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Synthesis, characterization and crystal structures of mono-, di- and trinuclear rhenium(I) tricarbonyl complexes with 2,3,5,6-tetra(2-pyridyl)pyrazine

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Abstract

A series of rhenium(I) tricarbonyl complexes with the ligand 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) were synthesized and characterized crystallographically. Two different coordination modes were found when tppz functions as a monobidentate ligand. Rhenium(I) may be bound to tppz through pyrazine and pyridyl nitrogens completing a 5-membered coordination ring when the reaction was carried out in toluene. However, the same reaction in methanol produced a yellow complex in which rhenium(I) was bound to tppz through two adjacent pyridyl nitrogens with a 7-membered coordination ring. In the presence of an excess amount of [ReBr(CO)₅], the dinuclear complex [{ReBr(CO)₃}₂(μ-tppz)] (**3**) was isolated, while the trinuclear complex [{ReCl(CO)₃}₃(μ-tppz)] (**4**) was obtained in the case of [ReCl(CO)₅]. Crystal data for **1**, C₂₇H₁₆ClN₆O₃Re·MeOH: monoclinic, *P*2₁/*n*, *a* = 9.2217(7), *b* = 10.7628(8), *c* = 26.932(2) Å, β = 94.130(1)°, *V* = 2666.1(3) Å³, *Z* = 4. **2**, C₂₇H₁₆BrN₆O₃Re: monoclinic, *P*2₁/*n*, *a* = 9.2931(6), *b* = 10.2387(7), *c* = 27.993(2) Å, β = 94.615(1)°, *V* = 2654.8(3) Å³, *Z* = 4. **1'**, C₂₇H₁₆ClN₆O₃Re·2H₂O: monoclinic, *C*₂/*c*, *a* = 18.584(4), *b* = 21.693(5), *c* = 15.392(4) Å, β = 122.328(3)°, *V* = 5243(2) Å³, *Z* = 8. **3**, C₃₀H₁₆Br₂N₆O₆Re₂: triclinic, *P* $\bar{1}$, *a* = 7.4668(6), *b* = 11.4902(10), *c* = 19.3736(16) Å, α = 73.659(2), β = 85.183(2), γ = 77.097(1)°, *V* = 1554.3(2) Å³, *Z* = 2. **4**, C₃₃H₁₆Cl₃N₆O₉Re₃·1/2C₆H₆: orthorhombic, *Pbca*, *a* = 18.828(1), *b* = 16.715(1), *c* = 25.366(2) Å, *V* = 7983.2(10) Å³, *Z* = 8.

Keywords

Crystal structures; Rhenium complexes; Carbonyl complexes; Bidentate complexes

1. Introduction

Polynuclear metal complexes with aromatic nitrogen heterocycles as bridging ligands have long been attractive for the study of photo-induced electron and energy transfer [1–4]. Complexes that incorporate polypyridine-type ligands are particularly attractive because

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5. Supplementary material

All atomic and thermal parameters and all interatomic angles are available from the author upon request. Crystallographic data (excluding structure factor) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 151994–151998 for compounds **1**, **2**, **1'**, **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

they form very stable complexes with a wide range of transition metals and also stabilize complexes in multiple oxidation states [5].

The ligand 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) was first reported by Goodwin et al. [6] and there have been reports on the synthesis and characterization of some mononuclear transition metal complexes with Sn, Fe, Ni, Co, Cu, Ru, Os, Pt and Pd in which tppz functions as a tridentate N₃ donor [6–9]. In addition, homo-bimetallic complexes utilizing tppz have also been recently reported [10–16]. As a consequence of the more facile first addition and the resulted kinetic control, it is possible to prepare asymmetric bridged dinuclear complexes of the donor/receptor type [17].

A recent investigation demonstrated that this versatile ligand may also function as a bis-bidentate ligand [18]. The reaction between the [Pt(PEt₃)Cl₂]₂ dimer and tppz led to the isolation of [{Pt(PEt₃)Cl}₂μ-(tppz)][Pt(PEt₃)Cl₃]₂. The Pt(II) sites in the cationic subunit of the complex are linked by the tppz ligand and coordinated in a bidentate mode to the adjacent pyridine nitrogens. As a continuation of our interest in exploring rhenium(I) tricarbonyl complexes of N-donor heterocyclic molecules [19], we report herein the synthesis and characterization of a series of mono-, di- and trinuclear rhenium(I) tricarbonyl complexes of tppz.

2. Experimental

2.1. General considerations

IR spectra were recorded as KBr pellets with a Perkin–Elmer Series 1600 FTIR. Elemental analysis for carbon, hydrogen and nitrogen were carried out by Oneida Research Services, Whitesboro, NY. Reagent grade solvents were used for all preparations, [ReCl(CO)₅], [ReBr(CO)₅] and 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) were obtained from the Aldrich Chemical Company.

2.2. Synthesis

2.2.1. Preparation of mononuclear complexes α-[ReX(CO)₃(tppz)] (1, X = Cl; 2, X = Br)—Tppz (39 mg, 0.1 mmol) was added to [ReX(CO)₅] (0.1 mmol) dissolved in toluene (50 cm³) in a 100 cm³ Erlenmeyer flask. The mixture was stirred at 100°C for 4 h, cooled to room temperature and the yellow polymeric precipitate was filtered off. The volume was condensed to 10 cm³ and upon slow cooling to 4°C, some wine-red microcrystalline solid was isolated from the toluene solution. X-ray quality crystals were obtained by recrystallization from methanol.

2.2.1.1. α-[ReCl(CO)₃(tppz)] · MeOH (1): Yield: 33 mg, 45%. FTIR (cm^{−1}, KBr pellet): 2024, 1917, 1880, 1601, 1444, 1400, 760, 587. *Anal.* Found: C, 46.5; H, 2.81; N, 11.6. Calc. for C₂₈H₂₀ClN₆O₄Re: C, 46.3; H, 2.75; N, 11.6%.

2.2.1.2. α-[ReBr(CO)₃(tppz)] (2): Yield: 28 mg, 38%. FTIR (cm^{−1}, KBr pellet): 2021, 1920, 1885, 1604, 1441, 1395, 763, 590. *Anal.* Found: C, 43.8; H, 2.21; N, 11.3. Calc. for C₂₇H₁₆BrN₆O₃Re: C, 43.9; H, 2.17; N, 11.4%.

2.2.2. Preparation of mononuclear complexes β-[ReX(CO)₃(tppz)] (1', X = Cl; 2', X = Br)—[ReX(CO)₅] (0.1 mmol) was added to tppz (39 mg) dissolved in methanol (50 cm³). The mixture was heated under gentle reflux for 40 min, upon which the solution turned to reddish brown and a yellow polymeric precipitate started to fall out of the solution. The reaction was cooled to room temperature, filtered and concentrated. Yellow crystals of

X-ray quality were grown by slow diffusion of ethyl ether into a solution of the compounds dissolved in minimum amount of CH_2Cl_2 .

2.2.2.1. β -[ReCl(CO)₃(tppz)] · 2H₂O (1'): Yield: 53 mg, 73%. FTIR (cm^{-1} , KBr pellet): 2025, 1921, 1891, 1587, 1568, 1487, 1393, 786, 774. *Anal.* Found: C, 44.6; H, 2.78; N, 11.3. Calc. for $\text{C}_{27}\text{H}_{20}\text{ClN}_6\text{O}_5\text{Re}$: C, 44.4; H, 2.74; N, 11.5%.

2.2.2.2. β -[ReBr(CO)₃(tppz)] (2'): Yield: 48 mg, 62%. FTIR (cm^{-1} , KBr pellet): 2025, 1924, 1889, 1588, 1567, 1393, 807, 785, 754, 552. *Anal.* Found: C, 44.1; H, 2.15; N, 10.9. Calc. for $\text{C}_{27}\text{H}_{16}\text{BrN}_6\text{O}_3\text{Re}$: C, 43.9; H, 2.17; N, 11.4%.

2.2.3. Preparation of the dinuclear complex [ReBr(CO)₃]₂(μ -tppz) (3)—Tppz (39 mg, 0.1 mmol) and [ReBr(CO)₅] (122 mg, 0.3 mmol) in toluene (50 cm^3) were refluxed overnight and subsequently cooled to room temperature. The dark-brown solution, which is sufficiently pure for analytical purposes, was filtered and a dark-red solid precipitated upon slow addition of pentane (150 cm^3). Crystals suitable for X-ray crystallography were grown by diffusion of pentane into solution of the complex in CH_2Cl_2 (yield: 31 mg, 29%). FTIR (cm^{-1} , KBr pellet): 2030, 1926, 1890, 1586, 1396, 1152, 756, 641, 544. *Anal.* Found: C, 33.4; H, 1.52; N, 7.65. Calc. for $\text{C}_{30}\text{H}_{16}\text{Br}_2\text{N}_6\text{O}_6\text{Re}_2$: C, 33.1; H, 1.47; N, 7.72%.

2.2.4. Preparation of the trinuclear complex [ReCl(CO)₃]₃(μ -tppz) · 1/2C₆H₆ (4)—Tppz (39 mg, 1 mmol) and [ReCl(CO)₅] (145 mg, 0.4 mmol) in benzene (50 cm^3) was refluxed for 24 h and allowed to cool to room temperature. The resulting solution was filtered and concentrated to dryness. The dark red residue was washed several times with cold methanol. Red needle crystals were separated by slow evaporation from benzene–methanol (yield: 35 mg, 26%). FTIR (cm^{-1} , KBr pellet): 2024, 1923, 1885, 1654, 1600, 1399, 914, 760. *Anal.* Found: C, 35.0; H, 1.45; N, 6.32. Calc. for $\text{C}_{36}\text{H}_{19}\text{Cl}_3\text{N}_6\text{O}_9\text{Re}_3$: C, 34.8; H, 1.41; N, 6.25%.

2.3. X-ray crystallography

The selected crystals of **1**, **2**, **1'**, **3**, and **4** were studied on a Bruker diffractometer equipped with the SMART CCD system [20] and using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All the data collections were carried out 89(5) K. The data were corrected for Lorentz and polarization effects, and absorption corrections were made using SADABS [21]. Neutral atom scattering factors were taken from Cromer and Waber [22], and anomalous dispersion corrections were taken from those of Creagh and McAuley [23]. All calculations were performed using SHELXL [24]. The structures were solved by direct methods [25] and all of the non-hydrogen atoms were located from the initial solution. After locating all the initial nonhydrogen atoms in each structure, the models were refined against F^2 , initially using isotropic and later anisotropic thermal displacement parameters until the final value of $\Delta/\sigma_{\text{max}}$ was less than 0.001. At this point the hydrogen atoms were located from the electron density difference map and a final cycle of refinements was performed, until the final value of $\Delta/\sigma_{\text{max}}$ was again less than 0.001. No anomalies were encountered in the refinement of any of the structures. The relevant parameters for crystal data, data collection, structure solution and refinement are summarized in Table 1, and important bond lengths and angles in Tables 2–4 Table 5. A complete description of the details of the crystallographic methods is given in the Supplementary material.

3. Results and discussion

The wine–red mononuclear complexes α -[ReX(CO)₃(tppz)] (**1**, X = Cl; **2**, X = Br) were prepared by treatment of [ReX(CO)₅] with tppz in refluxing toluene in the molar ratio 1:1.

In the metal carbonyl stretching region of the IR spectra, the complexes show three strong peaks consistent with a facial arrangement of the three carbonyl groups [26,27], which are assigned as the A' (1), A'' and A'(2) vibrations, respectively [28]. This indicates that tppz functions as a monobidentate chelate by substituting two equatorial carbonyl groups of the $[\text{ReX}(\text{CO})_5]$ compound. It is very surprising that 1:1 ratio of $[\text{ReX}(\text{CO})_5]$ and tppz in refluxing methanol resulted yellow crystalline solids with the same formula as those of **1** and **2**, which were confirmed from elemental analysis. Prolonged reaction time yielded polymeric yellow precipitates, which are insoluble in most of the organic solvents. Crystal structures for the red and yellow derivatives of **1** and **1'** were both available and different coordination modes of the $\{\text{Re}(\text{CO})_3\text{X}\}$ core toward the bidentate tppz ligand were observed. In the red crystal, Re(I) is coordinated to the nitrogen atoms of the pyrazine ring and of the adjacent pyridyl ring, forming a 5-membered coordination ring; whilst in the yellow crystal, Re(I) is coordinated to two adjacent pyridyl nitrogen atoms, forming a 7-membered coordination ring. In the presence of an excess amount of $[\text{ReBr}(\text{CO})_5]$, a dinuclear complex with the formula $[\{\text{ReBr}(\text{CO})_3\}_2(\mu\text{-tppz})]$ was obtained in which tppz acts in a bis-bidentate manner. We were unable to produce the dinuclear complex of the chloride analog, but rather an unexpected trinuclear Re(I) tricarbonyl complex $[\{\text{ReCl}(\text{CO})_3\}_3(\mu\text{-tppz})]$ was isolated.

In Fig. 1 the molecular structure of **1** is shown with the atom numbering scheme. Relevant bond lengths and angles are presented in Table 2. The coordination geometry at the Re atom is a distorted octahedral with three carbonyl ligands arranged in the facial fashion. The *trans* angles at the Re(I) site are in the range of $168.6(3)$ – $177.6(2)^\circ$, showing a slight deviation from an ideal octahedral arrangement. The Re–N bond lengths are typical of Re(I) diimine systems ($2.139(5)$ – $2.235(5)$ Å), with the deviations being attributable to the small differences in the π -back-bonding of pyridine and pyrazine nitrogen atoms [29]. The rhenium carbonyl bond lengths do not show any significant differences ($1.898(7)$ – $1.931(7)$ Å) and are consistent with those observed in similar complexes [30]. The N(1)–Re(1)–N(3) angle of $74.8(2)^\circ$ is significantly smaller than 90° , as a result of the small bite angle between pyridyl group and pyrazine ring. The uncoordinated pyridyl ring [C(15)–C(16)–C(17)–C(18)–C(19)–N(4)] is rotated, at an angle of 59.0° with respect to the pyrazine ring and 56.7° with respect to the coordinated pyridyl group. The coordinated pyridyl group is twisted 26.7° with respect to the pyrazine ring.

Selected bond distances and angles for complex **1'** are given in Table 3. A perspective view of this complex with the atomic numbering is presented in Fig. 2. The coordination environment around the Re ion in $[\text{Re-Cl}(\text{CO})_3(\text{tppz})]$ (**1'**) can be described as a slightly distorted octahedron with the equatorial plane defined by the two nitrogen atoms (N(3) and N(4)) belonging to the tppz ligand and by two carbon atoms (C(26) and C(27)) of two carbonyl ligands, the remaining carbonyl carbon atom and chlorine atom occupying the axial positions. In contrast to complex **1**, the tppz ligand is linked to the Re ion by the two nitrogen donors of the adjacent pyridyl rings. This produces a dihedral angle between the two planes of 69.3° , while it is 56.8° in the case of a nitrogen atom of pyrazine and one of the pyridyl ring nitrogen are linked in the metal. The coordinated pyridyl groups are twisted (40 and 59°) with respect to the pyrazine ring. N(3)–Re(1)–N(4) bond angle ($85.4(3)^\circ$) is smaller than 90° but significantly larger than the case of complex **1** which has a 5-membered coordination ring.

Selected bond distances and angles for complex **3** are given in Table 4. A perspective view of the complex with the atom numbering is given in Fig. 3. The heterocyclic ligand functions as a bis-bidentate ligand to two Re atoms each coordinated to a nitrogen atom of the pyrazine moiety and a pyridyl nitrogen atom. The coordination spheres about the rhenium atoms are slightly distorted from idealized octahedral geometry with two *cis*

carbonyl groups in the chelation plane, and the third carbonyl group and bromide atom occupying the axial positions. In the coordination sphere of Re(1), the least-squares plane through the atoms N(1), N(3), C(25) and C(27) (best plane) and in that of Re(2) the least squares plane through the atoms N(2), N(5), C(28) and C(30) (best plane) show very slight tetrahedral distortions (average deviation less than $\pm 9^\circ$). The two Re(I) sites in the complex project very slightly from the equatorial planes, with average out-of-plane distances of 0.025 Å. The source of distortion primarily reflects the acute ligand bite angles (average 74.5°), which are significantly smaller than the ideal value of 90° because of the constraints imposed by the 5-membered chelate rings. The ligand is distorted from planarity by steric interactions between the pyridyl rings. In complex **3**, the free pyridyl rings [C(10)–C(11)–C(12)–C(13)–C(14)–N(4)] and [C(20)–C(21)–C(22)–C(23)–C(24)–N(6)] are rotated at angles of 61.7° and 57.6° with respect to the pyrazine ring to minimize the steric interactions with the coordination spheres. The pyridyl rings coordinated to Re(1) and Re(2) are tilted 23.4° and 26.3° , respectively, from the pyrazine ring.

A perspective view (ORTEP) of complex **4** with the atom numbering is shown in Fig. 4; selected bond distances and angles are given in Table 5. The molecular geometry of complex **4** is of considerable interest, as the tppz ligand is highly distorted to accommodate three Re(I) tricarbonyl cores. The pyrazine ring in tppz shows a small deviation from planarity (0.07 Å). The dihedral angles between the least-squares planes of the pyridine rings and pyrazine are 39.6° , 59.7° , 97.6° and 24.8° , respectively. The coordination geometries at the three Re atoms are best described as distorted octahedral with three carbonyl ligands arranged in the facial fashion and Re atoms project slight from the equatorial planes, with out-of-plane distances of 0.096, 0.133 and 0.014 Å respectively. The bite angles ($74.2(4)^\circ$, $80.7(4)^\circ$ and $74.9(4)^\circ$) are significantly smaller than the ideal value of 90° because of the constraints imposed by the 5- and 7-membered chelation rings.

4. Conclusions

The ligand 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) may be exploited in the synthesis of mono-, di- and trinuclear complexes incorporating $\{\text{Re}(\text{CO})_3\text{X}\}$ cores. Curiously, two forms, α - and β -, of the mononuclear formulation $[\text{Re}(\text{CO})_3\text{X}(\text{tppz})]$ are observed depending on the details of the synthesis adopted. This observation demonstrates the remarkable coordination versatility of the ligand. In addition to the anticipated dinuclear complex $[\{\text{Re}(\text{CO})_3\text{Br}\}_2(\text{tppz})]$ (**3**), a remarkable trinuclear species, which exploits all nitrogen donor atoms on the tppz has been isolated, $[\{\text{Re}(\text{CO})_3\text{Cl}\}_3(\text{tppz})]$ (**4**). The isolation of the complete family of mono-, di- and trinuclear complexes reflects both the bonding versatility of the ligand and the coordination preferences and robustness of the $\{\text{Re}(\text{CO})_3\text{X}\}$ core.

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Fig. 1.
ORTEP drawing of [ReCl(CO)₃(tppz)]·MeOH (**1**), showing the atom numbering scheme and 50% probability ellipsoids.

Fig. 2. ORTEP drawing of $[\text{ReCl}(\text{CO})_3(\text{tppz})]\cdot 2\text{H}_2\text{O}$ (**1'**), showing the atom numbering scheme and 50% probability ellipsoids.

Fig. 3. ORTEP drawing of $[\{\text{ReBr}(\text{CO})_3\}_2(\mu\text{-tppz})]$ (**3**), showing the atom numbering scheme and 50% probability ellipsoids.

Fig. 4. ORTEP drawing of $[\{\text{ReCl}(\text{CO})_3\}_3(\mu\text{-tppz})]$ (4), showing the atom numbering scheme and 50% probability ellipsoids.

Table 1

Summary of crystal, intensity, collection, and refinement data for complexes [ReCl(CO)₃(tppz)]·MeOH (1), [ReBr(CO)₃(tppz)] (2), [ReCl(CO)₃(tppz)]·2H₂O (1'), [[ReBr(CO)₃]₂(μ-tppz)] (3) and [[ReCl(CO)₃]₃(μ-tppz)] (4)

	1	2	1'	3	4
Empirical formula	C ₂₈ H ₂₀ ClN ₆ O ₄ Re	C ₂₇ H ₁₆ BrN ₆ O ₃ Re	C ₂₈ H ₂₀ ClN ₆ O ₅ Re	C ₃₀ H ₁₆ Br ₂ N ₆ O ₆ Re ₂	C ₃₆ H ₁₉ Cl ₃ N ₆ O ₉ Re ₃
Formula weight	726.15	738.57	730.14	1088.71	1344.52
Crystal size (mm ³)	0.25×0.20×0.13	0.25×0.25×0.08	0.15×0.15×0.12	0.10×0.05×0.05	0.20×0.15×0.06
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> ₂ / <i>c</i>	<i>P</i> 1	<i>Pbca</i>
<i>a</i> (Å)	9.2217(7)	9.2931(6)	18.584(4)	7.4705(16)	18.8284(13)
<i>b</i> (Å)	10.7628(8)	10.2387(7)	21.693(5)	11.476(2)	16.7154(12)
<i>c</i> (Å)	26.932(2)	27.993(2)	15.392(4)	19.335(4)	25.3657(17)
<i>α</i> (°)				73.726(4)	
<i>β</i> (°)	94.130(1)	94.615(1)	122.328(3)	85.147(4)	
<i>γ</i> (°)				77.068(4)	
<i>V</i> (Å ³)	2666.1(3)	2654.8(3)	5243(2)	1550.5(6)	7983.2(10)
<i>Z</i>	4	4	8	2	8
<i>D</i> _{calc} (Mg m ⁻³)	1.809	1.848	1.850	2.332	2.237
<i>F</i> (000)	1416	1416	2848	1012	5000
<i>μ</i> (mm ⁻¹)	4.705	6.123	4.788	10.431	9.337
Final indices ^a (2σ data), <i>R</i> ₁ (<i>wR</i> ₂)	0.0387 (0.0753)	0.0449 (0.0903)	0.0715 (0.1998)	0.0787 (0.1653)	0.0456 (0.0931)
All data, <i>R</i> ₁ (<i>wR</i> ₂)	0.0813 (0.0990)	0.1391 (0.1208)	0.1026 (0.2225)	0.1691 (0.2090)	0.0754 (0.1015)

$$^a R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|, wR_2 = \left[\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)] \right]^{1/2}.$$

Table 2Selected bond distances ($\text{\AA}$) and angles ($^{\circ}$) for complexes **1** and **2**

	1	2
Re(1)–C(25)	1.918(8)	1.900(9)
Re(1)–C(26)	1.931(7)	1.959(11)
Re(1)–C(27)	1.898(7)	1.873(11)
Re(1)–N(1)	2.235(5)	2.249(7)
Re(1)–N(3)	2.139(5)	2.167(7)
Re(1)–X	2.490(2)	2.618(1)
C(27)–Re(1)–C(25)	90.5(3)	89.5(4)
C(27)–Re(1)–C(26)	87.6(3)	86.8(4)
C(25)–Re(1)–C(26)	88.7(3)	89.8(4)
C(27)–Re(1)–N(3)	95.8(2)	97.0(4)
C(25)–Re(1)–N(3)	94.8(3)	93.0(3)
C(26)–Re(1)–N(3)	175.1(2)	175.3(4)
C(27)–Re(1)–N(1)	168.6(3)	169.2(4)
C(25)–Re(1)–N(1)	96.7(2)	97.6(3)
C(26)–Re(1)–N(1)	101.4(2)	101.2(4)
N(3)–Re(1)–N(1)	74.8(2)	74.7(3)
C(27)–Re(1)–X	91.6(2)	91.9(3)
C(25)–Re(1)–X	177.6(2)	178.6(2)
C(26)–Re(1)–X	92.6(2)	90.6(3)
N(3)–Re(1)–X	83.8(1)	86.5(2)
N(1)–Re(1)–X	81.1(1)	81.0(2)

Table 3Selected bond distances (Å) and angles (°) for complex **1'**

Re(1)–C(25)	1.920(10)	Re(1)–N(3)	2.207(8)
Re(1)–C(26)	1.927(11)	Re(1)–N(4)	2.274(8)
Re(1)–C(27)	1.908(11)	Re(1)–Cl(1)	2.486(3)
C(27)–Re(1)–C(25)	89.7(4)	C(26)–Re(1)–N(4)	90.8(4)
C(27)–Re(1)–C(26)	90.5(4)	N(3)–Re(1)–N(4)	85.4(3)
C(25)–Re(1)–C(26)	86.9(4)	C(27)–Re(1)–Cl(1)	89.3(3)
C(27)–Re(1)–N(3)	93.0(4)	C(25)–Re(1)–Cl(1)	178.2(3)
C(25)–Re(1)–N(3)	96.3(4)	C(26)–Re(1)–Cl(1)	91.6(3)
C(26)–Re(1)–N(3)	175.2(4)	N(3)–Re(1)–Cl(1)	85.2(2)
C(27)–Re(1)–N(4)	175.0(4)	N(4)–Re(1)–Cl(1)	85.8(2)
C(25)–Re(1)–N(4)	95.2(4)		

Table 4Selected bond distances (Å) and angles (°) for complex **3**

Re(1)–C(25)	1.922(17)	Re(2)–C(28)	1.947(15)
Re(1)–C(26)	1.913(16)	Re(2)–C(29)	1.928(15)
Re(1)–C(27)	1.957(14)	Re(2)–C(30)	1.917(14)
Re(1)–N(1)	2.194(10)	Re(2)–N(2)	2.213(11)
Re(1)–N(3)	2.161(10)	Re(2)–N(5)	2.182(11)
Re(1)–Br(1)	2.619(2)	Re(2)–Br(2)	2.625(1)
C(27)–Re(1)–C(25)	91.0(6)	C(30)–Re(2)–C(29)	90.1(6)
C(27)–Re(1)–C(26)	90.0(6)	C(30)–Re(2)–C(28)	86.8(6)
C(25)–Re(1)–C(26)	88.4(6)	C(29)–Re(2)–C(28)	89.8(6)
C(27)–Re(1)–N(3)	94.3(5)	C(30)–Re(2)–N(5)	95.9(5)
C(25)–Re(1)–N(3)	95.0(5)	C(29)–Re(2)–N(5)	93.2(5)
C(26)–Re(1)–N(3)	174.5(5)	C(28)–Re(2)–N(5)	176.0(5)
C(27)–Re(1)–N(1)	96.7(5)	C(30)–Re(2)–N(2)	169.3(5)
C(25)–Re(1)–N(1)	167.3(5)	C(29)–Re(2)–N(2)	95.4(5)
C(26)–Re(1)–N(1)	101.6(5)	C(28)–Re(2)–N(2)	102.5(5)
N(3)–Re(1)–N(1)	74.4(4)	N(5)–Re(2)–N(2)	74.7(4)
C(27)–Re(1)–Br(1)	179.4(4)	C(30)–Re(2)–Br(2)	93.5(4)
C(25)–Re(1)–Br(1)	89.4(4)	C(29)–Re(2)–Br(2)	176.5(4)
C(26)–Re(1)–Br(1)	89.6(4)	C(28)–Re(2)–Br(2)	90.1(4)
N(3)–Re(1)–Br(1)	86.0(3)	N(5)–Re(2)–Br(2)	86.8(3)
N(1)–Re(1)–Br(1)	82.8(3)	N(2)–Re(2)–Br(2)	81.2(2)

Table 5Selected bond distances (Å) and angles (°) for complexes **4**

Re(1)–C(25)	1.892(15)	Re(2)–N(3)	2.253(10)
Re(1)–C(26)	1.951(17)	Re(2)–N(4)	2.237(10)
Re(1)–C(27)	1.892(15)	Re(2)–Cl(2)	2.490(3)
Re(1)–N(1)	2.213(10)	Re(3)–C(31)	1.893(15)
Re(1)–N(2)	2.217(9)	Re(3)–C(32)	1.903(17)
Re(1)–Cl(1)	2.482(3)	Re(3)–C(33)	1.889(14)
Re(2)–C(28)	1.927(14)	Re(3)–N(5)	2.205(11)
Re(2)–C(29)	1.903(13)	Re(3)–N(6)	2.176(10)
Re(2)–C(30)	1.921(16)	Re(3)–Cl(3)	2.471(3)
C(27)–Re(1)–C(25)	86.3(5)	C(28)–Re(2)–N(3)	92.3(5)
C(27)–Re(1)–C(26)	89.9(5)	N(4)–Re(2)–N(3)	80.7(4)
C(25)–Re(1)–C(26)	89.5(6)	C(30)–Re(2)–Cl(2)	173.2(4)
C(27)–Re(1)–N(2)	171.3(4)	C(29)–Re(2)–Cl(2)	85.9(4)
C(25)–Re(1)–N(2)	101.7(5)	C(28)–Re(2)–Cl(2)	85.0(4)
C(26)–Re(1)–N(2)	93.5(4)	N(4)–Re(2)–Cl(2)	87.0(3)
C(27)–Re(1)–N(1)	97.4(5)	N(3)–Re(2)–Cl(2)	87.3(3)
C(25)–Re(1)–N(1)	171.0(5)	C(33)–Re(3)–C(32)	82.3(6)
C(26)–Re(1)–N(1)	98.6(5)	C(33)–Re(3)–C(31)	86.9(5)
N(2)–Re(1)–N(1)	74.2(4)	C(32)–Re(3)–C(31)	88.4(9)
C(27)–Re(1)–Cl(1)	94.7(4)	C(33)–Re(3)–N(6)	98.1(5)
C(25)–Re(1)–Cl(1)	88.9(4)	C(32)–Re(3)–N(6)	177.8(7)
C(26)–Re(1)–Cl(1)	175.0(4)	C(31)–Re(3)–N(6)	93.8(6)
N(2)–Re(1)–Cl(1)	82.2(3)	C(33)–Re(3)–N(5)	173.0(5)
N(1)–Re(1)–Cl(1)	82.7(3)	C(32)–Re(3)–N(5)	104.7(5)
C(30)–Re(2)–C(29)	88.2(5)	C(31)–Re(3)–N(5)	92.8(5)
C(30)–Re(2)–C(28)	91.7(5)	N(6)–Re(3)–N(5)	74.9(4)
C(29)–Re(2)–C(28)	91.2(5)	C(33)–Re(3)–Cl(3)	97.2(4)
C(30)–Re(2)–N(4)	96.9(5)	C(32)–Re(3)–Cl(3)	93.4(7)
C(29)–Re(2)–N(4)	95.0(4)	C(31)–Re(3)–Cl(3)	175.8(4)
C(28)–Re(2)–N(4)	169.6(5)	N(6)–Re(3)–Cl(3)	84.4(3)
C(30)–Re(2)–N(3)	98.7(5)	N(5)–Re(3)–Cl(3)	83.0(3)
C(29)–Re(2)–N(3)	172.2(5)		