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FULL PAPER

Self-assembly of tetrametallic square $[Re_4(CO)_{12}Br_4(\mu\text{-pz})_4]$ (pz = pyrazine) from $[Re(CO)_4Br(pz)]$. A mechanistic approach †

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Self-assembly of the tetranuclear square $[Re_4(CO)_{12}Br_4(\mu\text{-pz})_4]$ (pz = pyrazine) from the monometallic complex $[Re(CO)_4Br(pz)]$ in acetone at room temperature has been investigated. The mechanistic pathway is examined and proved by both *in-situ* ^{1}H NMR and ES-MS studies. Both techniques are helpful to identify three species, $Re_2(CO)_8Br_2(\mu\text{-pz})$, $Re(CO)_3Br(pz)_2$ and $Re_2(CO)_7Br_2(\mu\text{-pz})(pz)$, as intermediates. The other intermediates, $Re_3(CO)_{11}Br_3(\mu\text{-pz})_2$, $Re_3(CO)_{10}Br_3(\mu\text{-pz})_2(pz)$, $Re_4(CO)_{14}Br_4(\mu\text{-pz})_3$ and $Re_4(CO)_{13}Br_4(\mu\text{-pz})_3(pz)$, detected by electrospray mass spectral techniques also support the proposed mechanistic pathway.

Introduction

The challenge of generating highly ordered supramolecular structures containing transition metals with specific coordination geometries particularly *via* the self-assembly process has been taken up by several groups of workers in this decade.[1–8] The metal-directed self-assembly of "molecular squares" by the simple combination of the square-planar and octahedral coordination geometry of Pd and Re complexes with pyridine-based bridging ligands forms the objective of Stang, Hupp, Sullivan, Lees and others.[9–15] In spite of the enormous amount of literature on the synthesis and characterization of metallo-macromolecules by the self-assembly processes, few attempts have been made to postulate a mechanistic pathway.[16–18] The gaining of knowledge on the mechanism of the self-assembly process from many components in solution is still a difficult task but it is of prime importance.

In the course of our studies on the synthesis, properties and applications of some metallomacromolecules, we have been interested in the study of the self-assembly process of rhenium-based supramolecules.[8] *In-situ* ^{1}H NMR spectroscopy and electrospray mass spectrometry (ES-MS) are the two most important tools available to monitor the self-assembly process.[17,19,20] Even though ES-MS has been used as a powerful tool for analyzing biomolecules, its application to inorganic and organometallic chemistry is limited.[21–32] This spectral technique helps us to detect unstable species which are generated in solution during the course of a chemical reaction.[33–42] ^{1}H NMR has been invariably used to identify the intermediates involved during the self-assembly mechanism.[16–19] These two important spectral techniques are judiciously used in the present study to understand the mechanism of the self-assembly of tetranuclear square $[Re_4(CO)_{12}Br_4(\mu\text{-pz})_4]$ (pz = pyrazine) from the monometallic rhenium compound $[Re(CO)_4Br(pz)]$ (**1**). The intermediates of this process have been detected and characterized, based on which we postulate a "step-by-step" pathway of self-assembly.

† Electronic supplementary information (ESI) available: crystallographic data and elemental analysis for compound **9**. See http://www.rsc.org/suppdata/dt/b1/b101992i/

Experimental

All the chemicals used in the present study were purchased from commercial sources and were used as received. All manipulations on the synthesis were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over CaH_2 or Na/benzophenone and freshly distilled before use. Infrared spectra were recorded on a Perkin Elmer 882 FT IR spectrophotometer.

Synthesis of $[Re(CO)_4Br(pz)]$ (1)

To a solution of $Re(CO)_5Br$ (406 mg, 1.00 mmol) in CH_2Cl_2 (100 ml) and CH_3CN (1 ml) at 0 °C was added a solution of Me_3NO (75 mg, 1.00 mmol) in CH_2Cl_2 (50 ml). The mixture was stirred at 0 °C for 2 h and filtered through a short column of silica gel. The solvent was removed under vacuum and the residue, $Re(CO)_4Br(NCMe)$, was redissolved in toluene (200 ml). To the resultant solution at 15 °C was added dropwise a solution of pyrazine (80 mg, 1.00 mmol) in toluene (50 ml). Stirring was continued and the completion of the reaction was checked by TLC and IR. The solvent was removed under vacuum and the residue was chromatographed on a silica gel TLC plate using a mixture of ethyl acetate and hexane (1 : 2) as eluent at 10 °C to afford the light yellow compound **1** (190 mg, 41%). IR (CH_2Cl_2): ν(CO) 2116(w), 2017(vs), 2001 (sh), 1943(s) cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): δ 9.29 (dd, ^3J = 3.0 Hz, ^4J = 1.5 Hz, 2 H, H^a), 8.93 (dd, ^3J = 3.0 Hz, ^4J = 1.1 Hz, 2 H, H^b); ^{13}C NMR (100 MHz, $(CD_3)_2CO$, 25 °C): δ 188.1, 186.4, 184.7 (1 : 2 : 1, CO), 150.5 (CH), 148.7 (CH).

In-situ ^{1}H-NMR analysis

Compound **1** (45.8 mg, 0.1 mmol) was dissolved in 0.5 ml of acetone-d_6 in an NMR tube under a nitrogen atmosphere and the chemical transformation was followed by *in-situ* ^{1}H-NMR techniques at 40 °C. NMR spectra of the sample were recorded every two hours on a Bruker AMX-400 FT-NMR spectrometer and the self-assembly of the tetranuclear square $[Re_4(CO)_{12}Br_4(\mu\text{-pz})_4]$ (**9**) was monitored.

ES-MS analysis

ES-MS was performed on a Finnigan LCQ quadrupole ion trap

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mass spectrometer (Finnigan MAT, San Jose, CA) equipped with a standard electrospray ionization source. The sample solution was prepared by dissolving $[Re(CO)_4Br(pz)]$ (**1**) in acetone under a nitrogen atmosphere and the temperature was maintained at 40 °C. The solution was delivered to the ESI sprayer by a syringe pump at a flow rate of 3 μl min^{-1}. An ESI high voltage of 4.5 kV was applied to produce a stable ion current. The temperature of the heated capillary was reduced to 50 °C to avoid further reaction and thermal decomposition of the reactant and products. Substantial fragmentation of the product was found at higher temperatures. To maintain gentle ionization conditions, the capillary-skimmer potential was kept at 10 V to minimize collisional fragmentation of the intermediates and products. The ion guide potential was optimized for maximum total ion intensity. The spectra were taken at 0.5 hour intervals over the first two hours and then every one hour afterwards. Calibration of the mass range (50–2000) was carried out according to the standard procedure and with reference to the compounds (caffeine, MRFA and Ultramark 1621) provided by the mass spectrometer manufacturer.

Crystallography

The crystallographic details of compound **9** are available as ESI. †

CCDC reference number 160973.

See http://www.rsc.org/suppdata/dt/b1/b101992i/ for crystallographic data in CIF or other electronic format.

Results and discussion

In-situ ^{1}H NMR study

Compound **1** in acetone-d_6 is transformed into the molecular square $[Re(CO)_3Br(\mu\text{-}pz)]_4$ (**9**) at 25 °C in two days, presumably *via* various intermediates. To ascertain the formation of the intermediates, the self-assembly of **9** from **1** was carried out in an NMR tube and the reaction was completed within 17 hours at 40 °C as observed by *in-situ* ^{1}H NMR spectroscopy. Exploration of the stack-plot (Fig. 1) points out several reaction intermediates. Initially the proton signals of **1** appear at δ 9.29 and 8.93. After two hours, the proton signals corresponding to the intermediates have emerged and the signals of the tetrametallic square **9** appeared at the fourth hour. The intermediates formed during this conversion are identified as $Re_2(CO)_8Br_2(\mu\text{-}pz)$ (**2**),[43] $Re(CO)_3Br(pz)_2$ (**3**) and $Re_2(CO)_7Br_2(\mu\text{-}pz)(pz)$ (**4**). Based on the concentration variation of the intermediates with time, we propose the self-assembly pathway shown in Scheme 1 which is also consistent with the ES-MS study (*vide infra*). During the course of the reaction the Re–N bond of **1** dissociates to give the reactive $Re(CO)_4Br$ species and pyrazine at ambient temperature. The species $Re(CO)_4Br$ may readily associate with **1** to form intermediate **2** followed by reaction with pyrazine to form another intermediate **4**. The postulation of these intermediates is supported by the appearance of the characteristic proton signals of **1**, **2**, **4** and free pyrazine (*cf*. the first plot of the NMR spectra in Fig. 1). Similarly, pyrazine is likely to react with **1** to form **3**, which on further reaction with **1** may afford the intermediate **4**. Fig. 1 also shows the presence of several minor peaks (δ 9.11, 9.08, 9.07, 9.04, 9.03 and 9.02) close to that of square **9**. We believe that these signals indicate the existence of other intermediates with higher molecular weight, which are eventually converted to the final product, molecular square **9**. Our postulation is in accordance with the logical conclusion of Hupp *et al.*[16] and others[44,45] that cyclic structures can be preferred over oligomeric ones based on enthalpy values. The assignment of the ^{1}H NMR signals of the intermediates is supported by the metal–ligand ratio (Table 1). For example, complex **1**, the intermediate **4** and the product **9** bear the same metal–ligand ratio (1 : 1) and the average

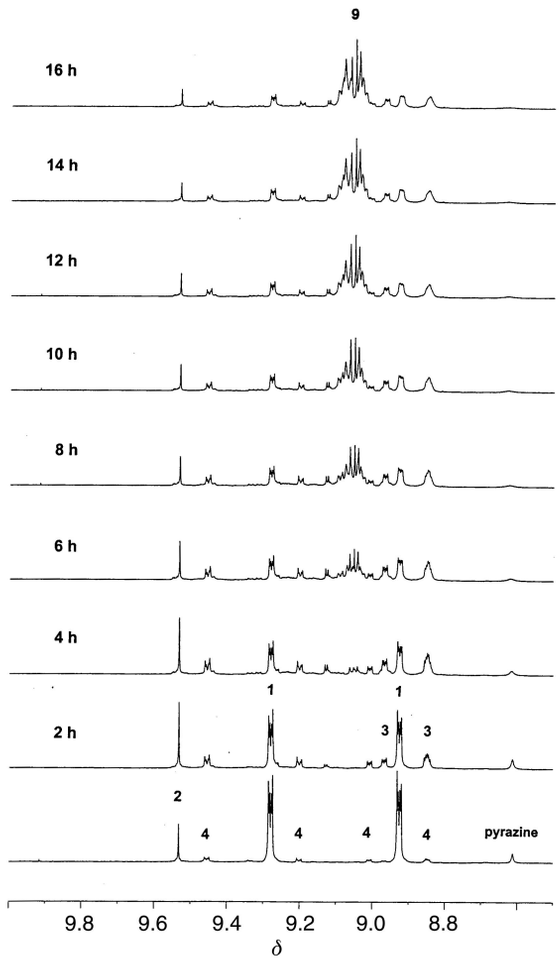


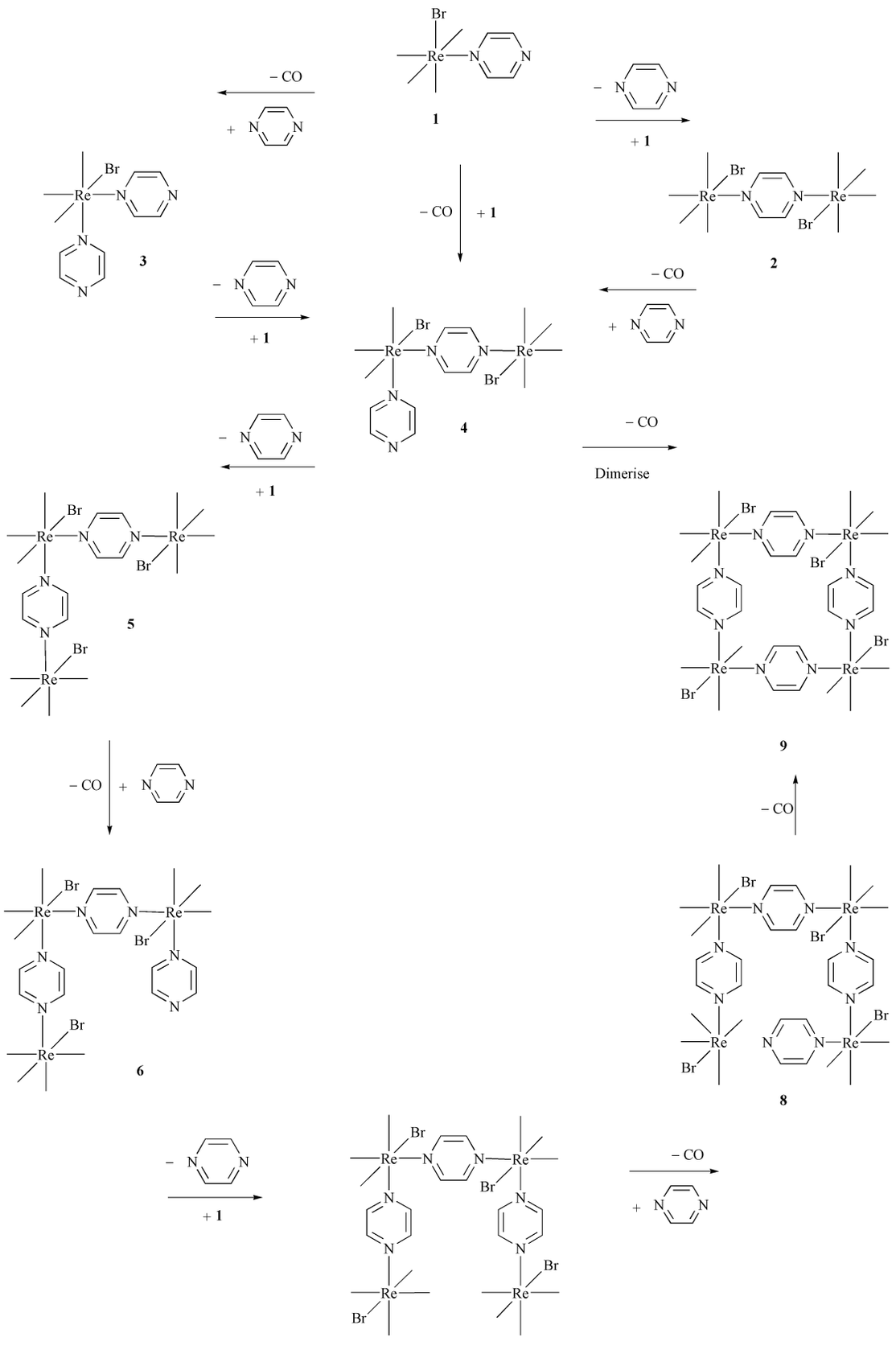
Fig. 1 Stack plot–time dependent ^{1}H NMR spectra showing the self-assembly of **9** (40 °C).

pyrazine proton signals of these species (**1**, δ 9.11; **4**, δ 9.13; **9**, δ 9.05) are very close. In addition, the average proton signals of **1**, **4**, and **9** are in between those of **2** (δ 9.55) and free pyrazine (δ 8.61) and their metal–ligand ratios are in the order of 2 : 1 : 0 as shown in Table 1. When a free pyrazine (δ 8.61) is coordinated to the Re center, the electrophilic nature of the metal will shift the proton signals of the coordinated pyrazine towards the low field region. Among the intermediates, **2** has the highest metal–ligand ratio and thus its proton signal appears in the most deshielded region.

Electrospray ionization mass spectral analysis

The conversion of the mononuclear rhenium complex $[Re(CO)_4Br(pz)]$ (**1**) to the tetranuclear square $[Re_4(CO)_{12}Br_4(\mu\text{-}pz)_4]$ (**9**) has also been studied by ES-MS analysis in acetone at room temperature. This study indicates the formation of other intermediates involved in the self-assembly process apart from those identified by the *in-situ* ^{1}H-NMR studies. Fig. 2 shows the time-dependent negative-ion ES-MS spectra in the range *m/e* 300–1900. Each spectrum was taken from an average of 10 consecutive scans. For organometallic compounds, transformation from neutral to cation by conventional ES-MS requires suitable functional groups for protonation. Due to the low basicity, the oxygen atom of the coordinated CO that possesses a lone-pair of electrons is not readily protonated. Though the free nitrogen atoms associated with the heterocyclic ligands seem available for protonation, neither the parent ion nor the other interpretable intermediates were found in the positive ion spectra. We believed that the formation of negative ions may attribute to the electrolytic nature of electrospray ionization. During a typical operation under high voltage, the

metal electrospray capillary can act as an electrolytic cell, forming cations or anions *via* oxidation or reduction.[46] The major ions identified from the observed ES-MS spectra are summarized in Table 2. The *m*/*e* values given in Table 2 are for the most intense peaks in each isotopic envelope. Assignment of the observed species is further confirmed by comparison of the calculated isotopic distribution with the high-resolution spectra (Zoom scan). To exclude the ambiguity between fragment ions resulting from dissociation in the gas phase and reaction intermediates, MS/MS measurements with tetranuclear square



Scheme 1 Proposed mechanistic pathway for the formation of **9** from **1**.

Table 1 The ^{1}H NMR signals of the pyrazine ligand and the metal–ligand ratio in **2**, **1**, **4**, **9** and **3**

Compound	^{1}H NMR signal (ppm)	Average ^{1}H NMR signal (ppm)	Metal–ligand ratio
2	9.55	9.55	2
1	9.29, 8.93	9.11	1
4	9.45, 9.20, 9.01, 8.85	9.13	1
9	9.05	9.05	1
3	8.97, 8.85	8.91	0.5
Pyrazine	8.61	8.61	0

Table 2 Reaction intermediates observed in the electrospray ionization mass spectra

Intermediate	Intermediate identified	*m/e*
2	$Re_2(CO)_8Br_2(\mu\text{-pz})$	836
3	$Re(CO)_3Br(pz)_2$	510
4	$Re_2(CO)_7Br_2(\mu\text{-pz})(pz)$	888
5	$Re_3(CO)_{11}Br_3(\mu\text{-pz})_2$	1266
6	$Re_3(CO)_{10}Br_3(\mu\text{-pz})_2(pz)$	1318
7	$Re_4(CO)_{14}Br_4(\mu\text{-pz})_3$	1696
8	$Re_4(CO)_{13}Br_4(\mu\text{-pz})_3(pz)$	1748

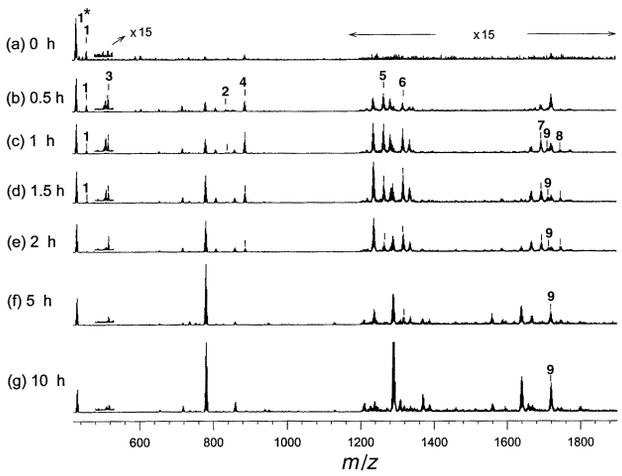


Fig. 2 Negative-ion electrospray spectra in the *m/e* range of 300–1900 (a) before heating the solution at 40 °C, (b) 0.5 h after reaction, (c) 1 h after reaction, (d) 1.5 h after reaction, (e) 2 h after reaction, (f) 5 h after reaction and (g) 10 h after reaction. Peak assignments are indicated and also listed in Table 2.

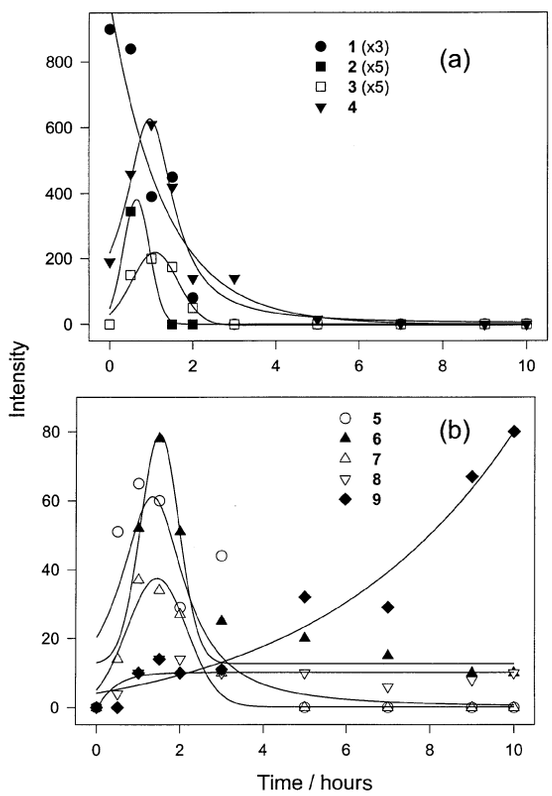


Fig. 3 Time dependence of the relative abundance in absolute intensity for the reactant and observed intermediates and product. (a) Species **1** (*m/e* 458), **2** (*m/e* 836), **3** (*m/e* 510) and **4** (*m/e* 888) (b) Species **5** (*m/e* 1266), **6** (*m/e* 1318), **7** (*m/e* 1696), **8** (*m/e* 1748) and **9** (*m/e* 1722).

$[Re_4(CO)_{12}Br_4(\mu\text{-pz})_4]$ (**9**) and all of the observed product ions were performed on the quadrupole ion-trap. The results indicate that the species $Re_2(CO)_6Br_2(\mu\text{-pz})$ (*m/e* 780), $Re_2(CO)_6Br_2(\mu\text{-pz})(pz)$ (*m/e* 860), $Re_3(CO)_9Br_3(\mu\text{-pz})_2(pz)$ (*m/e* 1290) and $Re_4(CO)_{12}Br_4(\mu\text{-pz})_3$ (*m/e* 1640), are the fragmentation products. All the species collected in Table 2 are truly produced during the reaction, and are not obtained from thermal or collisional dissociation of larger species present in the solution.

When compound **1** is dissolved in acetone, it eliminates either CO or a pyrazine molecule. (The intense peak 1* (*m/e* = 430), which emerges at 0 h and decreases in intensity with time, corresponds to the CO dissociation product of **1** during the ESI process.) The reactive species formed may react with either pyrazine or **1** (producing **3** or **2**) as shown in Scheme 1. After the elimination of pyrazine followed by the addition of one molecule of **1** (bearing the active site on pyrazine) the intermediate **4** forms $[Re_3(CO)_{11}Br_3(\mu\text{-pz})_2]$ (**5**). On subsequent elimination of one CO and addition of one pyrazine molecule, **5** produces the intermediate $[Re_3(CO)_{10}Br_3(\mu\text{-pz})_2(pz)]$ (**6**). Further, **6** surrenders one molecule of pyrazine and adds one molecule of **1** rendering the intermediate $[Re_4(CO)_{14}Br_4(\mu\text{-pz})_3]$ (**7**). This intermediate behaves in a way similar to **5** and gives the intermediate $[Re_4(CO)_{13}Br_4(\mu\text{-pz})_3(pz)]$ (**8**). Elimination of one CO from **8** facilitates the formation of the tetrametallic square **9**. The species with *m/e* = 1724 could not be designated with a definitive structure except for the possibility of a linear oligomer. A close scrutiny of Fig. 2 reveals that **9** becomes detectable one hour after the beginning of the reaction. The gradual development and disappearance (as and when **9** grows in intensity) of an intermediate with higher molecular weight **8**, clearly indicates the self-assembly pathway. One may visualise the possibility of the dimerisation of **4**, after eliminating one CO, leading to the formation of **9** even in the beginning of the self-assembly process.

To gain a clear insight into the self-assembly process, the time-dependent behaviour of the intermediates is plotted in Fig. 3. Based on these spectral observations, the sequence for the formation of the various intermediates shown in Scheme 1 is proposed for the self-assembly process. After 10 h, the molecular ion **9** and its fragments $Re_2(CO)_6Br_2(\mu\text{-pz})$ (*m/e* 780), $Re_2(CO)_6Br_2(\mu\text{-pz})(pz)$ (*m/e* 860), $Re_3(CO)_9Br_3(\mu\text{-pz})_2(pz)$ (*m/e* 1290) and $Re_4(CO)_{12}Br_4(\mu\text{-pz})_3$ (*m/e* 1640) dominate the whole *m/e* range, suggesting slow completion of the reaction towards the final product **9**. In the study of the self-assembly of tris-bipyridine ligands with iron(II), Lehn *et al.*[18] have pointed out that a linear kinetic product will be formed before the formation of the cyclic thermodynamic products, depending on the local and overall energy minimum in the potential energy surface. In a similar fashion, we postulate that various

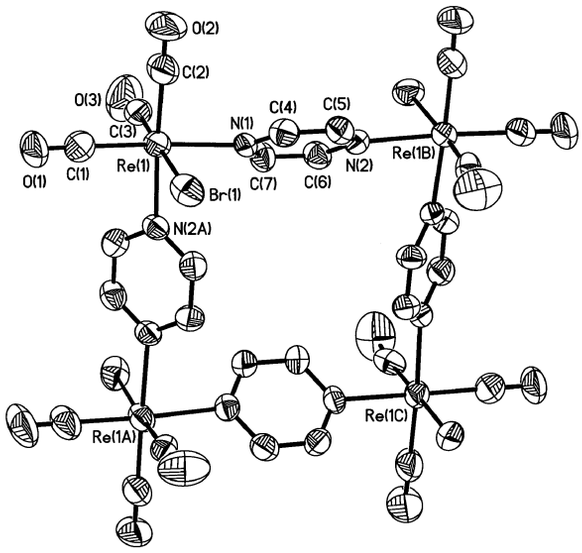


Fig. 4 ORTEP[47] diagram of $[Re_4(CO)_{12}Br_4(\mu\text{-}pz)_4]$ (**9**). Selected bond distances (Å) and angles (°): Re(1)–N(1) 2.197(6), Re(1)–N(2A) 2.198(7), Re(1)–C(1) 1.935(11), Re(1)–C(2) 1.954(11), Re(1)–C(3) 1.918(15), Re(1)–Br(1) 2.580(3); N(1)–Re(1)–N(2A) 85.4(2), N(1)–Re(1)–C(1) 177.6(4), N(1)–Re(1)–C(2) 91.3(3), N(1)–Re(1)–C(3) 91.9(8), N(1)–Re(1)–Br(1) 85.77(19).

intermediates observed in our study will be progressively transformed into a thermodynamically more stable cyclic product, the tetrametallic square **9**. The gradual disappearance of ions **7** and **8**, and the clear appearance of **9** and its fragment ions from 0.5 h to 10 h is strong evidence for the precursor identification and transformation processes. No species above *m/e* 1800 is found.

From the growth and decay of the observed species one can get important clues as to the key intermediates of the self-assembly. As seen in Fig. 3(a), the initial intermediates **2** and **4** which are in high concentration after 0.5 hour, diminish with time and reach a minimum concentration when the self-assembly process is almost complete; they are converted into intermediates **5** and **6**. This evolution is clearly demonstrated in Fig. 3. The concentration of intermediates **5** and **6** grows for the first 1.5 hours, then gradually diminishes in intensity. In addition, Fig. 2 illustrates the presence of two species, $Re_3(CO)_{10}Br_3(\mu\text{-}pz)_2$ (*m/e* 1238) and $Re_4(CO)_{13}Br_4(\mu\text{-}pz)_3$ (*m/e* 1667), which grow from 0.5–1.5 hours and start diminishing when the self-assembly is in progress and almost vanish after 5 hours. These detected species with reduced coordination sites may not be present in solution and may be formed in the gas phase during the electrospray ionisation process. Thus, the mechanistic pathway for the conversion of **1** to **9** can unambiguously be assigned by the time-dependent mass spectrometric behavior of the various intermediates **2**–**8**.

Structural characterization of $[Re_4(CO)_{12}Br_4(\mu\text{-}pz)_4]$ (9)

Dark red crystals of **9** were obtained from an acetone solution at 25 °C and an X-ray diffraction study was undertaken. The ORTEP diagram of **9** is shown in Fig. 4. The structure consists of a molecular square in which four $Re(CO)_4Br$ corners are bridged by four pyrazine ligands. The bonding of each Re atom to two pyrazine ligands, three terminally bonded CO groups and one Br atom gives the metal a distorted octahedral geometry. Atom Br(1) is disordered with the *trans* CO group in 67/33 occupancy.

Conclusions

In summary, a mechanistic pathway has been presented to explain the self-assembly of $Re_4(CO)_{12}Br_4(\mu\text{-}pz)_4$ from $Re(CO)_4Br(pz)$. *In-situ* ^1H NMR and ES-MS analysis are helpful for the identification of the various possible intermediates and the final product. In the vast area of supramolecular chemistry, this type of mechanistic approach will definitely aid the understanding of the process of self-assembly.

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