams, J.M. Kirschenbaum, S.S. Tubeh, R.J. English, *J. Nucl. Med.* 25 (1984) 1350.
- [6] a) R. Alberto, R. Schibli, A. Egli, A.P. Schubiger, U. Abram, T.A. Kaden, *J. Am. Chem. Soc.* 120 (1998) 7987; b) U. Abram, S. Abram, R. Schibli, R. Alberto, J.R. Dilworth, *Polyhedron* 17 (1998) 1303.
- [7] R. Alberto, R. Schibli, R. Waihel, P.A. Schubiger, *Coord. Chem. Rev.* 190-192 (1999) 901.
- [8] a) T.I.A. Gerber, D. Luzipo, P. Mayer, *J. Coord. Chem.* 57 (2004) 1393; I. Booyesen, T.I.A. Gerber, E. Hosten, D. Luzipo, P. Mayer, *J. Coord. Chem.* 60 (2007) 635; b) T.I.A. Gerber, P. Mayer, *J. Nucl. Radiochem. Sci.* 6 (2005) 165.
- [9] M. Glaser, H. Spies, R. Berger, F.E. Hahn, T. Lügger, B. Johannsen, *Inorg. Chim. Acta* 257 (1997) 143.
- [10] S.I. Murahashi, T. Yano, *J. Chem. Soc., Chem. Commun.* (1979) 270.
- [11] L. Wei, S.R. Banerjee, M.K. Levadala, J. Babich, J. Zubieta, *Inorg. Chim. Acta* 357 (2004) 1499.
- [12] D.S. Black, N.E. Rothnie, *Aust. J. Chem.* 36 (1983) 1141.
- [13] T.I.A. Gerber, E. Hosten, P. Mayer, Z.R. Tshentu, *J. Coord. Chem.* 59 (2006) 243.
- [14] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [15] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, G. Giacovazzo, A. Guagliardi, A.G.G. Moliterini, G. Polidoro, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [16] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.
- [17] Anal. Found (%): C, 69.41; H, 5.36; N, 16.33. Calcd.: C, 69.35; H, 5.24; N, 16.17. ¹H NMR δ (ppm): 9.59 (s, 2H, NH), 6.48 (s, 4H, NH₂), 7.64 (d, 2H, H18/33), 7.60 (t, 2H, H19/34), 7.24 (dd, 2H, H21/36), 7.18 (t, 2H, H20/35), 6.75 (d, 2H, H26/29), 6.53 (t, 2H, H27/28).
- [18] a) J. Granifo, *Polyhedron* 18 (1999) 1061; b) D.R. Gamelin, M.W. George, P. Glyn, F.W. Grevek, K. Schaffner, J.J. Turner, *Inorg. Chem.* 33 (1995) 3246.
- [19] L. Maria, C. Moura, A. Paulo, I.C. Santos, *J. Orgmet. Chem.* 691 (2006) 4773.
- [20] a) C. Melián, C. Kremer, L. Suescun, A. Mombrú, R. Mariezcurrena, E. Kremer, *Inorg. Chim. Acta* 306 (2000) 70; b) M. Chatterjee, B. Achari, S. Das, R. Banerjee, C. Chakrabarti, J.K. Dattagupta, S. Banerjee, *Inorg. Chem.* 37 (1998) 5424; c) G. Bandoli, A. Dolmella, T.I.A. Gerber, D. Mpinda, J. Perils, J.G.H. du Preez, *J. Coord. Chem.* 55 (2002) 823.
- [21] T.I.A. Gerber, P. Mayer, Z.R. Tshentu, *J. Coord. Chem.* 58 (2005) 1271