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Article

Synthesis and Characterization of New Trimeric Rhenium(I) Complexes. The Influence of Steric Factors on the Size of Pyrazolonaterhenium(I) Metallomacrocycles

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The reaction of [ReX(CO)$_5$] with thiosemicarbazones H_2L^R derived from β-keto esters (X = Cl, Br; R = Me, Ph) allowed the isolation of cyclic trimeric complexes [Re$_3$(pyz^R)$_3$(CO)$_9$], where pyz^R is the pyrazolonate corresponding to the thiosemicarbazone. Electron spray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS) monitoring of the reactions of H_2L^{Ph} in toluene confirmed that the trimer was formed in the reaction mixture and no higher oligomer was detected. These studies, together with the X-ray structures of the trimeric complexes, afford new insight into the factors influencing the self-assembly of pyrazolonaterhenium(I) complexes.

Introduction

The *fac*-Re^I(CO)$_3$ fragment has frequently been used for the construction of self-assembled metallomacrocycles with interesting photophysical, sensing, sieving, and catalytic properties.[1,2] The bridging ligands are usually bipyridine, pyrazine, and related N-donor ligands. However, the potentially N,O,O′-tridentate ligands 3-hydroxy-1,2,3-benzotriazine-4(3*H*)-one (bzt),[3] L-proline,[5] and *N*,*N*-dimethylglycine[5] and the potentially N,S,O-tridentate ligand 2,5-dihydro-3-methyl-5-oxo-1*H*-pyrazole-1-carbothiamide (Hpyz^H; see Scheme 1)[4] have also recently been shown to be suitable. In this last case,[4] the reaction of methyl acetoacetate (H_2L^H; Scheme 1) with [ReX(CO)$_5$] (X = Cl, Br) yielded the metallomacrocyclic tetramer [Re$_4$(pyz^H)$_4$(CO)$_{12}$] (**2a**), in which the pyrazolonate ligands coordinate to Re through their S and N3 atoms (forming a five-membered chelate ring), the *fac*-Re(CO)$_3$ fragments are located as if seated on the vertexes of a tetrahedron with their COs pointing outward, and the tetrameric structure is created by interaction between each metal atom and the O atom of a neighboring monomer.[6] In the analogous reaction between [ReBr(CO)$_5$] and ethyl 2-methylacetoacetate thiosemicarbazone (H_2L^B), isolation of [ReBr(CO)$_3$(Hpyz^B)], in which the pyrazolone ligand is not deprotonated, constitutes strong evidence that cyclization must occur following coordination of the thiosemicarbazone ligand to the metal.[4] In addition, isolation of the aqua complex [Re(pyz^B)(CO)$_3$(H_2O)] (by another route) suggests that the fragment [Re(pyz)(CO)$_3$], where pyz is a generic pyrazolonate, can itself act as a modular unit in Re^I chemistry.[4]

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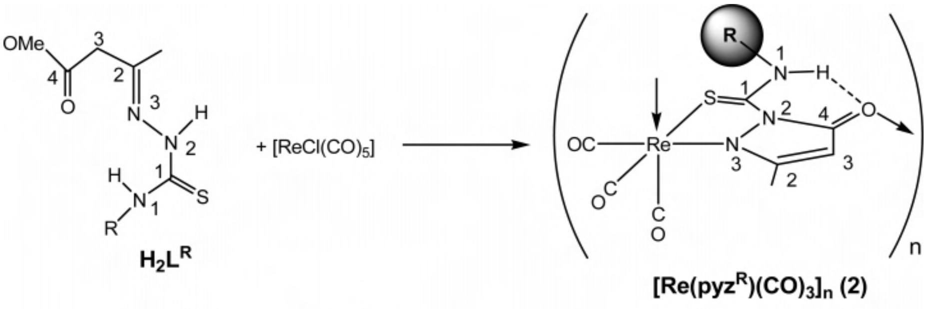
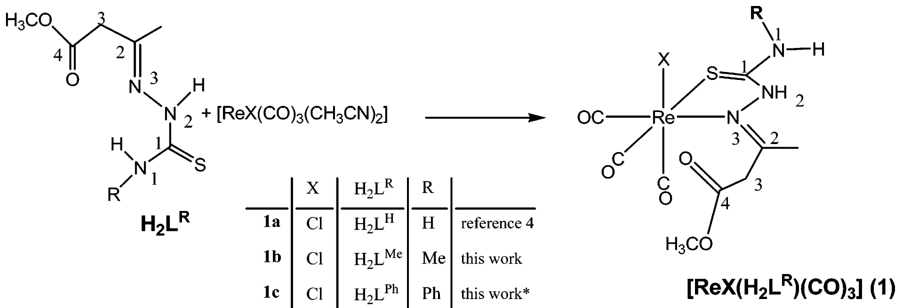
Scheme 1



	pyz^R-	n	
2a	pyz^H	4	reference 4
2b	pyz^Me	3	this work
2c	pyz^Ph	3	this work

Scheme 2



	X	H_2L^R	R	
1a	Cl	H_2L^H	H	reference 4
1b	Cl	H_2L^{Me}	Me	this work
1c	Cl	H_2L^{Ph}	Ph	this work*
1d	Br	H_2L^H	H	reference 4
1e	Br	H_2L^{Me}	Me	this work
1f	Br	H_2L^{Ph}	Ph	this work*

*Obtained as a mixture with other complexes

We have now investigated the reactions of $[ReX(CO)_5]$ (X = Cl, Br) with H_2L^{Me} and H_2L^{Ph} (Scheme 1), anticipating that the N1 substituents of these ligands might affect the formation, nuclearity, and structure of the resulting pyrazolone complexes. Because in our previous work[4] the reaction of H_2L^H with *fac*-$[ReX(CO)_3(CH_3CN)_2]$, while failing to achieve cyclization of H_2L^H to the pyrazolone, had given the thiosemicarbazone complexes $[ReX(CO)_3(H_2L^H)]$ (**1a**; see Scheme 2), we also investigated whether the N1 substituents of H_2L^{Me} and H_2L^{Ph} affected the formation of complexes of this latter type.

Results

Synthesis. The reaction of *fac*-$[ReX(CO)_3(CH_3CN)_2]$ (X = Cl, Br) with H_2L^{Me} in chloroform at room temperature yielded the thiosemicarbazone adducts **1b** and **1e** (Scheme 2) as pale-yellow solids. Their FAB(NBA) spectra display signals corresponding to the formula $[ReX(CO)_3\{H_2L^{Me}\}]$. Their IR spectra display three very strong ν(CO) bands in the 1891−2025-cm^{-1} region, which is indicative of *fac*-coordination geometry. In their ^{1}H NMR spectra, the hydrazinic proton singlets at 10.85 (**1a**) and 10.90 ppm (**1e**) confirm the S,N2-coordination of the undeprotonated thiosemicarbazone to the Re.[4,7]

By contrast, when H_2L^{Ph} was reacted with $[ReX(CO)_3(CH_3CN)_2]$ under the same conditions, IR and ^{1}H NMR studies showed the solids obtained to be mixtures of complexes involving both the thiosemicarbazone and pyrazolone resulting from its cyclization as in Scheme 1.

The reactions of H_2L^{Me} and H_2L^{Ph} with $[ReCl(CO)_5]$ at various concentrations in refluxing toluene afforded, after 20 h, the pyrazolonate complexes **2b** and **2c**, respectively. Compound **2c** was also obtained with methanol as the solvent. Elemental analyses showed both to have 1:1 stoichiometry, and their IR spectra showed two strong ν(CO) bands in the *fac*-$Re^I(CO)_3$ region (see above). Their FAB(NBA) spectra displayed signals corresponding to the trimer $[Re_3(pyz^R)_3(CO)_9]$ and no signals with higher *m*/*z* values, and X-ray crystallography confirmed their trimeric nature in the solid state (see below), but electron spray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS), which is sensitive to the nuclearity of Re oligomers,[8,9] showed that $^1/_2$ h after dissolution in dimethyl

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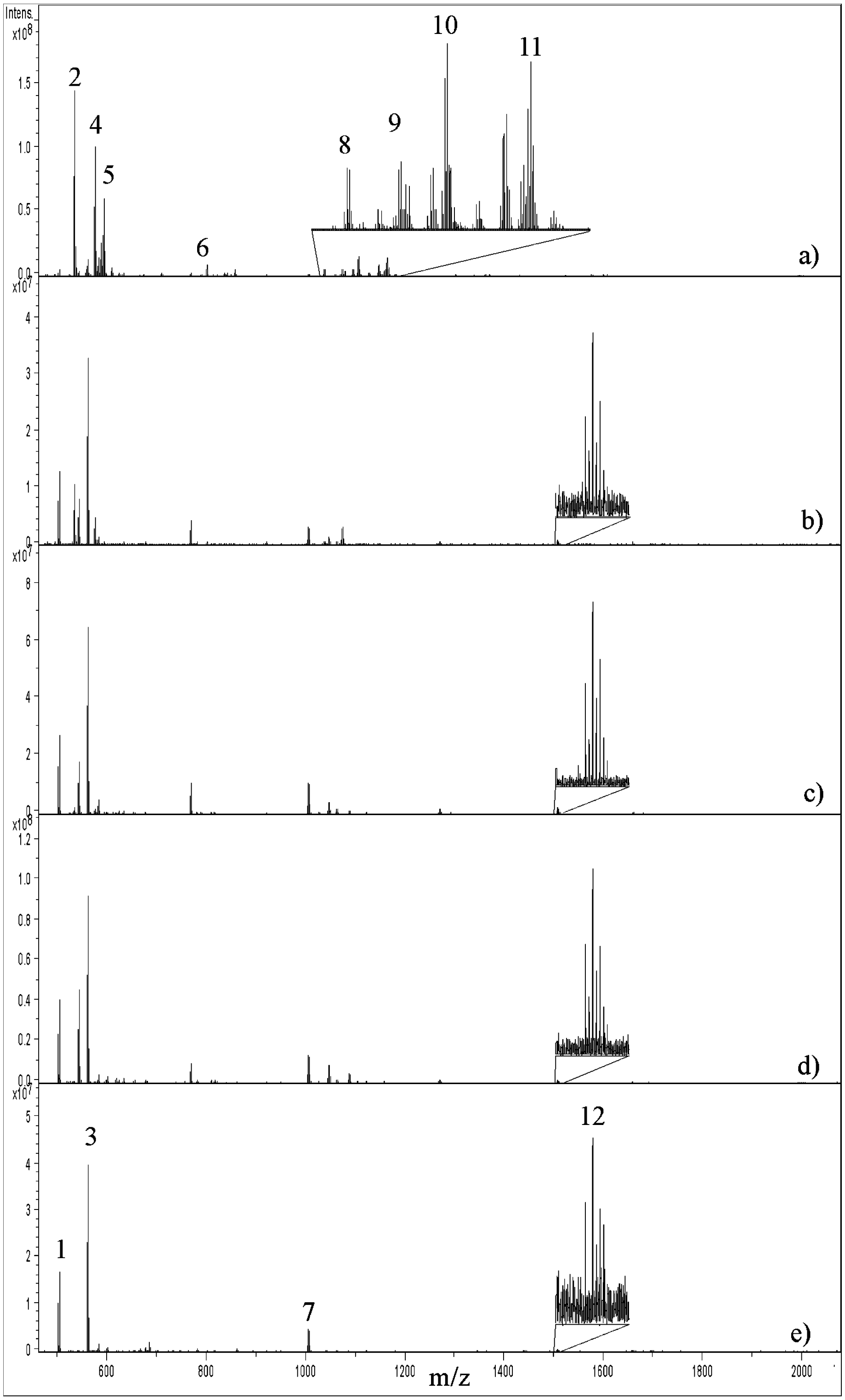

Figure 1. ESI-FTICR-MS spectra of the reaction of [ReCl(CO)$_5$] and H$_2$L^{Ph} in the *m*/*z* range of 490−2100 (a) at 0 h (a), 0.25 h (b), 2.5 h (c), 5.5 h (d), and 15 h (e) after the reaction mixture began to reflux. Peak assignments are listed in Table 1.

sulfoxide (DMSO) the only species present was the solvated monomer. ^{1}H NMR spectra showed no further decomposition in DMSO after several days of storage.

To determine whether trimers [Re$_3$(pyz^R)$_3$(CO)$_9$] were formed during the synthesis or only as a result of the crystallization process, we monitored the reactions of H$_2$L^{Ph} with [ReX(CO)$_5$] by ESI-FTICR-MS.[10] Figure 1 shows successive positive-ion spectra of the reaction of [ReCl(CO)$_5$]

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(10) To obtain a signal, it was necessary to protonate the [Re(pyz^{Ph})(CO)$_3$] fragment by the addition of formic acid to a reaction mixture diluted with acetone (see the Experimental Section).

Table 1. ESI-FTICR-MS Signal Identifications

peak	species	m/z X = Cl	m/z X = Br
1	$[\{Re(CO)_3(pyz^{Ph})\} + H]$	504	
2	$[Re(CO)_3(H_2L^{Ph})]$	536	
3	$[\{Re(CO)_3(pyz^{Ph})\} + \{(CH_3)_2CO\} + H]$	562	
4	$[Re_2X(CO)_6]$	577	
5	$[\{Re(CO)_3(H_2L^{Ph})\} + \{(CH_3)_2CO\}]$	594	
6	$[Re(CO)_3(H_2L^{Ph})_2]$	801	
7	$[\{Re_2(pyz^{Ph})_2(CO)_6\} + H]$	1005	
8	$[Re_2(pyz^{Ph})(CO)_6(H_2L^{Ph})]$	1037	
9	$[\{Re_2(pyz^{Ph})(CO)_6X(H_2L^{Ph})\} + H]$	1075	1119
10	$[Re_2(CO)_6X(H_2L^{Ph})_2]$	1107	1151
11	$[\{Re_2(CO)_6X(H_2L^{Ph})_2\} + \{(CH_3)_2CO\}]$	1165	1226
12	$[\{Re_3(pyz^{Ph})_3(CO)_9\} + H]$	1508	

in the range m/z 200−2100 (see also Table 1, and for the spectra of the reaction of $[ReBr(CO)_5]$, see the Supporting Information). No signals attributable to a tetramer were observed at any time. Signals at m/z 504 and 1005 corresponding to the monomer $[\{Re(pyz^{Ph})(CO)_3\} + H]$ and the dimer $[\{Re_2(pyz^{Ph})_2(CO)_6\} + H]$ were already present in the first spectrum run and attained their maximum intensity after 1 h, while the trimer signal at m/z 1508 also appeared within the first 1 h of reaction.

The ESI-FTICR-MS spectra also throw light on the ligand cyclization process. Signals due to the monomeric complex with uncyclized H_2L^{Ph}, and to its acetone solvate, appear and attain their maximum intensity within 10 min of the start of the reaction, as do signals due to species based on the dinuclear fragment $[Re_2X(CO)_6]^+$, with or without two H_2L^{Ph} ligands or a H_2L^{Ph} ligand and a pyz^{Ph} ligand. The monomer signals disappear within 3 h, and 7 h later, the spectra are clearly dominated by species containing only the pyrazolonate ligand. These processes are discussed below.

Crystal and Molecular Structures. The Kitaigorodskii packing indices of crystals of **2b**$\cdot{}^1/_2C_7H_8$ and **2c**$\cdot 2C_7H_8$ are 49.1% and 53.2%, respectively, if their solvent molecules are ignored (the solvent of **2b**$\cdot{}^1/_2C_7H_8$ is disordered, and the index of solvated **2c**$\cdot 2C_7H_8$, 65.5%, is in the usual range for organometallic complexes). The fact that **2b**$\cdot{}^1/_2C_7H_8$ has the lower "desolvated" index is due to its trimers being associated by $C_{methyl}{-}H\cdots O_{carbonyl}$ interactions in sheets with large hexagonal holes (Figure 2A). When **2c** crystallizes in solvent-free form, its packing is likewise mainly determined by $C{-}H\cdots O$ interactions, but its main voids are quite narrow channels running along crystallographic axis b (Figure 2B); these voids are sufficient for its packing index to be only 55.7% (considerably smaller than that of solvated **2c**$\cdot 2C_7H_8$, for example), but even so, this index is larger than those of "desolvated" **2b**$\cdot{}^1/_2C_7H_8$ and **2c**$\cdot 2C_7H_8$. The hexagonal holes in the sheets of "desolvated" **2b**$\cdot{}^1/_2C_7H_8$ do not jointly create channels perpendicular to the sheets because successive sheets are shifted so that each hides the holes in the sheet below (Figure 2A).

The molecular structures of **2b**$\cdot{}^1/_2C_7H_8$, **2c**, and **2c**$\cdot 2C_7H_8$ are very similar (see the Supporting Information and Figure 3); Table 2 lists selected bond lengths and angles, together with data for **2a** for comparison. The asymmetric unit consists of three crystallographically independent $[Re(pyz^R)(CO)_3]$ complexes, in each of which the pyrazolonato ligand is coordinated to the Re center through its S and N3 atoms (Scheme 1), forming a five-membered chelate ring. As in **2a**,[4] the interaction linking the $[Re(pyz^R)(CO)_3]$ monomers together to form an oligomer involves the metal center and the O atom of a neighboring monomer. The resulting coordination polyhedron around the Re atom is in each case a slightly distorted octahedron. The R groups on the thioamide N atoms lie on the same side of the plane defined by the Re atoms, so that the trimer adopts the general form

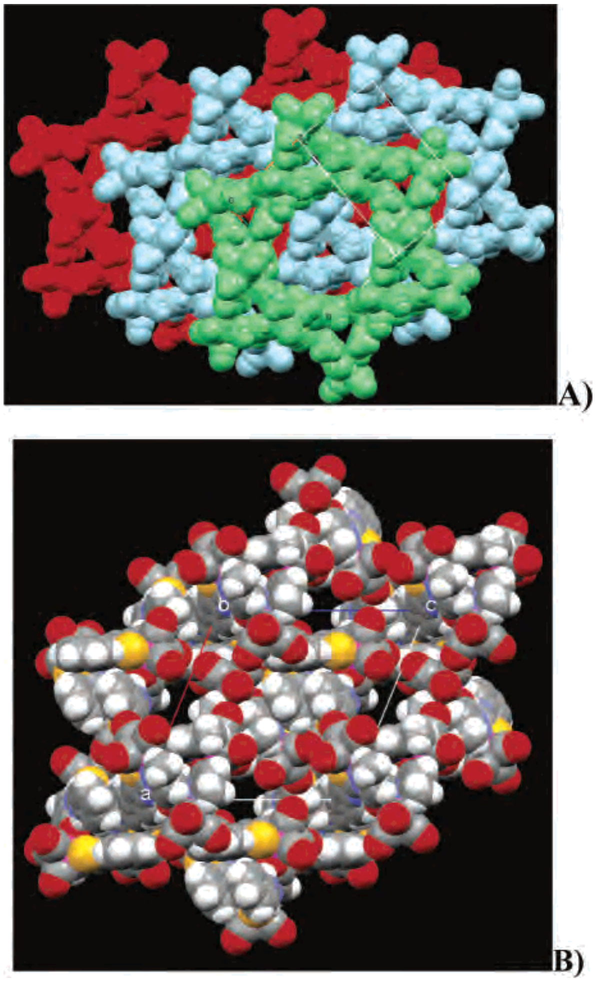

Figure 2. Crystal packing in **2b**$\cdot{}^1/_2C_7H_8$ (A) and **1c** (B).

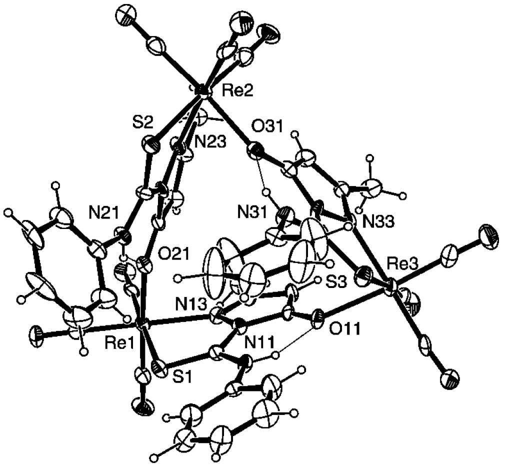

Figure 3. Ellipsoidal representation of **2c** (H atoms, except those attached to the thioamide N atom, are omitted by clarity).

Table 2. Relevant Interatomic Distances (Å) and Angles (deg) in **2b**·$^{1}/_{2}C_7H_8$, **2c**, **2c**·$2C_7H_8$, and the Tetragonal Form of **1a**[a]

	2a[a]	**2b**·$^{1}/_{2}C_7H_8$	**2c**·$2C_7H_8$	2c
Re1−N13	2.180(10)	2.15(2)	2.173(9)	2.162(10)
Re1−O21	2.172(8)	2.143(17)	2.173(6)	2.190(9)
Re1−S1	2.446(3)	2.454(6)	2.461(3)	2.479(4)
Re2−N23		2.21(2)	2.170(8)	2.146(11)
Re2−O31		2.29(2)	2.169(7)	2.192(9)
Re2−S2		2.437(8)	2.470(3)	2.450(4)
Re3−O11		2.132(18)	2.205(7)	2.197(10)
Re3−N33		2.15(3)	2.143(8)	2.168(11)
Re3−S3		2.422(8)	2.461(3)	2.470(4)
Re1−Re2	7.456	7.3791(17)	7.4368(8)	7.4615(10)
Re1−Re3		7.3791(17)	7.4630(7)	7.4717(10)
Re2−Re3		7.4420(17)	7.4696(7)	7.4332(9)
O21−Re1−N13	77.5(3)	80.4(8)	81.2(3)	78.9(4)
O21−Re1−S1	84.3(2)	80.3(4)	80.88(18)	79.6(2)
N13−Re1−S1	79.2(2)	80.4(6)	78.8(2)	78.9(3)
N23−Re2−O31		84.3(9)	80.4(3)	82.9(4)
N23−Re2−S2		78.5(6)	78.2(2)	78.1(3)
O31−Re2−S2		80.9(8)	80.03(19)	80.5(2)
O11−Re3−N33		80.3(8)	81.9(3)	79.3(4)
O11−Re3−S3		78.5(5)	80.06(19)	81.8(3)
N33−Re3−S3		80.8(7)	78.5(3)	78.6(3)

[a] See ref 4.

of a metallocalix. However, the involvement of the $N_{thioamide}$ hydrogen atoms in strong intramolecular H bonds with the pyrazolonate O atom (vide infra) would probably prevent the use of these compounds for binding anions or other electron-rich substrates.

Compounds **2a**, **2b**·$^{1}/_{2}C_7H_8$, **2c**, and **2c**·$2C_7H_8$ all have very similar Re−N, Re−S, and C−S distances, and with one exception their Re−N distances are slightly shorter than the 2.195(8) Å found in [ReBr(CO)$_3$(Hpyz^B)], in which the pyrazolone ligand is not deprotonated.[4] The Re−O distances are more varied but are close to those found in rhenium(I) alkoxides,[11a,b] in monomeric and dimeric 8-quinolato complexes,[11c] in the aqua complexes *mer,trans*-[Re(CO)$_3$-(H$_2$O)(L)$_2$]$^+$ [2.214(6)−2.263(8) Å; L = a phosphonite or phosphinite ligand],[11d] in the pyrazolonate derivative [Re-(pyz^B)(CO)$_3$(H$_2$O)] [2.203(6) and 2.216(5) Å],[4] and in the trimeric benzotriazine complex [Re$_3$(CO)$_9$(bzt)$_3$] [2.168(10) and 2.163(9) Å].[3] That this Re−O interaction must be mainly dative is suggested by the C(4)−O(1) distances in **2a**−**c** being longer than that in free Hpyz^H [1.240(2) Å;[12a] see Tables S2−S4 in the Supporting Information].

The Re−O=C angles (about 130°) and Re−Re distances [7.3791(17)−7.471(2) Å in this work and 7.4566(13) Å in tetragonal **2a**] are also similar in the four complexes. However, the difference between the trimers and the tetramer is seen in the S−Re−O=C torsion angle (146−148° in this work and 93.4° in tetragonal **2a**).

Like the free ligand Hpyz^H and its 3-methylated derivative,[12] complexes **2** have a strong intraligand N1−H···O interaction (it completes a six-membered ring)[13] that makes the pyrazole and carbothioamide fragments coplanar and prevents rotation around the C1−N1 bond (average H-bond values: 0.86, 1.92, and 2.61 Å and 136.0° in **2b**·$^{1}/_{2}C_7H_8$; 0.86, 1.89, and 2.617 Å and 142.4° in **2c**·$2C_7H_8$; 0.86, 1.87, and 2.611 Å and 143.3° in **2c**; full data are listed in Table S5 in the Supporting Information). However, the new complexes naturally lack the bonds formed by the other N1 hydrogen atoms of **2a** with S atoms in its own and neighboring tetramers, which in the within-tetramer case of the tetragonal form of **2a** probably help to stabilize the tetramer, despite their weakness [N1···S, 2.82 and 3.517(12) Å and 139.8°; expected for N···S=C<,[14] 2.51(1) and 3.43(1) Å and 157(1)°].[4]

Discussion

The N1 substituents of H$_2$L^{Me} and H$_2$L^{Ph} did not prevent the formation of pyrazolonate complexes when they were reacted with [ReX(CO)$_5$] in toluene (X = Cl, Br), but the complexes formed were trimers rather than the tetramers obtained in the reactions of H$_2$L^H.[4] Although the ESI-FTICR-MS spectra of the reactions of H$_2$L^{Ph} did not show whether monomers, dimers, or trimers predominated among metalated species at the end of the reactions (because the trimer underwent fragmentation under the ESI conditions), no signals attributable to a tetramer were observed at any time. Because the stability of **2c** is attested to by being able to isolate it from the methanol solution (see the Experimental Section), it seems likely that trimers predominate in the final reaction mixture.

The fact that the reagent concentration did not influence the identity of the products of the reaction suggests that the formation of oligomers rather than polymers was thermodynamically favored, as has been observed in the case of complexes of *fac*-Re^I(CO)$_3$ with bis-monodentate ligands.[1,2,15] The predominance of square tetramers among the latter has been attributed to the combination of the rigidity of the ligands and the tendency of the *fac*-Re^I(CO)$_3$ unit to enforce 90° donor−Re−donor angles if the ligands so allow. However, the possibility of trimers being formed by ligands that are more flexible and/or impose a different donor−Re−donor angle has already been pointed out by Fujita et al.[16a] In fact, recent evidence[16b] suggests that trimers and tetramers probably have similar energies of formation per monomer, the preference for one or the other possibly depending not only on the above factors but also on steric interactions. In the present case, because the CO groups of the [Re(pyz^R)-

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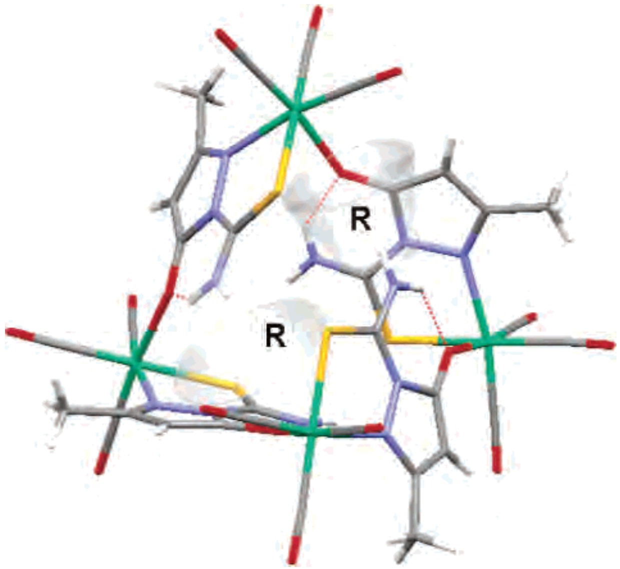

Figure 4. Structure of **2a**, with an indication of the steric hindrance to the adoption of this structure by [Re(pyz^R)(CO)$_3$] (R = Me, Ph) due to the R groups (here represented by truncated cones).

(CO)$_3$] units must point "outward" from the oligomer for steric reasons, the association of [Re(pyz^{Me})(CO)$_3$] or [Re(pyz^{Ph})(CO)$_3$] monomers in tetramers such as those of **2a**, in which adjacent monomers have opposite chiralities, appears to be prevented by the steric interactions that there would be between each monomer and the Me or Ph of one of its neighbors (see Figure 4). Thus, the size of the metallomacrocycles formed of [Re(pyz^R)(CO)$_3$] units appears to be determined by the presence of R groups on N1. Which halogen is present in the [ReX(CO)$_5$] precursor appears to have no influence on the metallomacrocycle size.

Although the signal due to protonated [Re$_3$(pyz^{Ph})$_3$(CO)$_9$] appeared after only 15 min in the ESI-FTICR-MS spectra of the reactions of H$_2$L^{Ph} with [ReCl(CO)$_5$] and [ReBr(CO)$_5$], the fact that signals for monomers and dimers containing H$_2$L^{Ph} reached their maximum intensity within 10 min, about 1 h before the corresponding complexes of pyz^R, suggests that cyclization occurred following the coordination of H$_2$L^{Ph} (Table 1). This was not unexpected given our previous experience with **2a**.[4] Nor was the appearance of dimeric [Re$_2$X(CO)$_6$] units very surprising because halogen-bridged dimers [Re$_2$(μ-X)$_2$(CO)$_8$] are known to result when the corresponding [ReX(CO)$_5$] species is heated in an inert solvent,[17] and [Re$_2$(μ-Br)$_2$(CO)$_6$(NCCH$_3$)$_2$] has been isolated as a byproduct of the reaction of [ReBr(CO)$_3$(NCCH$_3$)$_2$] with H$_2$L^H in toluene.[18] It is nevertheless worth noting that their faster substitution reactions (relative to those of [ReX(CO)$_5$]^{17}) appear to allow the coordination and cyclization of H$_2$L^{Ph} to take place at these dinuclear species: note in Figure 1 the behavior of peaks 4, 10, 8, 9, and 7. Thus, in toluene dimerization may either precede or follow coordination and cyclization of the thiosemicarbazone ligand, whereas it must surely follow coordination and cyclization in more polar solvents such as acetone, in which the halogen-bridged dimers are unlikely to be formed.

It is interesting that in **2b**·$^1/_2$C$_7$H$_8$, **2c**, and **2c**·2C$_7$H$_8$ all three [Re(pyz^R)(CO)$_3$] monomers of each trimer have the same chirality; indeed, crystals of **2b**·$^1/_2$C$_7$H$_8$ are enantiomerically pure. Thus, the structures isolated in this work, like previously reported Ru and Re metallacycles,[5,19] have the greatest symmetry possible for a cyclic trimer (C_3) and **2a** has the greatest symmetry possible for a nonplanar cyclic tetramer (S_4).

Finally, although both H$_2$L^{Me} and H$_2$L^{Ph}, like H$_2$L^H,[4] afforded [ReX(CO)$_3$(H$_2$L^R)] in their reactions with *fac*-[ReX(CO)$_3$(CH$_3$CN)$_2$] in chloroform, in the case of H$_2$L^{Ph} (but not the others) we were unable to obtain the thiosemicarbazone complex unaccompanied by the corresponding pyrazolonate complex. The phenyl substituent thus appears to facilitate the cyclization of the coordinated thiosemicarbazone. This behavior contrasts with that of N1-phenylated ferrocenylcarbaldehyde[7a] and 4-acetylpyridine[7b] thiosemicarbazones, in which the phenyl group has no effect whatsoever on the reactivity of the Re^I-coordinated thiosemicarbazone ligand. Pending information on, for example, the acidity constants of these ligands, it is difficult to hazard a guess as to the origin of this difference, but if N2 is more acidic in acetoacetate thiosemicarbazones than in ferrocenylcarbaldehyde[7a] and 4-acetylpyridine[7b] thiosemicarbazones, then one possibility might be conjugation of the lone pair on N1 with the phenyl π system: cyclization would be facilitated if the conjugation-induced loss of charge on N1 were transmitted inductively to N2, so increasing the acidity of the latter because deprotonation of N2 is postulated as the first step in the cyclization mechanism.[4,6]

In conclusion, the present results and those of our earlier work[4] indicate that whereas in polar solvents (acetone, methanol, and DMSO) the main product of the reactions of H$_2$L^R with [ReX(CO)$_5$] are monomers [Re(pyz^R)(CO)$_3$], in refluxing toluene the main products are the result of the assembly of these monomers in metallomacrocyclic oligomers. The size of the metallomacrocycle (trimer or tetramer) appears to depend on the R group, which determines whether the tetramer is stabilized by within-oligomer H bonds or destabilized by steric interactions. Work is in progress to determine how the presence of substituents on the pyrazole ring may influence the size and/or symmetry of the metallomacrocycle.

Experimental Section

Materials and Methods. All operations performed in the synthesis and isolation of the compounds were carried out under an atmosphere of dry Ar. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled in an Ar atmosphere.[20a] [ReX(CO)$_5$] and [ReX(CO)$_3$(CH$_3$CN)$_2$] were synthesized by published methods.[20b] Thiosemicarbazone ligands were obtained by the method of Jayasree and Aravindakshan.[20c,d]

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Elemental analyses were carried out on a Fisons EA-1108. Melting points (mp's) were determined on a Gallenkamp MFB-595 and are uncorrected. IR spectra were recorded from KBr pellets on a Bruker Vector 22FT spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker AMX 400 spectrometer from acetone-d_6 solutions. FAB mass spectra were recorded on a VG Autospec Micromass spectrometer using nitrobenzyl alcohol matrixes.

ESI-FTICR-MS spectra were run on an actively shielded 4.7-T Apex III ESI-FTICR-MS mass spectrometer from Bruker Daltonik (Bremen, Germany). Data acquisition, processing, apodization, deconvolution, and mass calculation were performed or controlled using Bruker Daltonik XMASS version 6.1.2 software. The number of data points was 512 000 for acquisition and 2 million for processing within a mass range of 200−2500 Da, and to optimize the signal-to-noise ratio, 16 scans were accumulated. External four-point calibration was carried out using an ES Tuning Mix from Hewlett-Packard (Waldbronn, Germany). The experimental procedure was as follows. A mixture of $[ReX(CO)_5]$ (X = Cl, Br) and H_2L^{Ph} in refluxing toluene (7.5 μL) was diluted in 1 mL of a 97:3 mixture of acetone and 1% formic acid, and this solution was delivered to the ESI sprayer. An ESI high voltage of 4.5 kV was applied to produce a stable ion current. The temperature of the capillary was 150 °C. To maintain gentle ionization conditions and minimize collisional fragmentation of the intermediates and products, the capillary skimmer potential was kept at 2 eV. The ion guide potential was optimized for maximum total ion intensity. The solid reagents were completely dissolved by the time the mixture began to reflux, after which spectra were run at about 15-min intervals over the next 2 h and at 1-h intervals thereafter.

All spectroscopic measurements were performed at the CACTI facilities of the University of Vigo.

Synthesis of Compounds 1. Compounds $[ReX(CO)_3(H_2L^{Me})]$ (X = Cl, Br) were synthesized as described in ref 4 for the corresponding complexes of H_2L^H, by stirring solutions of equal amounts of *fac*-$[ReCl(CO)_3(CH_3CN)_2]$ and H_2L^{Me} in chloroform at room temperature. Under similar reaction conditions, the ligand H_2L^{Ph} failed to yield a pure product (see above).

Data for 1b. Yield: 78 mg (61%). Mp: >170 °C (dec). Anal. Calcd for $C_{10}H_{13}N_3O_5SClRe$: C, 23.6; H, 2.6; N, 8.3; S, 6.3. Found: C, 23.6; H, 2.5; N, 8.2; S, 6.3. MS [*m/z* (%)]: 509 (13) $[M]^+$, 474 (49) $[M - Cl]^+$, 445 (21) $[M - \{X,CO,H\}]^+$, 418 (7) $[M - \{X,2CO\}]^+$. IR data (KBr, cm^{-1}): 3444m, 3274m, 3145m ν(N−H); 2025vs, 1914vs, 1892vs ν(CO); 1741s ν(C═O); 1610m ν(C═N); 1211m ν(C−O); 760w ν(C═S). ^{1}H NMR data (DMSO-d_6, ppm): 10.85s (1H) δ(N(2)−H); 8.29s,a (1H) δ(N(1)−H); 4.23ds (1H), 3.97d(1H) δ(C(3)−H); 3.59s (3H) δ(O−CH_3); 2.76d (3H) δ(N(1)−CH_3); 2.31s (3H) δ(C(2)−CH_3).

Data for 1e. Yield: 81 mg (63%). Mp: >170 °C (dec). Anal. Calcd for $C_{10}H_{13}N_3O_5SBrRe$: C, 21.7; H, 2.4; N, 7.6; S, 5.8. Found: C, 22.8; H, 2.4; N, 7.5; S, 5.8. MS [*m/z* (%)]: 553 (28) $[M]^+$, 474 (100) $[M - Cl]^+$, 445 (32) $[M - \{X,CO,H\}]^+$, 418 (15) $[M - \{X,2CO\}]^+$. IR data (KBr, cm^{-1}): 3456m, 3260s, 3136m ν(N−H); 2025vs, 1916vs, 1891vs ν(CO); 1749s ν(C═O); 1581m ν(C═N); 1209m ν(C−O); 759w ν(C═S). ^{1}H NMR data (DMSO-d_6, ppm): 10.90s (1H) δ(N(2)−H); 8.26s,a (1H) δ(N(1)−H); 4.22ds (1H), 3.96d(1H) δ(C(3)−H); 3.56s (3H) δ(O−CH_3); 2.72d (3H) δ(N(1)−CH_3); 2.40s (3H) δ(C(2)−CH_3).

Synthesis of 2b. A mixture of $[ReCl(CO)_5]$ (150 mg, 0.42 mmol) and H_2L^{Me} (84.5 mg, 0.42 mmol) in freshly distilled toluene (8 mL) was refluxed for 20 h. The pale-green precipitate was filtered out, washed with dry chloroform, and vacuum-dried until, after several days, elemental analyses became stable. Single crystals of each compound were obtained from the corresponding mother liquor.

Yield: 85 mg (47%). Mp: >260 °C (dec). Anal. Calcd for $C_{27}H_{24}N_9O_{12}S_3Re_3$: C, 24.54; H, 1.83; N, 9.54; S, 7.28. Found: C, 24.40; H, 1.81; N, 9.32; S, 7.29. MS [*m/z* (%)]: 1320 (10) $[Re_3(pyz^{Me})_3(CO)_9]^+$, 881 (19) $[Re_2(pyz^{Me})_2(CO)_6]^+$, 441 (73) $[Re(pyz^{Me})(CO)_3]^+$. IR data (KBr, cm^{-1}): 3151m, 3072m ν(N−H); 2024vs, 1894vs,b ν(CO); 1609s ν(C═O); 753m ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 11.95s (1H) δ(N(1)−H); 4.88s (1H) δ(C(3)−H); 2.44d (3H) δ(N(1)−CH_3); 2.24s (3H) δ(C(2)−CH_3). UV−vis {CH_3CN, λ (nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: 240 (53.7), 256 (39.1), 313 (14.4), 351 (14.6).

Synthesis of 2c. A mixture of $[ReCl(CO)_5]$ (150 mg, 0.42 mmol) and H_2L^{Ph} (110 mg, 0.42 mmol) in freshly distilled toluene (10 mL) was refluxed for 20 h, allowed to cool slowly, and stored at room temperature for several days. The yellow crystals formed were filtered out, washed with dry chloroform, and vacuum-dried. More product was obtained from the mother liquor after storage for a few more days. Nonsolvated crystalline samples of **2c** were obtained similarly using methanol as the solvent in the reaction.

Data for 2c·2C_7H_8. Yield: 111 mg (53%). Mp: >285 °C (dec). Anal. Calcd for $C_{56}H_{46}N_9O_{12}S_3Re_3$: C, 39.76; H, 2.74; N, 7.45; S, 5.68. Found: C, 39.55; H, 2.84; N, 7.63; S, 5.69. MS [*m/z* (%)]: 1507 (10) $[Re_3(pyz^{Ph})_3(CO)_9]^+$, 1005 (16) $[Re_2(pyz^{Ph})_2(CO)_6]^+$, 503 (69) $[Re(pyz^{Ph})(CO)_3]^+$. IR data (KBr, cm^{-1}): 3443m ν(N−H); 2026vs, 1900vs,b ν(CO); 1610m,sh ν(C═O); 754m ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 11.06s (1H) δ(N(1)−H); 7.60−7.12m (5H) δ(N(1)−Ph); 5.11s (1H) δ(C(3)−H); 2.30s (3H) δ(C(2)−CH_3). UV−vis {CH_3CN, λ(nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: 240 (63.8), 284 (36.2), 332 (24.4), 380 (10.0).

Crystal Structure Determination. Single crystals were mounted in a Bruker Smart CCD 1000 diffractometer with a graphite-monochromated Mo Kα radiation source (λ = 0.710 73 Å). For **2b**·$^1/_2C_7H_8$, contributions from disordered solvent molecules were removed by the SQUEEZE[21a] routine of *PLATON*,[21b] and the number of toluene molecules was estimated from the number of electrons so excluded per unit cell. All crystallographic data were corrected for Lorentz and polarization effects using *SAINT*, and multiscan absorption corrections were applied using *SADABS*.[21c] The structures were solved by direct methods and refined by full-matrix least squares on F^2 using *SHELX97*.[21d] All non-H atoms were refined anisotropically except for the C and O atoms of the carbonyl ligands on Re3 in **2b**·$^1/_2C_7H_8$ and the C atoms of toluene molecules in **2c**·2C_7H_8, which were fixed or refined with common anisotropic factors. H atoms were placed at their geometrically ideal positions and refined as riders. Graphics were produced with *PLATON* and *MERCURY*.[21e]

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Supporting Information Available: ESI-FTICR-MS spectra of the reaction of [ReBr(CO)$_5$] and H_2L^{Ph} and, for compounds characterized by X-ray diffractometry, CIF files, tables of crystal and structure refinement data, interatomic bond lengths and angles, and H-bond data. This material is available free of charge via the Internet at http://pubs.acs.org.

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