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Coordination of bidentate aniline derivatives to the *fac*-$[Re(CO)_3]^+$ core

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ABSTRACT

A series of rhenium(I) tricarbonyl complexes, containing bidentate derivatives of aniline, was synthesized and structurally characterized. With 1,2-diaminobenzene (Hpda) the ‘2+1’ complex salt *fac*-$[Re(CO)_3(Hpda)_2]Br$ was isolated. The neutral complex $[Re(CO)_3(Hapa)Br]$ was formed with 2-aminodiphenylamine (Hapa) as ligand. 2-Aminophenol (Hopa) also produced the neutral ‘2+1’ complex $[Re(CO)_3(opa)_2(Hopa)]$, but with 2-mercaptophenol (Hspo) the bridged dimer $[Re_2(CO)_7(spo)_2]$ was found. In the complex $[Re(CO)_3(Htpn)Br]$ (Htpn = N′-{(2-methylthio)benzylidene}benzene-1,2-diamine) the potentially tridentate ligand Htpn is coordinated via the methylthio sulfur and imino nitrogen atoms only, with a free amino group.

1. Introduction

The nuclear properties of the ^{99m}Tc and $^{186/188}Re$ isotopes have made them ideal for application as diagnostic and therapeutic radiopharmaceuticals respectively [1]. Initially most research efforts were focussed on the $[M^{V}O]^{3+}$ core (M = Tc, Re), since it could easily be obtained from the permetalate, but since the discovery of the cardiac imaging agent $[^{99m}Tc(MIBI)_6]^+$ (MIBI = 2-methoxy-2-methylpropylisocyanide) [2] and the easy preparation of the synthons $[M(CO)_3(H_2O)_3]^+$ and $[M(CO)_3X_3]^{2-}$ (X = Cl, Br), the research efforts have shifted to the +I oxidation state [3]. Studies on these synthons have illustrated a high substitution lability of the three halides and water molecules, with a concomitant stability of the three carbonyl ligands [4]. It was therefore not surprising that tridentate chelates with a combination of oxygen, sulfur, nitrogen and phosphorus donor atoms were initially investigated as possible ligands for the $[M(CO)_3]^+$ core [5].

In this paper we report on the synthesis and structural characterization of the rhenium(I) complexes formed by the reaction of $[Re(CO)_5Br]$ and the potentially bi- and tridentate ligands depicted in Scheme 1.

2. Experimental

2.1. Materials and instrumentation

All materials were commercially available and used as received. $[Re(CO)_5Br]$, 1,2-diaminobenzene (Hpda), 2-aminodiphenylamine (Hapa), 2-aminophenol (Hopa) and 2-mercaptophenol (Hspo) were obtained from Aldrich. The ligand Htpn was synthesized by the simple condensation of equimolar amounts of (2-methylthio) benzaldehyde with 1,2-diaminobenzene in ethanol/toluene [6].

Infrared (IR) spectra were recorded on a Digilab FTS 3100 Excalibur HE spectrophotometer and were run as KBr pellets. ^1H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solutions in DMSO-d_6 at 25 °C, using TMS as internal standard. Microanalyses were obtained on a Carlo Erba EA1108 elemental analyzer, and melting points were determined on an Electrothermal IA-900 apparatus. Conductivity measurements (in the unit $ohm^{-1}\,cm^{-2}\,mol^{-1}$) were carried out with 10^{-3} M solutions in methanol at 293 K with a Phillips PW 9509 conductometer.

2.2. Synthesis of the complexes

2.2.1. General method

The ligands Hpda, Hapa, Hopa, Hspo and Htpn (490 µmol) were added to a solution of $[Re(CO)_5Br]$ (100 mg, 246 µmol) in 20 mL of toluene, and the mixtures were heated at reflux for an hour under nitrogen. After cooling to room temperature, the solutions were filtered and left to evaporate slowly at room temperature. After 3 days light yellow crystals, suitable for X-ray diffraction studies, were collected from the mother liquor. They were washed with diethyl ether and dried under vacuum.

*2.2.1.1. $[Re(CO)_3(Hpda)_2]Br$ (**1**).* Yield 0.079 g (57%), m.p. 252 °C. *Anal.* Calc. for $C_{15}H_{16}N_4O_3BrRe$: C, 31.8; H, 2.8; N, 9.9. Found: C, 31.8; H, 3.0; N, 9.7%. IR (cm^{-1}): $\nu(NH_2)$ 3104m, 3169m, 3194m, 3245m; $\nu(C{\equiv}O)$ 2031s, 1925s, 1880s; $\nu(Re{-}N)$ 528m, 513m, 484m. ^1H NMR (ppm): 7.14–7.34 (m, 4H), 6.48 (d, 1H, *H*12), 6.17 (m, 3H). Conductivity: 126.

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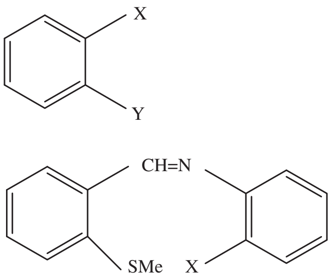

X	Y	Abbv
NH_2	NH_2	Hpda
NH_2	C_6H_5NH	Hapa
NH_2	OH	Hopa
SH	OH	Hspo
NH_2		Htpn
OH		Hons

Scheme 1. Structures of the ligands used in the study.

*2.2.1.2. [Re(CO)$_3$(Hapa)Br] (**2**).* Yield 0.083 g (62%), m.p. 131 °C. *Anal.* Calc. for $C_{15}H_{12}N_2O_3BrRe{\cdot}0.125C_7H_8$: C, 34.9; H, 2.4; N, 5.1. Found: C, 34.7; H, 2.6; N, 5.0%. IR (cm^{-1}): ν(NH, NH_2) 3170m, 3192m, 3267m; ν(CO) 2032s, 1926s, 1882s; ν(ReN) 533m, 513m. ^{1}H NMR (ppm): 7.10–7.35 (m, 5H, *H*6, *H*7, *H*12, *H*13, *H*14), 6.55 (d, 2H, *H*5, *H*8), 6.20 (d, 2H, *H*11, *H*15), 3.47 (br s, 3H, N(1)H_2, N(2)*H*). Conductivity: 37.

*2.2.1.3. [Re(CO)$_3$(opa)(Hopa)] (**3**).* Yield 0.078 g (65%), m.p. >300 °C. *Anal.* Calc. for $C_{15}H_{13}N_2O_5Re$: C, 37.0; H, 2.7; N, 5.7. Found: C, 36.8; H, 2.7; N, 2.6%. IR (cm^{-1}): ν(NH_2) 3273m, 3207m; ν(CO) 2029s, 1925s, 1882s; ν(ReN) 416m. ^{1}H NMR (ppm): 7.76–7.83 (m, 4H, *H*6, *H*7, *H*8, *H*9), 7.27–7.34 (m, 4H, *H*12, *H*13, *H*14, *H*15), 6.50 (s, 4H, 2 × NH_2), 3.23 (s, 1H, O*H*). Conductivity: 32.

*2.2.1.4. [Re$_2$(CO)$_7$(spo)$_2$] (**4**).* Yield 0.062 g (62%), m.p. 155 °C. *Anal.* Calc. for $C_{19}H_{10}O_9S_2Re_2$: C, 27.9; H, 1.2. Found: C, 27.8; H, 1.5%. IR (cm^{-1}): ν(CO) 2016s, 1932s, 1914s, 1887s; ν(Re—O) 472m; ν(Re—S) 357m. ^{1}H NMR (ppm): 7.12 (d, 1H, *H*6), 7.04 (d, 1H, *H*12), 6.84–6.91 (m, 2H, *H*4, *H*10), 6.61–6.66 (m, 2H, *H*5, *H*11), 6.44 (d, 2H, *H*3, *H*9). Conductivity: 33.

*2.2.1.5. [Re(CO)$_3$(Htpn)Br] (**5**).* Yield 0.096 g (66%), m.p. 195–197 °C. *Anal.* Calc. for $C_{17}H_{14}N_2O_3SBrRe$: C, 34.5; H, 2.4; N, 4.7. Found: C, 34.6; H, 2.6; N, 4.9%. IR (cm^{-1}): ν(NH_2) 3064m; ν(CO) 2033s, 1923s, 1896s; ν(ReS) 354m. ^{1}H NMR (ppm): 9.36 (s, 1H, *H*11), 7.89–7.33 (m, 5H), 7.11 (t, 1H), 6.72 (t, 1H), 6.55 (t, 1H), 3.08 (s, 3H, SCH_3). Conductivity: 75.

2.3. X-ray crystallography

X-ray diffraction studies on the crystals of compounds **1**, **2**, **3** and **5** were performed at 200(2) K on a Nonius Kappa CCD detector system using the ω scan technique with Mo Kα radiation. Crystals of **4** were studied with a Bruker Kappa Apex II diffractometer. In complex **1** the monodentate Hpda ligand is disordered, and a split model was applied with a *sof* ratio of 0.7:0.3. The non-hydrogen atoms of the main part were refined anisotropically, and those of the minor part isotropically. The structures were solved by direct methods applying SIR97 [7] and refined by full-matrix least-squares procedures using the SHELXL-97 package [8]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were calculated in idealized geometrical positions. Crystal and structure refinement data are given in Table 1, with selected bond distances and angles in Table 2.

3. Results and discussion

3.1. Synthesis and characterization

The compounds **1**–**5** were synthesized by the reactions of [Re(CO)$_5$Br] with the corresponding ligands in toluene.

The complex salt [Re(CO)$_3$(Hpda)$_2$]Br (**1**) was formed by the substitution of two carbonyls and the bromide from [Re(CO)$_5$Br]. The substitution of two carbonyls only from [Re(CO)$_5$Br] by 2-aminodiphenylamine (Hapa) produced the neutral complex [Re(CO)$_3$(Hapa)Br] (**2**), with bidentate coordination of Hapa. Although reasonably good yields of [Re(CO)$_3$(opa)(Hopa)] (**3**) were obtained from a 2:1 molar ratio of 2-aminophenol (Hopa) and [Re(CO)$_5$Br], the best yield (81%) was achieved with a 5:1 molar ratio. The reaction of 2-mercaptophenol (Hspo) with [Re(CO)$_5$Br] formed the neutral dimeric complex [Re$_2$(CO)$_7$(spo)$_2$] (**4**), with a deprotonated sulfur atom of each spo ligand forming a double bridge. The potentially tridentate ligand Htpn is coordinated as a neutral bidentate chelate in the complex [Re(CO)$_3$(Htpn)Br] (**5**).

Table 1
Crystal and structure refinement data for the complexes.

	1	2	3	4	5
Chemical formula	$C_{15}H_{16}N_4O_3BrRe$	$C_{15}H_{12}N_2O_3BrRe$	$C_{15}H_{13}N_2O_5Re$	$C_{19}H_{10}S_2O_9Re_2$	$C_{17}H_{14}N_2O_3SBrRe$
Formula weight	566.42	545.96	487.48	818.83	592.48
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	8.3815(2)	12.3607(4)	13.2298(2)	12.5117(5)	7.0339(1)
b (Å)	10.5477(2)	14.4372(5)	13.0295(4)	9.1612(3)	19.7023(3)
c (Å)	10.8571(3)	19.8623(7)	19.1889(5)	18.9629(8)	12.8887(2)
α (°)	108.126(2)	92.841(3)			
β (°)	92.235(2)	97.270(3)	104.588(1)	94.910(1)	94.362(1)
γ (°)	105.478(2)	99.281(3)			
V (Å^3)	871.28(4)	3461.1(2)	3201.1(1)	2165.6(1)	1781.0(1)
Z	2	8	8	4	4
D_{calc} (g cm^{-1})	2.151	2.091	2.023	2.511	2.210
μ (mm^{-1})	9.287	9.344	7.618	11.411	9.202
F(0 0 0)	532	2042	1856	1512	1120
θ Range (°)	3.2–27.5	4.1–25.3	3.3–27.5	2.9–28.3	3.2–27.5
Index ranges	−10/10, −13/13, −14/14	−15/15, −11/18, −24/24	−17/17, −16/15, −24/22	−16/16, −7/12, −25/25	−9/9, −25/25, −16/16
Reflections measured	18 983	24 861	50 739	20 003	46 334
Independent/observed reflections	3971/3587	12 476/7612	7306/5054	5316/5012	4076/3769
Data/parameters	3971/222	12 476/809	7306/415	5316/289	4076/227
Goodness-of-fit on F^2	1.06	0.73	1.03	1.13	1.06
Final *R* indices ($I > 2\sigma(I)$)	0.0213, 0.0452	0.0309, 0.0441	0.0303, 0.0640	0.0432, 0.1112	0.0193, 0.0458
Largest peak/hole (e Å^{-3})	0.92/−0.71	0.80/−0.77	1.53/−1.25	3.20, −4.19	0.87/−1.04

Table 2
Selected bond lengths (Å) and angles (°) for the complexes.

1			
Re–C(13)	1.906(4)	Re–N(1)	2.211(3)
Re–C(14)	1.906(4)	Re–N(2)	2.224(3)
Re–C(15)	1.904(4)	Re–N(3)	2.256(3)
N(1)–C(1)	1.456(5)	N(3)–C(7)	1.501(9)
N(4)–C(8)	1.41(2)	O(1)–C(13)	1.162(5)
N(1)–Re–N(2)	76.8(1)	N(1)–Re–C(13)	176.3(1)
Re–N(3)–C(7)	115.8(2)	N(2)–Re–C(14)	171.6(1)
C(13)–Re–C(15)	87.9(2)	N(3)–Re–C(15)	178.1(2)
2			
Re–Br(1)	2.6429(8)	Re–N(1)	2.202(4)
Re–C(1)	1.873(9)	Re–N(2)	2.217(5)
N(1)–Re–N(2)	76.1(2)	N(1)–Re–C(3)	171.7(2)
C(9)–N(2)–C(10)	114.2(5)	N(2)–Re–C(1)	172.9(3)
3			
Re(1)–N(1)	2.213(4)	Re(1)–N(2)	2.259(4)
Re(1)–O(1)	2.133(3)	Re(1)–C(2)	1.908(6)
O(2)–C(11)	1.363(6)	Re(2)–N(4)	2.270(4)
O(1)–Re(1)–N(1)	77.2(1)	Re(1)–N(2)–C(10)	119.2(3)
O(1)–Re(1)–C(2)	172.6(2)	O(1)–Re(1)–C(1)	96.4(2)
N(2)–Re(1)–C(3)	174.9(2)	N(2)–Re(1)–C(2)	94.6(2)
4			
Re(1)–S(11)	2.488(1)	Re(1)–S(21)	2.522(1)
Re(2)–S(11)	2.527(1)	Re(2)–S(21)	2.516(1)
Re(1)–O(12)	2.220(5)	Re(1)–C(2)	1.895(6)
O(12)–C(12)	1.397(8)	O(22)–C(22)	1.377(8)
Re(1)–C(1)	1.912(6)	Re(2)–C(4)	1.931(6)
Re(2)–C(5)	2.003(7)	Re(2)–C(6)	2.007(7)
Re(1)–S(11)–Re(2)	98.65(5)	S(11)–Re(1)–S(21)	81.63(4)
Re(1)–S(21)–Re(2)	98.06(5)	S(11)–Re(2)–S(21)	80.98(4)
S(21)–Re(1)–C(1)	168.9(2)	C(5)–Re(2)–C(6)	178.0(3)
S(11)–Re(1)–C(3)	172.7(2)	S(11)–Re(2)–C(4)	175.4(2)
5			
Re–Br(1)	2.6263(3)	Re–C(1)	1.934(3)
Re–N(1)	2.202(2)	Re–C(2)	1.924(3)
Re–S(1)	2.4684(8)	Re–C(3)	1.911(3)
N(1)–C(11)	1.287(4)	N(2)–C(13)	1.361(4)
N(1)–Re–C(2)	177.0(1)	Br(1)–Re–S(1)	85.31(2)
S(1)–Re–C(1)	175.7(1)	Br(1)–Re–N(1)	83.35(6)
Br(1)–Re–C(3)	175.2(1)	Br(1)–Re–C(1)	93.0(1)
C(1)–N(1)–C(12)	114.3(2)	Br(1)–Re–C(2)	93.8(1)
C(4)–S(1)–C(5)	99.7(2)	C(2)–Re–C(3)	90.9(1)

All the complexes **1**–**5** are stable in air. They are soluble in a wide variety of solvents like methanol, DMF, DMSO, acetonitrile and acetone, but insoluble in dichloromethane and chloroform. Their IR spectra are characterized by three intense bands around 2030, 1925 and 1880 cm^{-1}, typical of v(C$\equiv$O) of the *fac*-$[Re(CO)_3]^+$ unit [9]. The ^1H NMR spectra clearly establish the diamagnetism and presence of the chelates in the complexes, but due to the overlapping of peaks in the aromatic region the assignment of signals could not be made with confidence. However, the methine proton C(11)*H* in **5** occurs the furthest downfield at δ 9.36 ppm. All of them (except **1**, which is a 1:1 electrolyte) are non-electrolytes in methanol.

3.2. Description of the structure of complex 1

A perspective view of the asymmetric unit of **1** is shown in Fig. 1. The X-ray results show that the rhenium(I) complex cation contains the chemically robust *fac*-$[Re(CO)_3]^+$ core in a distorted octahedral geometry. The rhenium(I) is coordinated to three carbonyl donors in a *facial* orientation, to the two amino nitrogen atoms N(1) and N(2) of one Hpda ligand, and to one nitrogen atom N(3) of a second Hpda. The amino group N(4)H_2 is uncoordinated. The Re—C bond distances [average of 1.905(4) Å] fall in the range observed [1.900(2)–1.928(2) Å] for similar complexes [10]. The two Re—N bond lengths of the bidentate ligand is similar [average of 2.218(3) Å, and noticeably shorter than the Re—N(3) length [2.256(3) Å] (see Table 2). However, all three lengths are typical for Re—N(amino) bonds [11].

Table 3
Hydrogen bond data (Å) for complexes **1**, **3** and **5**.

D—H···A	d(D—H)	d(H···A)	d(D···A)	∠(DHA)
1				
N(1)H(1A)···Br(1)	0.92	2.64	3.529(3)	163
N(1)H(1B)···Br(1)	0.92	2.53	3.422(3)	164
N(2)H(2A)···Br(1)	0.92	2.66	3.495(3)	151
N(2)H(2A)···O(1)	0.92	2.58	2.893(4)	100
N(2)H(2B)···O(1)	0.92	2.39	2.893(4)	115
N(3)H(3A)···Br(1)	0.92	2.60	3.506(3	167
N(3)H(3A)···N(4)	0.92	2.48	2.827(6)	103
N(3)H(3B)···Br(1)	0.92	2.52	3.428(3)	168
3				
N(1)H(1A)···O(2)	0.92	2.06	2.867(5)	146
O(2)H(2)···O(3)	0.84	1.73	2.566(4)	169
N(2)H(2A)···O(2)	0.92	2.31	2.683(5)	104
N(3)H(3B)···O(4)	0.92	2.00	2.821(5)	148
O(4)H(4)···O(1)	0.84	1.73	2.533(4)	160
N(4)H(4B)···O(4)	0.92	2.36	2.703(4)	102
5				
N(2)H(2B)···Br(1)	0.88	2.59	3.457(2)	167
N(2)H(2B)···N(1)	0.88	2.56	2.868(3)	101

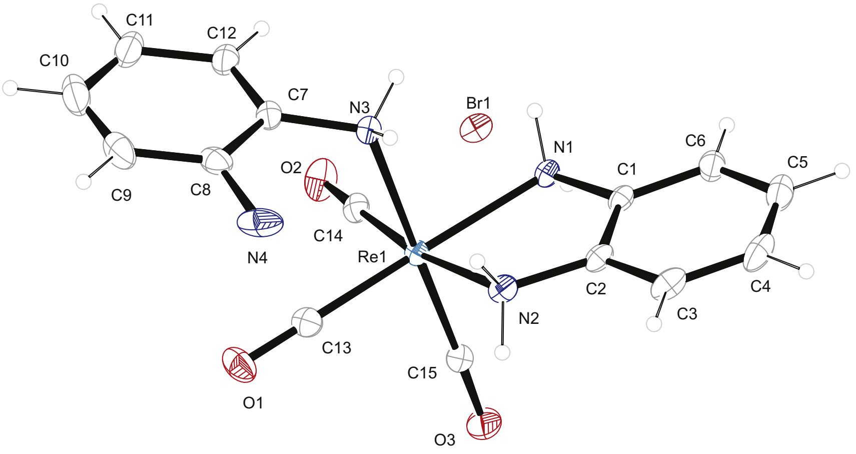

Fig. 1. ORTEP view of complex **1**, showing 40% probability displacement ellipsoids and the atom-labeling.

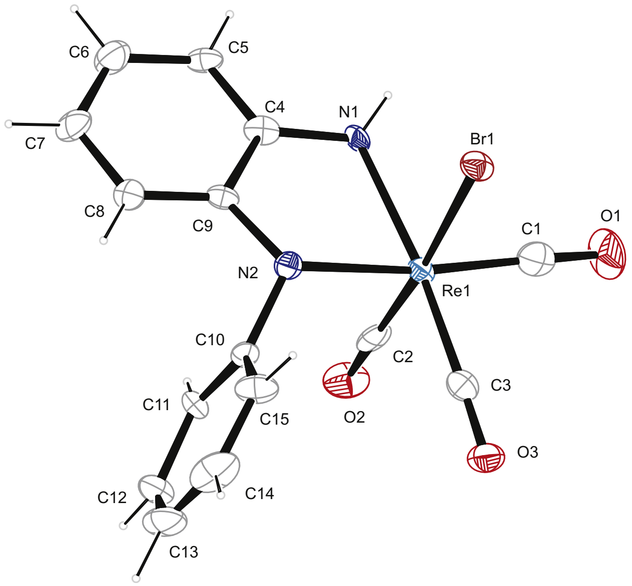

Fig. 2. Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity.

The distortion from octahedral ideality is mainly the result of the *trans* angles, with N(1)—Re—C(13) = 176.3(1)°, N(2)—Re—C(14) = 171.6(1)° and N(3)—Re—C(15) = 178.1(2)°. These distortions are the result of the constraints imposed by the bidentate ligand, which forms a five-membered [N(1)—Re—N(2) = 76.8(1)°] metalloring. This argument is manifested in the larger (closer to linearity) bond angle between the *trans* monodentate ligand/donor C(15)O and $N(3)H_2$. The average C—Re—C bond angle is 88.6(2)°.

A comparison of the N(4)—C(8) bond length [1.41(2) Å] with the longer N(3)—C(7) one [1.445(4) Å] clearly shows the effect of coordination on this type of bond.

The bromide counter-ion is involved in a series of hydrogen bonds in the lattice (see Table 3).

The formation of $[Re(CO)_3(Hpda)_2]Br$ (**1**) is surprising since neutral bidentate nitrogen-donor ligands usually form neutral complexes of the type $[Re(CO)_3(NN)Br]$ [11–13]. The preparation of *cationic* Re(I) complexes (containing the $[Re(CO)_3]^+$ core) under mild conditions by the simple ligand substitution of $[Re(CO)_5X]$ (X = Cl, Br) is unusual. For example, the reaction of 2,2′:6;2″-terpyridine (terpy) with $[Re(CO)_5Cl]$ led to the formation of $[Re(CO)_3(\sigma^2\text{-terpy})Cl]$. Only by drastic action (by refluxing with silver perchlorate in acetonitrile overnight) could the cationic complex $[Re(CO)_3(\sigma^2\text{-terpy})(CH_3CN)]^+$ be formed [14]. Complex **1** is a unusual example of a '2+1' compound with the $[Re(CO)_3]^+$ core prepared in an one-pot procedure. A similar example is the complex $[Re(CO)_3(phen)(pyridine)]^+$, which was synthesized under harsh conditions in a two-step process [15]. The fact that complex **2**, $[Re(CO)_3(Hapa)Br]$, contains only one Hapa ligand, illustrates that electronic and steric factors play a role in its dissimilarity to complex **1**.

3.3. Description of the structure of 2

The asymmetric unit contains four molecules of $[Re(CO)_3(Hapa)Br]$. The rhenium(I) is coordinated to three carbonyl donors in a *facial* orientation, to the two amino nitrogens N(1) and N(2), and a bromide (Fig. 2). The Re—N(2) bond [2.217(5) Å] is significantly longer than Re—N(1) [2.202(4) Å], and they are both typical for Re—N(amino) bonds [11]. The bite angle [N(1)—Re—N(2)] of Hapa is 76.1(2)°, which delineates the *trans* angles [N(1)—Re—C(3) = 171.7(2)°, N(2)—Re—C(1) = 172.9(3)°] (see Table 2). The Re-N(1)—C(4) and Re—N(2)—C(9) bond angles are 113.6(3)° and 111.7(4)° respectively, with the C(9)—N(2)—C(10) angle at 114.2(5)°.

3.4. Description of the structure 3

The crystal structure consists of pi-dimer stacks (Fig. 3) and the asymmetric unit consists of four of these dimer units. The distance between the ring centroids of these pi-stacks is 4.419 Å.

Each metal is coordinated to three carbonyl donors in a *facial* orientation, to a neutral amino nitrogen (N(2) or N(4) of Hopa) and to a neutral amino nitrogen (N(1) or N(3)), and a deprotonated phenolate oxygen (O(1) or O(3)) of opa. The phenolate oxygens O(2) and O(4) are protonated and uncoordinated.

Focussing on the structure around Re(1), there is a notable difference in the $Re—NH_2$ bond lengths [Re(1)—N(1) = 2.213(4) Å; Re(1)—N(2) = 2.259(4) Å] of the coordinated opa and Hopa ligands. The Re(1)—O(1) bond length of 2.133(3) Å is considerably longer

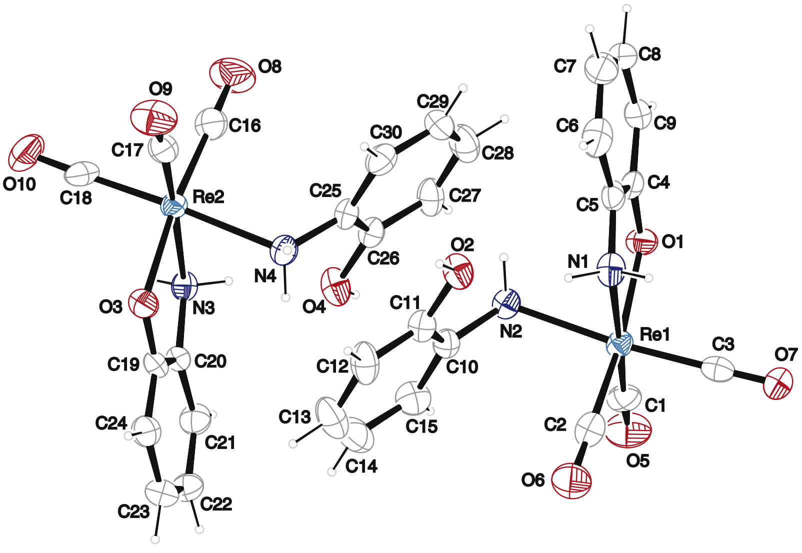

Fig. 3. A perspective view of the asymmetric unit of complex **3**.

than that found for bidentate *N*,*O*-donor ligands in Re(V) complexes (usually around 2.00 Å), but is similar to other Re(I)—O bond lengths, which occur in the range 2.120(8)–2.152(9) Å [11,16,17].

The bite angle of opa [N(1)—Re(1)—O(1) = 77.2(1)°] results in the *trans* angles falling in the narrow range of 172.6(2)–174.9(2)°. The packing of the complexes in the unit cell is complemented by an extensive network of hydrogen bonds (Table 3).

$[Re(CO)_3(opa)(Hopa)]$ (**3**) is another example of a '2+1' complex containing the $[Re(CO)_3]^+$ core. In order to obtain neutrality, the Hopa ligand coordinates via the neutral amino nitrogen, rather than through the neutral O(2)H group, an example of which is also shown in complex **4**. The preference for the amino nitrogen is understandable, since the d^6 system would have a lower affinity for the more electronegative oxygen donor atom, which prefers ionic interaction with the metal. This feature was observed in the '2+1' complex $[Re(CO)_3(ons)(Hopa)]$ (Hons = 2-[(2-methylthio)benzylideneimino]phenol; Scheme 1), with ons coordinated bidentately as a N,O^--donor, and Hopa monodentately via the neutral amino nitrogen [18]. Although the deprotonation of phenylamino groups occurs readily in rhenium(V) complexes (due to the hard acidic properties of Re(V)), it is not observed for the $[Re(CO)_3]^+$ core [18,19].

3.5. Description of the structure of **4**

The structure is shown in Fig. 4. The dimeric molecule has a rhombic $(\mu\text{-}S)_2Re_2$ unit at the center. Each sulfido-bridge is symmetrical, with unequal Re—S distances of 2.488(1) [Re(1)—S(11)], 2.522(1) [Re(1)—S(21)], 2.527(1) [Re(2)—S(11)] and 2.516(1) Å [Re(2)—S(21)]. The Re—Re distance across the rhombus is 3.8038(3) Å, implying no Re—Re bonding.

The dimer consists of two different halves. Each rhenium is in a distorted octahedral environment. Re(1) is coordinated to the carbon atoms of three carbonyls, the two charged sulfur atoms S(11) and S(21), and the phenolic oxygen O(12). The Re(1)—O(12) bond length of 2.220(5) Å intimates that this oxygen is neutral, and thus protonated. As stated above for complex **3**, the length of a rhenium(I)—phenoxy bond falls in the range 2.120(8)–2.152(9) Å [16]. The bite angle of the bidentate ligand is 77.0(1)° [S(11)—Re(1)—O(12)], leading to *trans* angles in the range 168.9(2)–174.4(2)°.

In the second half of the molecule Re(2) is bonded to four carbonylic carbons and the two sulfido bridging atoms. The O(22)H group is not coordinated. The Re(2)—C(4) and Re(2)—C(7) bond lengths are practically identical, as are Re(2)—C(5) and Re(2)—C(6) (see Table 2). The difference between the C(22)—O(22) [1.377(8) Å] and C(12)—O(12) [1.397(8) Å] lengths are small. The C(4)—Re(2)—C(6) [90.4(3)°], C(4)—Re(2)—C(5) [91.5(3)°] and C(4)—Re(2)—C(7) [90.5(3)°] are close to orthogonality.

The potentially bidentate ligand Hspo provides somewhat of a dilemma for the $[Re(CO)_3]^+$ core, since both the OH and SH groups can be deprotonated. However, in the complex $[Re_2(CO)_7(spo)_2]$ only the mercapto sulfur atoms are deprotonated. The different coordination behavior of the two spo ligands is surprising, since bidentate coordination of both would have led to the symmetrical complex $[Re(CO)_3(spo)]_2$, with sulfide bridges. A second possibility would be to form the symmetrical dimer $[Re(CO)_4(spo)]_2$, with sulfide bridges and free OH groups. We cannot explain this anomalous behavior. Interestingly, with tropolone (Htrp) the anionic monomer $[Re(CO)_3(trp)Br]^-$ was isolated [20].

3.6. Description of the structure of **5**

The X-ray results show that the bidentate ligand Htpn is coordinated via the imino nitrogen N(1) and the thioethereal sulfur S(1) to the metal, which resides in a distorted octahedral environment (Fig. 5). The Re—N(1) bond length of 2.202(2) Å is typical of rhenium(I)—imine bonds [12], and the Re—S(1) length of 2.4684(8) Å is in the range observed for similar bonds [21]. The N(1)—C(11) bond is double, with a length of 1.287(4) Å, and the angle C(11)—N(1)—C(12) [114.3(2)°] is slightly smaller than would be expected around a sp^2-hybridized nitrogen atom. The smaller bite angle of Htpn [N(1)—Re—S(1) = 86.18(7)°] results in larger *trans* angles [175.2(1)–177.0(1)°], when compared to the other complexes in the study.

One of the hydrogen atoms of the free amino group is involved in two hydrogen bonds to Br(1) and N(1) (Table 3). These interactions may be responsible for the remarkable value of −0.2(4)° for the N(1)—C(12)—C(13)—N(2) torsion angle.

Whereas in complex **5** the potentially tridentate N_2S-donor ligand Htpn coordinates as a bidentate N,S-donor (with a free amino group), the very similar NSO-donor ligand Hons (see Scheme 1) coordinates as a NO-donor (via the imino nitrogen and deprotonated oxygen with a free methylthio group) in the complex $[Re(CO)_3(ons)(Hopa)]$ [18]. Complexes with the *fac*-$[Re(CO)_3]^+$ core have been well studied with potentially tridentate ligands, which commonly contain N, O and S donor atoms from amine [22], pyridyl [23], carboxyl [24] or thioether [25] groups in octahedral

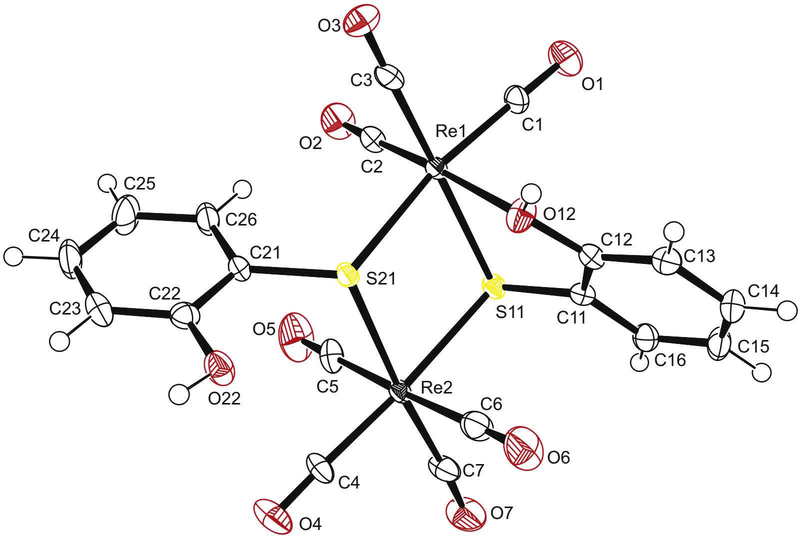

Fig. 4. Structure of complex **4**.

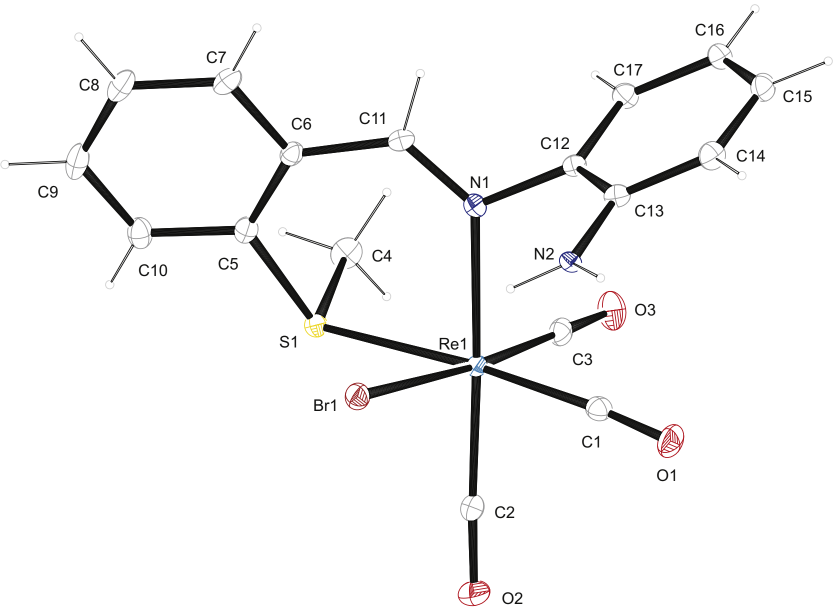

Fig. 5. View of the structure of **5**, showing the atom-numbering and 40% thermal ellipsoids.

complexes of the type $[Re(CO)_3L]X$ (X = Cl, Br, PF_6). Conclusions have been made that nitrogen donor ligands are preferred by the $[Re(CO)_3]^+$ core above sulfur donor ligands, which is in contradiction with the results found in complex **5** [23,25].

4. Conclusion

This study was a systematic attempt to study the reaction of $[Re(CO)_5Br]$ with a series of potentially bidentate ligands with an aromatic backbone. The ligands were varied in terms of different donor atoms, and to be coordinated as neutral, monoanionic or dianionic chelates in the rhenium(I) complexes. The reaction of the N,N-donor ligand 1,2-diaminobenzene (Hpda) with $[Re(CO)_5Br]$ gives the '2+1' complex salt $[Re(CO)_3(Hpda)_2]Br$ (**1**). Increasing the steric bulk of the diamine by using 2-aminodiphenylamine (Hapa) as ligand produces the neutral complex $[Re(CO)_3(Hapa)Br]$ (**2**). Changing the ligand to the monoanionic bidentate 2-aminophenol (Hopa), the neutral '2+1' complex *fac*-$[Re(CO)_3(opa)(Hopa)]$ (**3**) was found. With the dianionic bidentate ligand 2-mercapto-phenol the di(sulfido) bridged species $[Re_2(CO)_7(spo)_2]$ (**4**) was isolated. Giving the $[Re(CO)_3]^+$ core a choice of donor atoms in the ligand Htpn, a thioether sulfur donor atom is preferred to an amino nitrogen as donor atom in the complex $[Re(CO)_3(Htpn)Br]$ (**5**).

Appendix A. Supplementary data

CCDC 815130, 815131, 815132, 815134, and 768100 contain the supplementary crystallographic data for complexes **1**–**5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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