Inorg. Chem. **2003**, *42*, 6395–6403

Rhenium(I)-Induced Cyclization of Thiosemicarbazones Derived from β-Keto Esters

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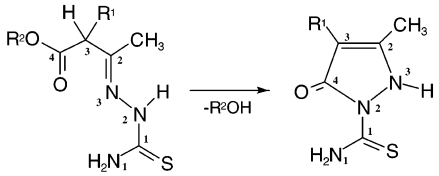
Received May 9, 2003

The reactions of methylacetoacetate and ethyl 2-methylacetoacetate thiosemicarbazones (H_2L^A and H_2L^B, respectively) with $[ReX(CO)_5]$ and $[ReX(CO)_3(CH_3CN)_2]$ (X = Cl, Br) were explored under various experimental conditions. Besides the adducts *fac*-$[ReX(CO)_3(H_2L)]$, in which the rhenium is coordinated to three carbonyl groups, the X anion, and the N,S-bidentate thiosemicarbazone ligand, the following complexes were also isolated: *fac*-$[ReBr(CO)_3(Hpyz^B)]$, the tetrameric complexes *fac*-$[Re(pyz^A)(CO)_3]_4$ and *fac*-$[Re(pyz^B)(CO)_3]_4$, and *fac*-$[Re(pyz^B)(CO)_3(H_2O)]$ (where $Hpyz^A$ and $Hpyz^B$ are pyrazolones derived by cyclization of H_2L^A and H_2L^B, respectively). The cyclization reactions were monitored by ^1H NMR spectroscopy and the complexes isolated were identified by elemental analysis, mass spectrometry, IR and ^1H NMR spectroscopy, and in some cases by X-ray diffractometry. The isolation and the full structural identification of the rather unusual *fac*-$[ReBr(CO)_3(Hpyz^B)]$, which contains the enol form of the pyrazolone ligand, affords new insight into the cyclization of thiosemicarbazones derived from β-keto esters.

Introduction

Monothiosemicarbazones derived from 1,3-dicarbonyl compounds can undergo chain−ring tautomerism, as has recently been discussed by Zelenin and Alekseyev.[2] In the case of monothiosemicarbazones derived from β-keto esters (H_2L), the cyclization gives pyrazolones (Hpyz, Scheme 1) a class of compounds that includes certain nonsteroidal anti-inflammatory drugs (NSAIDs).[3] The cyclization process is influenced by both compositional and extrinsic factors. The most important compositional factor is substitution at N(2) because it prevents the intramolecular addition of N(2)−H to the C(4)═O bond. Catalytic extrinsic factors include basic pH,[4a,b] sonication,[4c] and performance of the reaction in refluxing 2-propanol containing sodium,[4d] and we have also found[5] that zinc(II) and cadmium(II) acetates strongly promote the formation of the pyrazolone at room temperature, which opens the way to a rather smooth synthesis of this type of molecule. For example, reaction of methyl acetoacetate thiosemicarbazone with $Zn(OAc)_2{\cdot}2H_2O$ affords 2,5-dihydro-3-methyl-5-oxo-1*H*-pyrazole-1-carbothioamide,[5b] which was found to show promising anti-inflammatory activity against carrageenan-induced edema in Sprague−Dawley rat paw.[5]

Scheme 1



H_2L	R^1	R^2	Hpyz
H_2L^A	H	CH_3	$Hpyz^A$
H_2L^B	CH_3	CH_2CH_3	$Hpyz^B$

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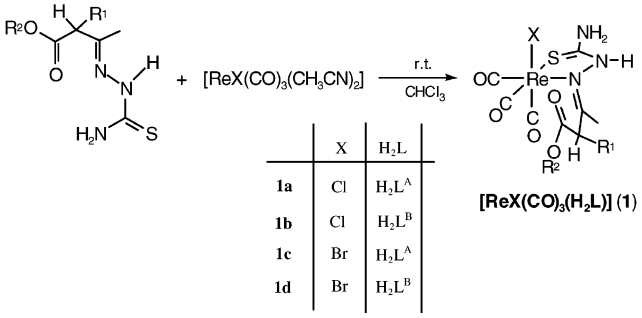
10.1021/ic030154q CCC: $25.00
Published on Web 08/30/2003

Scheme 2



	X	H_2L
1a	Cl	H_2L^A
1b	Cl	H_2L^B
1c	Br	H_2L^A
1d	Br	H_2L^B

In continuance of our work on the induction of cyclization by metal centers, we have now investigated the fragment *fac*-$Re(CO)_3$ as a possible inducer of chain−ring tautomeric conversion of two β-keto ester monothiosemicarbazones, methylacetoacetate and ethyl 2-methylacetoacetate thiosemicarbazones (H_2L^A and H_2L^B, respectively, Scheme 1). Our working hypothesis was that the rigidity of the *fac*-$Re(CO)_3$ unit would hinder geometrical rearrangement in the coordination sphere during cyclization and might thereby allow inspection of previously inaccessible stages of the reaction mechanism.

Results

Synthesis. Reaction of *fac*-$[ReX(CO)_3(CH_3CN)_2]$ with the H_2L ligands in chloroform at room temperature yielded the thiosemicarbazone adducts **1** within 30 h as pale yellow solids (Scheme 2). Their IR spectra display three very strong ν(CO) bands in the 2035−1900 cm^{-1} region, which is indicative of fac-coordination geometry. In their ^1H NMR spectra, there is a hydrazinic proton singlet at 11.20 ppm in the H_2L^A derivatives and near 11.00 ppm in the H_2L^B derivatives that is strongly shifted (by 2.0 and 1.8 ppm, respectively) with respect to its positions in the spectra of the free ligands, confirming the coordination of the undeprotonated thiosemicarbazone to the rhenium. Similar shifts of the hydrazinic proton signals are observed in the spectra of the adducts $[ReBr(CO)_3(HFFcRTSC)]$ (HFFcRTSC = a ferrocenylcarbaldehyde thiosemicarbazone).[6]

When $[ReX(CO)_5]$ (X = Cl, Br) was reacted with the H_2L ligands in refluxing toluene, IR and ^1H NMR studies showed the solids isolated to contain a mixture of complexes involving both the thiosemicarbazone and the pyrazolone resulting from its cyclization (Scheme 3), and in some cases we were able to isolate single crystals of one or both of these complexes (see Experimental Section). Specifically, when H_2L^A and $[ReBr(CO)_5]$ were refluxed for 0.5 h, the mother liquor afforded single crystals of two different types, pale yellow crystals of the adduct *fac*-$[ReBr(CO)_3(H_2L^A)]\cdot{}^1/_2C_7H_8\cdot{}^1/_2H_2O$ (**1c**·$^1/_2C_7H_8$·$^1/_2H_2O$) and garnet-colored crystals of the tetrameric complex $[Re(pyz^A)(CO)_3]_4\cdot C_7H_8$ (**3a**·C_7H_8). By contrast, crystallization of the solid obtained by an analogous 2-h reaction between H_2L^B and $[ReBr(CO)_5]$ afforded only single crystals of *fac*-$[ReBr(CO)_3(Hpyz^B)]$ (**2d**). Analytically pure **3** could only be obtained by prolonged refluxing of the ligand with $[ReCl(CO)_5]$ (20 h); the IR spectra of these products confirm the fac geometry around the rhenium atom and their ^1H NMR spectra the deprotonation and cyclization of the ligands, and X-ray studies of single crystals obtained from the mother liquor of **3a** also confirm the tetrameric structure of $[Re(pyz^A)(CO)_3]_4\cdot C_7H_8$.

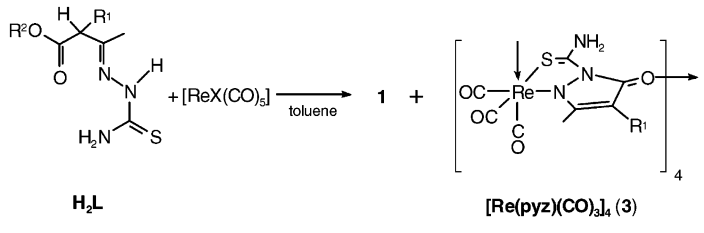
Since the free H_2L ligands transform into pyrazolones spontaneously in basic media, we also attempted to obtain **3** by reacting **1** with NaOMe. Again, the spectroscopic studies of the isolated solids showed a mixture of **3** and other products, but single crystals of $[Re(pyz^B)(CO)_3(H_2O)]$ (**4b**) were isolated from the aqueous solution obtained in washing the precipitate formed in the reaction of **1d** so as to remove NaBr.

Structure of *fac*-$[ReBr(CO)_3(H_2L^A)]\cdot{}^1/_2C_7H_8\cdot{}^1/_2H_2O$ (1c·$^1/_2C_7H_8$·$^1/_2H_2O$). The numbering scheme used is shown in Figure 1a, and selected bond lengths and angles are listed in Table 1. The asymmetric unit consists of two molecules of complex denoted A and B in Table 1, which differ just slightly in bond lengths and angles, a toluene molecule (really two symmetrically independent half molecules), and a water molecule.

The rhenium atom lies in an octahedral coordination environment formed by three fac carbonyl groups, a bromine atom, and the azomethine nitrogen and sulfur atoms of the thiosemicarbazone ligand. This coordination mode, which is common among thiosemicarbazone complexes,[7] creates a five-membered chelate ring and changes the C(1)−N(2) bond from the E configuration observed in the free ligand[5] to Z. There are only small changes in the bond lengths around the azomethine nitrogen, the largest affecting the N−C bond. The Re−Br and Re−C distances are close to those found in *fac*-$[ReBr(CO)_3(HFFcRTSC)]$.[6]

The thiosemicarbazone ligand retains the configuration around the $N_{azomethine}$−C bond that is observed in the free ligand, and the ester group lies parallel to the S−Re−C(112) fragment, so that C(14)═O(12) is parallel to Re−Br, with the Br and O atoms on the same side of the S/N(13)/C(111)/C(112) plane. Steric hindrance is probably responsible for the thiosemicarbazide chain not being coplanar with the plane defined by Re, C(111), and C(112) (these planes form an

Scheme 3



	pyz^-
3a	pyz^A
3b	pyz^B

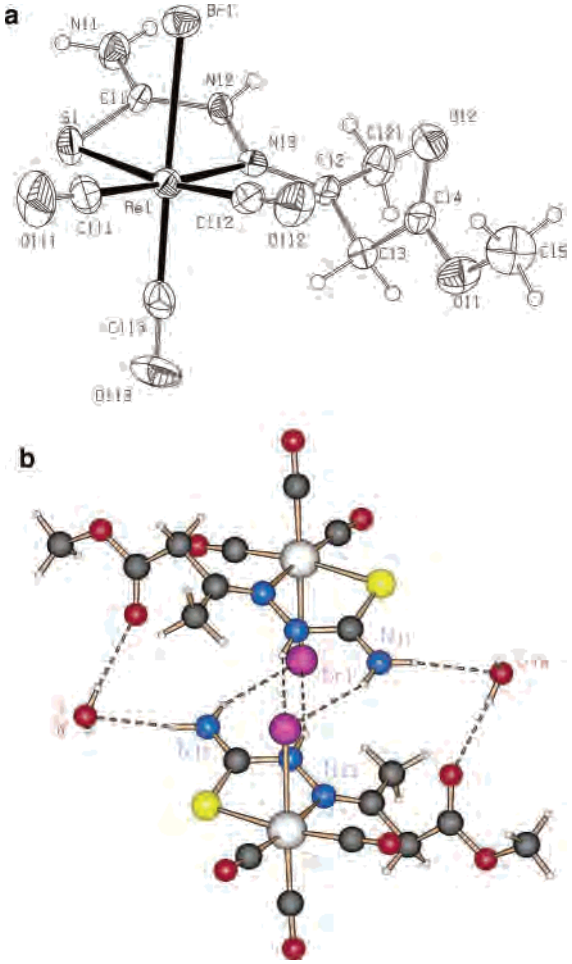


Figure 1. (a) PLATON drawing of molecule **1c** (ellipsoids at the 30% probability level). (b) SCHAKAL diagram showing the dimerizing hydrogen bonds.

angle of 30.3(3)° in molecule A and 15.9(3)° in molecule B) even though the C_{trans}−Re−X angles (X = S or N) are, as expected, close to 180°. An additional cause of this noncoplanarity may be the intermolecular hydrogen bonds between the bromine atom and the thioamide and hydrazinic NH groups, which give rise to pseudodimers (Figure 1b). Hydrogen bonds also seem to be largely responsible for the crystal packing, a water molecule acting both as a hydrogen donor in a bond with C(14)═O(12) and also as an acceptor in a bond with the thioamide group of the other molecule in the dimer. As mentioned above, the crystal also contains two toluene molecules at special positions. Since we were unable to find a statistical model for the disorder of one of them, the program SQUEEZE[8] was used to correct its diffuse scattering data. The other one lies on the 2-fold axis (*e* position in Wyckoff notation for the group *C*2/*c*) between two molecules B (Table 1), establishing a *nonclassical*[9] hydrogen bond with a carbonyl group.

Table 1. Main Structural Parameters of **1c**·$^1/_2C_7H_8$·$^1/_2H_2O$ (Lengths in Å and Angles in deg)

molecule A		molecule B	
Re(1)−C(111)	1.916(11)	Re(2)−C(211)	1.921(10)
Re(1)−C(112)	1.917(11)	Re(2)−C(212)	1.899(10)
Re(1)−C(113)	1.909(10)	Re(2)−C(213)	1.891(10)
Re(1)−N(13)	2.244(6)	Re(2)−N(23)	2.251(6)
Re(1)−S(1)	2.461(2)	Re(2)−S(2)	2.446(2)
Re(1)−Br(1)	2.6623(9)	Re(2)−Br(2)	2.6543(10)
C(111)−Re(1)−C(112)	86.5(4)	C(211)−Re(2)−C(212)	85.5(4)
C(111)−Re(1)−C(113)	88.5(4)	C(211)−Re(2)−C(213)	87.8(4)
C(112)−Re(1)−C(113)	91.9(4)	C(213)−Re(2)−C(212)	91.1(4)
C(111)−Re(1)−N(13)	174.3(3)	C(211)−Re(2)−N(23)	172.3(3)
C(112)−Re(1)−N(13)	98.7(3)	C(212)−Re(2)−N(23)	101.2(3)
C(113)−Re(1)−N(13)	93.6(3)	C(213)−Re(2)−N(23)	95.9(3)
C(111)−Re(1)−S(1)	96.6(3)	C(211)−Re(2)−S(2)	94.7(3)
C(112)−Re(1)−S(1)	172.3(3)	C(212)−Re(2)−S(2)	176.2(3)
C(113)−Re(1)−S(1)	95.3(3)	C(213)−Re(2)−S(2)	92.7(3)
N(13)−Re(1)−S(1)	77.95(18)	N(23)−Re(2)−S(2)	78.43(16)
C(111)−Re(1)−Br(1)	92.0(3)	C(211)−Re(2)−Br(2)	91.3(3)
C(112)−Re(1)−Br(1)	86.6(3)	C(212)−Re(2)−Br(2)	89.0(3)
C(113)−Re(1)−Br(1)	178.4(3)	C(213)−Re(2)−Br(2)	179.1(3)
N(13)−Re(1)−Br(1)	86.11(15)	N(23)−Re(2)−Br(2)	85.00(15)
S(1)−Re(1)−Br(1)	86.22(6)	S(2)−Re(2)−Br(2)	87.22(7)
S(1)−C(11)	1.702(8)	S(2)−C(21)	1.686(8)
N(12)−C(11)	1.328(9)	N(22)−C(21)	1.340(9)
N(12)−N(13)	1.396(8)	N(22)−N(23)	1.384(8)
N(13)−C(12)	1.296(9)	N(23)−C(22)	1.289(9)
N(11)−C(11)−S(1)	120.6(6)	N(21)−C(21)−S(2)	119.4(7)
N(12)−C(11)−S(1)	122.0(6)	N(22)−C(21)−S(2)	123.3(6)
N(11)−C(11)−N(12)	117.3(7)	N(21)−C(21)−N(22)	117.3(7)
C(11)−N(12)−N(13)	121.1(6)	C(21)−N(22)−N(23)	120.1(6)
C(12)−N(13)−N(12)	115.9(6)	C(22)−N(23)−N(22)	115.1(6)

Structure of [ReBr(CO)$_3$(Hpyz^B)] (2d). Figure 2a shows the molecule **2d** with the numbering scheme used. The main bond lengths and angles are listed in Table 2. The rhenium is octahedrally coordinated to three carbonyl carbon atoms in fac arrangement, a bromine atom, and the N(3) and S atoms of the pyrazolone ligand, with which the metal forms a five-membered chelate ring. The pyrazolone adopts its enol form, as was confirmed by the localization of the hydrogen from the Fourier difference map and successful refinement and by the lengthening of the C(4)−O(1) bond to 1.335(12) Å from the 1.2468(19) Å of free Hpyz^B.[10] In keeping with the neutral character of the ligand, the Re−Br, Re−S, and Re−N(3) distances are similar to those found in the adduct **1c** described above. Bonds that do change in length (apart from C(4)−O(1)) are C(2)−C(3), which is lengthened, and C(2)−N(3) and C(3)−C(4), which are shortened (cf. lengths of 1.367(2), 1.350(2), and 1.414(2) Å, respectively, in Hpyz^B).[10] All these changes are attributable to differences in electronic distribution associated with the formation of the enol. This enol form of pyrazolones with thiocarbonyl groups on N(2) has previously been detected by NMR spectroscopy in solutions of free pyrazolones,[11a−b] but unlike their N(2)-alkyl analogues,[11c] these pyrazolones have hitherto always crystallized in HN form[11d] (Scheme 4). As far as we know, this is the first time that an HO tautomer, whether as

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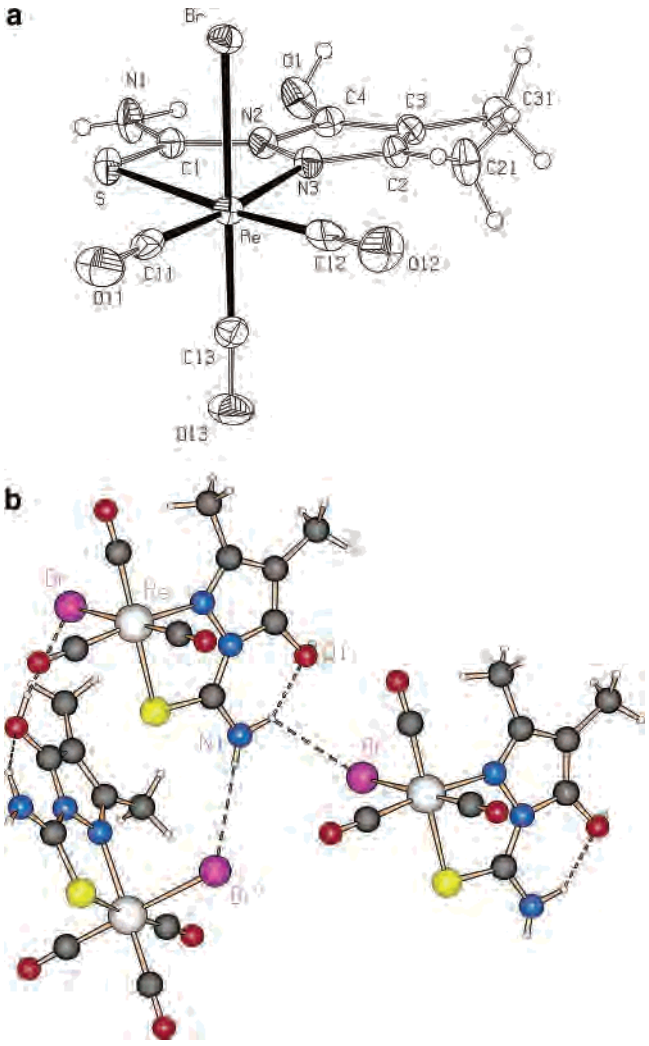


Figure 2. (a) PLATON drawing of **2d** (ellipsoids at the 30% probability level). (b) SCHAKAL drawing showing the hydrogen bonding.

Table 2. Main Structural Parameters of **2d** (Lengths in Å and Angles in deg)

Re−N(3)	2.195(8)	N(2)−C(1)	1.357(10)
Re−S	2.462(3)	N(2)−N(3)	1.391(10)
Re−Br	2.6553(9)	N(2)−C(4)	1.400(11)
O(1)−C(4)	1.335(12)	N(3)−C(2)	1.330(11)
S−C(1)	1.679(10)	C(4)−C(3)	1.334(13)
N(1)−C(1)	1.349(13)	C(3)−C(2)	1.399(14)
N(3)−Re−S	78.4(2)	N(3)−N(2)−C(4)	107.8(7)
N(3)−Re−Br	86.83(18)	N(1)−C(1)−N(2)	118.0(9)
S−Re−Br	86.21(6)	N(1)−C(1)−S	120.5(7)
C(1)−S−Re	100.4(3)	N(2)−C(1)−S	121.4(7)
C(1)−N(2)−N(3)	120.6(8)	C(2)−N(3)−N(2)	105.3(8)
C(1)−N(2)−C(4)	131.5(8)		

ligand or uncomplexed compound, has been characterized structurally by X-ray diffractometry.

Hydrogen bonds also play a role in the structure of **2d**. In addition to the intramolecular interaction involving one of the thioamide hydrogens and the oxygen atom, intermolecular

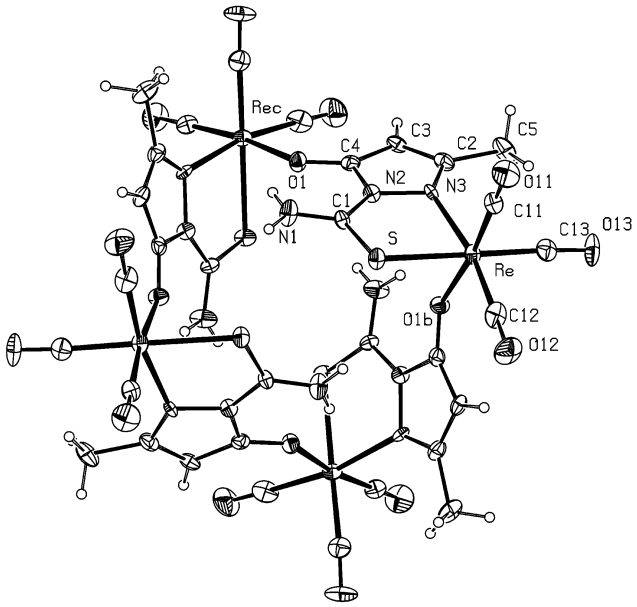
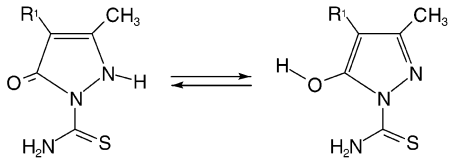


Figure 3. PLATON drawing of the tetramer $[Re(pyz^A)(CO)_3]_4$ in **3a**·C_7H_8 (tetragonal form, ellipsoids at the 30% probability level).

Scheme 4



interactions of the thioamide and OH groups with neighboring Br atoms associate the molecules in chains parallel to the *b* axis (Figure 2b).

Structure of the Tetramer $[Re(pyz^A)(CO)_3]_4$·C_7H_8 (3a·C_7H_8). The two different syntheses of **3a** (see Experimental Section) afforded different forms of **3a**·C_7H_8: monoclinic crystals were obtained in the reaction that also afforded **1c**·$^1/_2C_7H_8$·$^1/_2H_2O$, and tetragonal crystals were obtained from the mother liquor of the 20-h reaction of $[ReCl(CO)_5]$ and H_2L^A. In both cases, four "*fac*-$Re(CO)_3$" units and four bridging pyrazolonato ligands form a tetramer (Figure 3). In the monoclinic form, the asymmetric unit is constituted by the self-assembled metallomacrocycle[12a] and a toluene molecule, and in the tetragonal form the metallomacrocycle is centered at a −4 rotoinversion axis (position *a* in Wyckoff notation), making the toluene molecule disordered (see Experimental Section). However, the differences in interatomic distances and angles between the monomers in the two structures fall within the statistical error.

In each *fac*-$[Re(pyz^A)(CO)_3]$ unit, the pyrazolonato ligand coordinates to rhenium through its sulfur and N(3) atoms, forming a five-membered chelate ring. The tetrameric

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structure is created by the interaction of the rhenium atom with the exocyclic oxygen of a neighboring molecule at the position occupied by the halogen ligands of **1c** and **2d**. The resulting coordination polyhedron around the rhenium atom is a slightly distorted octahedron. Unlike other tetrameric structures based on nitrogen heterocycles and "*fac*-$Re(CO)_3$" corners,[12b] that of **3a** is nonplanar. In fact, it can best be described as the result of sitting the "*fac*-$Re(CO)_3$" fragments on the vertexes of a tetrahedron with their CO groups pointing outward. This nonplanarity is probably due to the nonlinearity of the Re−O−C4 angle (around 130°) combined with the relative positions of the donor atoms O(1) and N(3), which are determined by the pyrazolonate ring and lead to the O(1)−C(4) and N(3)−Re vectors to form an angle of roughly 150°.[12c,d] The Re−Re distance is 7.456 Å in the tetragonal form but ranges from 7.41 to 9.36 Å in the monoclinic form, giving rise to a more irregular polyhedron probably because of the intratetrameric hydrogen bonds between the NH_2 group and the oxygen and sulfur atoms of the pyrazolonate in this form.

The Re−N bonds are slightly shorter than those in **2d**, while the Re−S and C(1)−S distances are statistically equivalent in the two molecules. The Re−O distances are close to those found in the tetrameric alkoxide $[Re_2(OCH_3)_2(CO)_6(4,4'\text{-bipy})]_2$ (2.149(7) and 2.136(7) Å),[13] in the alkoxide and aryloxide monomers $[Re(OR)(CO)_3(L_2)]$ (2.120−2.143Å; $L_2 = 2PPh_3$, *diars*; R = *p*-cresol, $OCH(CF_3)_2$),[14] and in the dimeric and monomeric complexes $[Re_2L_2(CO)_6]$ (2.164(7) and 2.209(6) Å) and $[ReL(CO)_3(py)]$ (2.099 Å, L = 8-quinolato)[15] but shorter than those found in the aqua complexes *mer*,*trans*-$[Re(CO)_3(H_2O)(L)_2]^+$ (2.216−2.263 Å; L = a phosphonite or phosphinite ligand)[16] and in the pyrazolonate derivative **4b** (see below). In agreement with the mainly dative nature of this interaction, the C(4)−O(1) distance (1.281(5) and 1.266(4) Å in the monoclinic and tetragonal forms, respectively) is just slightly longer than that in the free ligand (1.240(2) Å).[5a]

Of the slight alterations in pyrazolonato bond lengths and angles caused by its deprotonation and coordination to the rhenium, the most significant are the shortening of the N(2)−N(3) distance and the narrowing of the N(2)−N(3)−C(2) angle, which are 1.376(2) Å and 108.6(2)°, respectively, in $Hpyz^A$.[5a]

In the monoclinic form, the tetramers are associated by weak hydrogen bonds, some of which involve the toluene molecule.

Structure of *fac*-[Re(pyz^B)(CO)$_3$(H$_2$O)] (4b). This compound crystallized in the monoclinic space group $P2_1/n$. The two independent molecules in the asymmetric unit form an enantiomeric pair which differ slightly in bond lengths and angles (Table 4). Figure 4 shows the molecular structure of the *anticlockwise* enantiomer[17] together with the atomic numbering scheme used.

In both molecules, the rhenium atom is coordinated to the carbon atoms of three fac carbonyl groups, the sulfur and nitrogen atoms of a pyrazolonato ligand, and the oxygen atom of a water ligand. The Re−S and Re−N distances are similar to those found in the tetramer described above, and the Re−O distance is similar to those found in the cationic derivatives *mer*,*trans*-$[Re(CO)_3(H_2O)(L)_2]^+$ (2.216−2.263 Å).[16] The effects of deprotonation and coordination on the pyrazolonato ligand, relative to free $Hpyz$,[B 10] are similar to those observed in **3a**, i.e., shortening of the N−N distance and narrowing

Table 3. Main Structural Parameters of the Two Structures of *fac*-$[Re(pyzA)(CO)_3]_4 \cdot C_7H_8$ (**3a**·C_7H_8) (Lengths in Å and Angles in deg)

	monoclinic form[a]	tetragonal form[b]
Re−N(3)	2.167(4)	2.180(10)
Re−O(1)#1	2.182(3)	2.172(8)
Re−S	2.468(2)	2.446(3)
S−C(1)	1.683(5)	1.695(13)
O(1)−C(4)	1.281(5)	1.266(14)
N(1)−C(1)	1.310(5)	1.284(15)
N(2)−C(1)	1.368(6)	1.368(15)
N(2)−N(3)	1.395(5)	1.421(13)
N(2)−C(4)	1.414(5)	1.439(15)
N(3)−C(2)	1.332(5)	1.345(15)
C(2)−C(3)	1.385(6)	1.392(17)
C(3)−C(4)	1.364(6)	1.353(17)
N(3)−Re−S	78.5(1)	79.2(2)
O(1)#1−Re−S	83.83(10)	84.3(2)
N(3)−Re−O(1)#1	76.7(1)	77.5(3)
C(1)−N(2)−N(3)	119.2(4)	121.2(9)
C(1)−N(2)−C(4)	129.6(4)	128.4(10)
N(3)−N(2)−C(4)	110.8(4)	110.4(9)
C(2)−N(3)−N(2)	104.0(4)	103.4(9)
C(4)−O(1)−Re#2	130.1(3)	135.6(8)
C(1)−S−Re	99.5(2)	101.1(4)

[a] Monoclinic form. Data are average values and standard deviations are estimated as $(\Sigma\sigma_i/n)/n^{1/2}$. Symmetry transformations: #1 $x - 1/2$, $-y + 1/2$, $z + 1/2$; #2 $x - 1/2$, $-y + 1/2$, $z - 1/2$. [b]Tetragonal form. Symmetry transformations:#1 $y + 1/2$, $-x + 1$, $-z$; #2 $-y + 1$, $x - 1/2$, $-z$.

Table 4. Main Structural Parameters of **4b** (Lengths in Å and Angles in deg)

	X = 1 (OC-6-44A)	*X* = 2 (OC-6-44C)
Re(X)−N(X3)	2.145(6)	2.166(6)
Re(X)−O(XW)	2.216(5)	2.203(6)
Re(X)−S(X)	2.477(2)	2.469(2)
O(X1)−C(X4)	1.289(8)	1.269(9)
S(X)−C(X1)	1.700(8)	1.676(8)
N(X1)−C(X1)	1.307(9)	1.317(9)
N(X2)−C(X1)	1.361(8)	1.373(9)
N(X2)−N(X3)	1.403(8)	1.392(8)
N(X2)−C(X4)	1.432(9)	1.422(9)
N(X3)−C(X2)	1.346(8)	1.350(8)
N(X3)−Re(X)−O(XW)	81.9(2)	80.6(2)
N(X3)−Re(X)−S(X)	78.82(17)	78.95(17)
O(XW)−Re(X)−S(X)	82.32(15)	84.52(17)
C(X1)−S(X)−Re(X)	99.2(3)	99.7(3)
C(X1)−N(X2)−N(X3)	121.2(6)	120.5(6)
C(X1)−N(X2)−C(X4)	126.8(6)	128.0(7)
N(X3)−N(X2)−C(X4)	111.1(6)	111.4(6)
C(X2)−N(X3)−N(X2)	103.6(6)	104.7(6)
N(X1)−C(X1)−S(X)	122.7(6)	122.3(6)
N(X2)−C(X1)−S(X)	119.8(6)	121.2(6)

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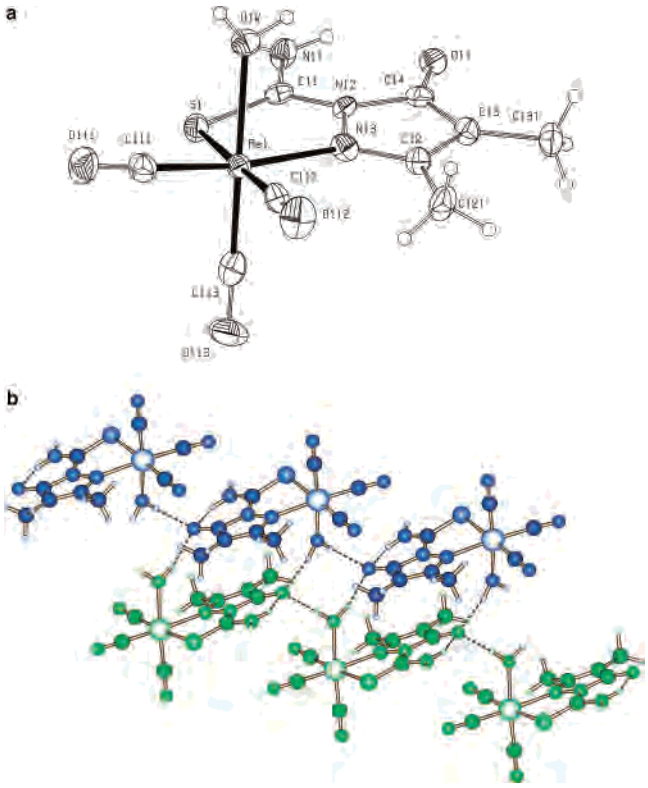

Figure 4. (a) PLATON drawing of **4b** (ellipsoids at the 30% probability level). (b) SCHAKAL drawing showing the H···O hydrogen bonding.

of the N(X2)−N(X3)−C(X2) angle, which are 1.3801(18) Å and 108.22(13)°, respectively, in $Hpyz^B$.[10]

Hydrogen bonds are also present in the crystal structure. Besides the intramolecular N−H···O interaction usually present in the free ligand,[5,10] the coordinated water bridges between two other molecules of the complex by interacting with the carbonyl oxygens of their pyrazolonato ligands, creating pseudotetrameric structures (Figure 4b). Also, the sulfur and the oxygen atoms of the carbonyl ligands are involved in weak interactions with thioamide groups.

UV−vis Data. Electronic absorption data for **1** are reported in the Experimental Section. In the ultraviolet region, two main bands are observed at positions that are hardly affected by the identities of the halogen and thiosemicarbazone bound to the rhenium. For solutions of each complex in acetonitrile and dichloromethane, the band of shorter wavelength lies at nearly the same position as a more intense band in the spectrum of the free ligand in the same solvent, suggesting an intraligand (IL) origin; in methanol this band (which appears at the same position as in CH_3CN, CH_2Cl_2) is probably due to methanol behaving as a donor in hydrogen bonds with the coordinated thiosemicarbazone (see, for example, ref 18). The position of the longer-wavelength band depends more markedly on the solvent, suggesting a metal−ligand charge transfer (MLCT) origin;[19] similar behavior has been found in other *fac*-$[ReX(CO)_3L_2]$ complexes.[20] The indifference of this band to the identity of the halogen and thiosemicarbazone is consistent with the similar indifference of the intensities and positions of the Re-bound CO-stretching bands to the identity of the halogen; both findings suggest that these ligands must have little effect on the charge density on the rhenium in the ground state.[20]

Similar considerations hold for **3**, the spectra of both of which feature both bands in the near-UV region (probably due to the IL transition) and a low-energy band around 360 nm that is tentatively attributed to an MLCT transition.

Monitoring the Cyclization Process. The cyclization of **1** in acetone-d_6 at 50 ± 3 °C was studied by monitoring the evolution of the ^{1}H NMR signals of the CH_3 group on C(2), the R^1 and R^2 groups, and the byproduct R^2OH (see Scheme 1). It was not possible to monitor the signals of N(2)H, $N(1)H_2$, and C(3)H because these groups were deuterated by the solvent after 7 h.

In all experiments, cyclization was detected within 7 h, but the rate clearly depended on the halogen, being greater with Cl than Br. The reaction rate did not depend on R^1. In similar experiments when the free-ligand cyclization did not occur within 24 h, neither did the deuteration of NH_2, NH, or C(3)H.

Discussion

That the cyclization of thiosemicarbazones derived from β-keto esters can be favored by coordination to metals has previously been reported for M^{II} cations of group 12.[5] The process was found to depend on the nature of the metal and on the ligand substituents R^1 and R^2, and dependence on the solvent and on the counterion of the metal was also surmized. Cyclization appeared to be favored by M^{II} essentially because the thiosemicarbazonato ligand of the intermediate was N(2) deprotonated, which must favor nucleophilic attack by N(2) on C(4)═O.[5] As explained in the Introduction, in the present study we investigated the behavior of H_2L (Scheme 1) with the group 7 metal rhenium(I) in *fac*-$Re(CO)_3$ because we hoped that the rigidity of this unit might lead to the manifestation of previously unknown aspects of the reaction mechanism.

Isolation of the adducts $[ReX(CO)_3(H_2L)]$ (**1a**−**d**) allowed their cyclization in acetone-d_6 at 50 °C to be monitored by ^{1}H NMR (at room temperature the reactions were very slow). Since the UV−vis results for **1** suggest that the electron density on the rhenium does not depend on the halogen (see above), the finding that the identity of the halogen was the main determinant of the cyclization rate, which was faster with chlorine than with bromine, suggests that the rate is determined largely by steric factors. In keeping with this hypothesis, the structure of **1c** (Figure 1a) shows that a number of steric barriers have to be crossed by the thiosemicarbazone carbonyl group in its approach to N(2) (which involves rotation around the C(2)−N(3) bond) and that successful approach must be easier in the chloro complexes **1a** and **1b** than in the bromo complexes **1c** and **1d** because of the smaller size of the chloro ligand.

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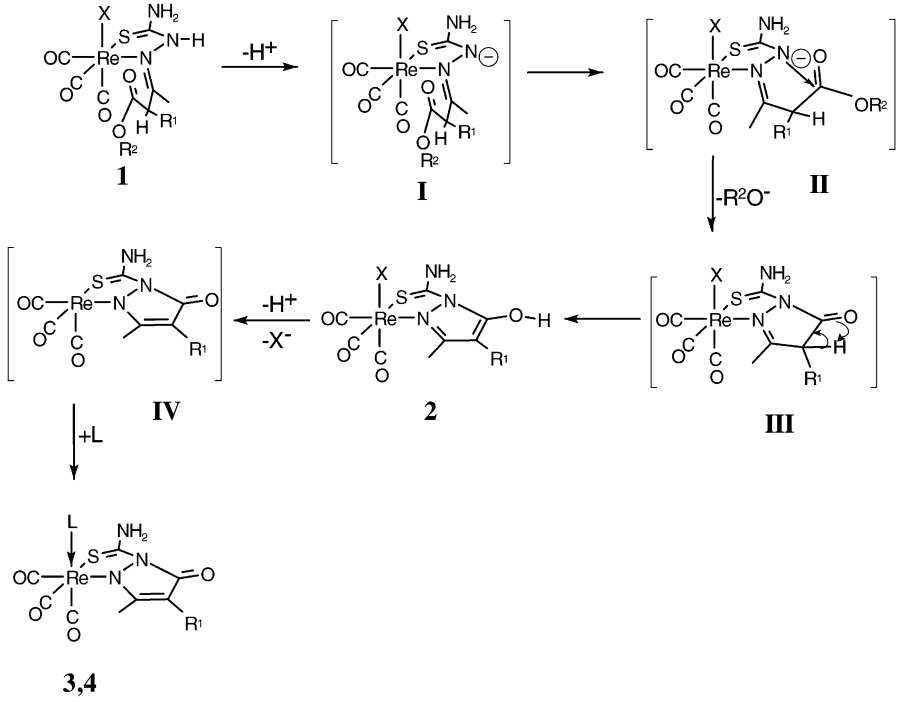
Scheme 5



As in the case of the M^{II}-induced cyclizations studied previously,[5] we assume that nucleophilic attack on C(4)═O by N(2) is essentially initiated by the deprotonation of the latter. However, whereas the thiosemicarbazonato ligand of the intermediate M^{II} complex is already deprotonated, in this work this assumption means that complexes **1** require deprotonation before cyclization can occur. Factors affecting this deprotonation can therefore modify the overall reaction time. For instance, although the UV−vis and IR results suggest that the inductive effects of Cl and Br transmitted via the rhenium atom to the thiosemicarbazone ligand must be very weak in species **1** of Scheme 5, they can be greater in some transition state between **1** and **I**. In that case, the observed dependence of the overall cyclization rate on the nature of the halogen would be due not only to the steric effects discussed above but also to the greater electronegativity of Cl making deprotonation faster for **1a** and **1b** than for **1c** and **1d**.

Perhaps a more striking difference between the M^{II}- and Re^{I}-catalyzed cyclizations is that whereas the M^{II} intermediate equivalent to **II** in Scheme 5 appears to evolve directly to the final pyrazolonate by simultaneous loss of the C(3) hydrogen and the C(4) substituent, in the present case the isolation of **2d** suggests that **II** evolves by loss of the negatively charged R^2O^- group, leaving C(3) with a hydrogen that immediately migrates to the neighboring carbonyl. Note that with this mechanism the halogen remains in the coordination sphere throughout the cyclization process; it is not labilized by deprotonation of N(2) as it is in the adducts *fac*-[ReBr(CO)$_3$(HFFcRTSC)].[6] The formation of compounds **3** and **4b** is nevertheless explicable by loss of HX from **2** and reaction of the resulting coordinatively and electronically unsaturated 16e complex [Re(pyz)(CO)$_3$] (**IV** in Scheme 5) with a 2e-donating oxygen, that of pyz in **3** and that of a water molecule in **4b**.

In view of the final stages of the above mechanism, in our future work we plan to study **3** not only as regards to their capacity to bind guest molecules and ions within the cavity created by their tetrameric structure[12b,21] but also as sources of 16e rhenium(I) reaction intermediates.

Experimental Section

Materials and Methods. All operations performed in the synthesis and isolation of the compounds were carried out under an atmosphere of dry argon. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled in an Ar atmosphere.[22]

$Re_2(CO)_{10}$ (ABCR), methylacetoacetate, *R*,*S*-2-ethylacetoacetate, and thiosemicarbazide (all from Aldrich) were used as supplied, without any further purification. Thiosemicarbazone ligands were obtained by the method of Jayasree and Aravindakshan,[23] and [ReX(CO)$_5$] and [ReX(CO)$_3$(CH$_3$CN)$_2$] were likewise synthesized by published methods.[24]

Elemental analyses were carried out on a Fisons Instruments EA-1108. Melting points (mp) were determined on a Sanyo Gallenkamp PLC MPD350 and are uncorrected. Mass spectra were recorded on a VG Autospec Micromass spectrometer operating under fast atom bombardment conditions (nitrobenzyl alcohol matrix). Infrared

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spectra were recorded from KBr pellets on a Bruker Vector 22FT spectrometer. ^{1}H NMR spectra were obtained from acetone-d_6 solutions on a Bruker AMX 400 spectrometer. UV−vis spectra were recorded in a CECIL CE2021 apparatus. UV−vis data for free thiosemicarbazone and pyrazolone ligand and ^{1}H NMR data for thiosemicarbazone ligands in acetone are included for comparison.

Data for H_2L^A. ^{1}H NMR data (acetone-d_6, ppm): 9.18 s (1H) δ(N(2)−H); 7.60 s,b, 7.40 s,b (2H) δ(N(1)−H_2); 4.40 d, 4.14 d (2H) δ(C(3)−H_2); 3.74 s (3H) δ(C(5)−CH_3); 2.50 s (3H) δ(C(2)−CH_3). UV−vis {solvent, λ (nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: CH_3CN, 276 (15.5); CH_2Cl_2, 279 (32.1); CH_3OH, 271 (28.9).

Data for H_2L^B. ^{1}H NMR data (acetone-d_6, ppm): 9.11 s (1H) δ(N(2)−H); 7.51 s,b, 7.38 s,b (2H) δ(N(1)−H_2); 3.45 q (1H) δ-(C(3)−H_2); 4.13 q (2H) δ(C(5)−H_2); 2.04 s (3H) δ(C(2)−CH_3); 1.33 d (3H) δ(C(3)−CH_3); 1.22 t (3H) δ(C(6)−H_3). UV−vis {solvent, λ (nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: CH_3CN, 276 (37.7); CH_2Cl_2, 279 (40.8); CH_3OH, 272 (22.5).

UV−vis Data for Pyrazolone Ligands in CH_3CN. {λ(nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: Hpyz^A, 276 (9.4); Hpyz^B, 279 (18).

General Synthesis of Complexes *fac*-[ReX(CO)$_3$(H_2L)] (X = Cl, Br; H_2L = H_2L^A, H_2L^B) (1). The four **1** complexes were obtained as follows. [ReX(CO)$_3$(CH_3CN)$_2$] (150 mg, 0.387 mmol for X = Cl; 100 mg, 0.231 mmol for X = Br) and the equimolar amount of the corresponding ligand were dissolved in 3 mL of freshly distilled chloroform by stirring for 10−15 min. The solution was stirred for 1 h more at room temperature, concentrated by vacuum to half volume, and stored in the refrigerator. The pale yellow precipitate was then filtered out, washed with dry chloroform, and vacuum dried.

Data for 1a (X = Cl; H_2L^A). Yield: 110 mg (57.3%). Mp: 185 °C (dec). Anal. Found: C, 21.6; H, 2.2; N, 8.3; S, 6.4. $C_9H_{11}O_5N_3$-SClRe requires: C, 21.8; H, 2.2; N, 8.9; S,6.5. Mass spectrum [*m*/*z* (%)]: 495 (11.02) |M|$^+$, 460 (91.12) |M − Cl|$^+$, 431 (30.70) |M − Cl,CO,H|$^+$, 404 (17.74), |M − Cl,2CO|$^+$. IR data (KBr, cm^{-1}): 3452 s, 3269 s, 3177 m ν(N−H); 2029 vs, 1923 vs, 1901 vs ν-(CO); 1730 s ν(C═O); 1608 s ν(C═N); 1426 m δ(−OCH_3); 1211 m ν(C−O); 761 w ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 11.20 s (1H) δ(N(2)−H); 8.60 s,b, 8.15 s,b (2H) δ(N(1)−H_2); 4.35 d, 4.14 d (2H) δ(C(3)−H_2); 3.72 s (3H) δ(O−CH_3); 2.47 s (3H) δ(C(2)−CH_3). UV−vis {solvent, λ(nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: CH_3CN, 302 (5.1), 270 (7.6); CH_2Cl_2, 318 (3.0), 272 (4.5); CH_3OH, 351 (2.0), 287 (6.9).

Data for 1b (X = Cl; H_2L^B). Yield: 135 mg (66.5%). Mp: 200 °C (dec). Anal. Found: C, 25.2; H, 2.8; N, 8.0; S, 6.2. $C_{11}H_{15}O_5N_3$-SClRe requires: C, 25.3; H, 2.9; N, 8.0; S,6.1. Mass spectrum [*m*/*z* (%)]: 523 (12.45) |M|$^+$, 488 (100) |M − Cl|$^+$, 459 (44.25) |M − Cl,CO,H|$^+$, 432 (36.14) |M − Cl,2CO|$^+$. IR data (KBr, cm^{-1}): 3359 m, 3272 m, 3182 m ν(N−H); 2033 vs, 1916 vs, 1901 vs ν(CO); 1693 s ν(C═O); 1624 s ν(C═N); 1233 m ν(C−O); 1088 m, 754 w ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 11.00s (1H) (N(2)−H; 8.40s,b, 8.00s,b (2H) δ(N(1)−H_2); 4.59q (1H) δ(C(3)−H); 4.10q (2H) δ(O−CH_2); 2.24s (3H) δ(C(2)−CH_3); 1.37q (3H) δ(C(3)−CH_3); 1.14t (3H) δ(C(6)−H_3). UV−vis {solvent, λ (nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: CH_3CN, 309 (4.0), 270 (6.1); CH_2Cl_2 324 (4.0), 276 (4.2); CH_3OH 351 (1.9), 289 (6.9).

Data for 1c (X= Br; H_2L^A). Yield: 46 mg (37.0%). Mp: 190 °C (dec). Anal. Found: C, 19.9; H, 2.1; N, 7.7; S, 6.0. $C_9H_{11}O_5N_3$-SBrRe requires: C, 20.0; H, 2.1; N, 7.8; S, 5.9. Mass spectrum [*m*/*z* (%)]: 539 (21.04) |M|$^+$, 460 (72.0) |M − Br|$^+$, 431 (23.90) |M − Br,CO,H|$^+$, 404 (12.46) |M − Br,2CO|$^+$. IR data (KBr, cm^{-1}): 3452 s, 3287 s, 3177 m ν(N−H); 2029 vs, 1922 vs, 1904 vs ν(CO); 1729 s ν(C═O); 1607 s ν(C═N); 1426 m δ(−OCH_3); 1209 m ν(C−O); 759 w ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 11.20 s (1H) δ(N(2)−H); 8.60 s,b, 8.15 s,b (2H) δ(N(1)−H_2); 4.40 d, 4.14 d (2H) δ(C(3)−H_2); 3.74 s (3H) δ(O−CH_3); 2.50 s (3H) δ(C(2)−CH_3). UV−vis {solvent, λ (nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: CH_3CN, 315 (4.6), 278 (7.6); CH_2Cl_2, 323 (4.0), 273 (6.3); CH_3OH, 350 (2.8), 292 (6.1). Single crystals of this compound were obtained by reaction of [ReBr(CO)$_5$] and H_2L^A in toluene as described below.

Data for 1d (X = Br; H_2L^B). Yield: 63 mg (47.8%). Mp: 190 °C (dec). Anal. Found: C, 23.3; H, 2.4; N, 7.3; S, 5.5. $C_{11}H_{15}O_5N_3$-SBrRe: C, 23.3; H, 2.7; N, 7.4; S, 5.7. Mass spectrum [*m*/*z* (%)]: 567 (20.03) |M|$^+$, 488 (100) |M − Br|$^+$, 459 (45.38) |M − Br,-CO,H|$^+$, 432 (26.42) |M − Br,2CO|$^+$. IR data (KBr, cm^{-1}): 3350 m, 3268 m, 3180 m ν(N−H); 2033 vs, 1916 vs, 1901 vs ν(CO); 1694 s ν(C═O); 1623 s ν(C═N); 1232 m ν(C−O); 1087 m, 754 w ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 11.06 s (1H) δ(N(2)−H); 8.65 s,b, 7.99 s,b (2H) δ(N(1)−H_2); 4.66 c (1H) δ(C(3)−H); 4.18 c (2H) δ(O−CH_2); 2.33 s (3H) δ(C(2)−CH_3); 1.45 c (3H) δ(C(3)−CH_3); 1.22 t (3H) δ(C(6)−H_3). UV−vis {solvent, λ (nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: CH_3CN, 315 (4.0), 278 (7.6); CH_2-Cl_2, 320 (4.0), 274 (5.3); CH_3OH, 350 (2.3), 290 (7.9).

Short (0.5 h) Reactions of [ReX(CO)$_5$] and H_2L^Y. X = Br and Y = A. A mixture of 104 mg (0.55 mmol) of H_2L^A and 193 mg (0.48 mmol) of [ReBr(CO)$_5$] in 10 mL of toluene was refluxed for 0.5 h. The orange solid formed was filtered out and vacuum dried. Elemental analysis and the IR and ^{1}H NMR spectra of the solid suggested the presence of both thiosemicarbazone and pyrazolone complexes. Single crystals of both [ReBr(CO)$_3$(H_2L^A)]·$^1/_2C_7H_8$·$^1/_2H_2O$ and [Re(pyz^A)(CO)$_3$]$_4$·C_7H_8 were obtained from the mother liquor after storage for a few days at 0 °C.

X = Cl or Y = B. These reactions were performed by the same general procedure as above and likewise yielded mixtures of thiosemicarbazone and pyrazolone complexes, but we were unable to obtain single crystals.

Longer (2 h) Reactions of [ReX(CO)$_5$] and H_2L^Y. X = Br and Y = B. A suspension of 500 mg (1.23 mmol) of [ReBr(CO)$_5$] and 238 mg of H_2L^B in 15 mL of freshly distilled toluene was refluxed for 2 h under Ar. The solid formed was filtered out and vacuum dried. Since its IR and NMR spectra showed the presence of complexes of both the thiosemicarbazone ligand and some cyclic derivative, a sample was dissolved in 1:1 acetone/toluene and this solution was concentrated in a sandbath until it afforded pale yellow crystals which were separated by hand and identified by X-ray studies as [ReBr(CO)$_3$(Hpyz^B)] (**2d**). Mp: 220 °C (dec). IR data (KBr, cm^{-1}): 3445 m,b ν(O−H); 3333 m, 3238 m, 3110 m ν(N−H); 2027 vs, 1940 vs, 1912 vs ν(CO); 1607 s ν(C═O); 811 m ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 10.07 s, 9.58 s (2H) δ(NH_2); 2.48 s (3H) δ(C(2)−CH_3); 2.10 s (3H) δ(C(3)−CH_3). The crystals obtained were too few for elemental analysis.

X = Cl or Y = A. These reactions were performed by the same general procedure as above and likewise yielded mixtures of thiosemicarbazone and pyrazolone complexes, but we were unable to obtain single crystals.

Synthesis of Complexes *fac*-[Re(pyz)(CO)$_3$]$_4$ [L = pyz^A (3a), pyz^B (3b)]. The following synthesis of **3a** was typical. A mixture of [ReCl(CO)$_5$] (150 mg, 0.415 mmol) and H_2L^A (78.5 mg, 0.415 mmol) in freshly distilled toluene (7.5 mL) was refluxed for 20 h. The pale green (**3a**) or yellow (**3b**) precipitate was filtered out, washed with dry chloroform, and vacuum dried.

Data for 3a. Yield: 153 mg (86.0%). Mp: 250 °C (dec). Anal. Found: C, 22.8; H, 1.4; N, 9.8; S, 7.5. $C_8H_6N_3O_4SRe$ requires: C, 22.5; H, 1.4; N, 9.9; S, 7.5. Mass spectrum [*m*/*z* (%)]: 427 (28) |M/4|$^+$. IR data (KBr, cm^{-1}): 3406 m, 3379 w ν(N−H); 2027 vs, 1920 vs, 1891 vs ν(CO); 1618 s ν(C═O); 1580 m, 1485 m ν(ring);

Table 5. Crystal and Structure Refinement Data

	1c·$^1/_2C_7H_8$·$^1/_2H_2O$	**2d**	**3a**·C_7H_8	**3a**·C_7H_8	**4b**
chemical formula	$C_{12.5}H_{16}O_{5.5}N_3BrReS$	$C_9H_9O_4N_3BrSRe$	$C_{39}H_{32}O_{16}N_{12}S_4Re_4$	$C_{39}H_{32}O_{16}N_{12}S_4Re_4$	$C_9H_{10}O_5N_3SRe$
formula weight	594.45	521.36	1797.81	1797.81	458.46
crystal system	monoclinic	monoclinic	monoclinic	tetragonal	monoclinic
space group	*C*2/*c*	$P2_1/c$	$P2_1/n$	*P*4/*n*	$P2_1/n$
a (Å)	14.3705(9)	8.6123(7)	13.9390(8)	17.562(3)	11.8361(8)
b (Å)	30.862(2)	8.4047(7)	23.4550(14)	17.562(3)	7.7421(5)
c (Å)	17.4628(11)	19.1452(16)	16.2538(10)	8.144(2)	30.004(2)
β (deg)	105.4270(10)	95.665(2)	90.3800(10)	−	93.110(2)
V (Å^3)	7465.7(8)	1379.0(2)	7643.3(12)	2511.8(9)	2745.4(3)
Z	16	4	4	2	8
D_X (Mg m^{-3})	2.116	2.511	2.247	2.377	2.218
temperature (K)	293	293	293	293	293
λ (Mo Kα)/D	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	8.792	11.872	9.315	9.854	9.023
reflections measured	21637	8082	29848	12281	16182
independent reflections (R_{int})	8490 (0.0582)	3189 (0.0845)	11939 (0.0696)	2987 (0.0870)	6368 (0.0827)
R1/wR2 ($I > 2\sigma(I)$)	0.0403/0.0773	0.0467/0.0947	0.0449/0.0599	0.0617/0.1242	0.0418/0.0626

1033 m, 763 m ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 10.18 s, 9.79 s (2H) δ(N(1)−H$_2$); 4.98 s (1H) δ(C(3)−H); 2.32 s (3H) δ(C(2)−CH$_3$). UV−vis {CH$_3$CN, λ(nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: 355 (23.4), 318 (21.0). Single crystals of **3a**·C_7H_8 (tetragonal form) were obtained from the mother liquor after storage for a few days at 0 °C.

Data for 3b. Yield: 126 mg (70.0%). Mp: 255 °C (dec). Anal. Found: C, 25.0; H, 1.7; N, 9.4; S, 7.2. $C_9H_8N_3O_4SRe$ requires: C, 24.5; H, 1.8; N, 9.5; S, 7.3. Mass spectrum [*m*/*z* (%)]: 441 (27) |M/4|$^+$. IR data (KBr, cm^{-1}): 3439 m, 3380 w, 3326 w ν(N−H); 2026 vs, 1907 s, 1885 sh ν(CO); 1628 s ν(C═O); 1578 m, 1502 m ν(ring); 1029 w, 763 w ν(C═S). ^{1}H NMR data (DMSO-d_6, ppm): 11.10 s, 10.27 s (2H) δ(N(1)−H$_2$); 2.08 s (3H) δ(C(3)−CH$_3$); 1.50 s (3H) δ(C(2)−CH$_3$). UV−vis {CH$_3$CN, λ (nm) ($\epsilon \times 10^{-3}$ dm^3 mol^{-1} cm^{-1})}: 376 (20.0), 308 (20.1).

Reaction of 1*x* with NaOMe. *x* = d. NaOMe (4.8 mg) was added to a stirred solution of 50 mg (0.09 mmol) of **1d** in 3 mL of freshly distilled acetone, and the resulting mixture was refluxed for 1.5 h. The acetone was then removed by vacuum, and the yellow solid obtained was washed with water. Its IR and ^{1}H NMR spectra and elemental analysis suggested the presence of impure **3b**, but slow concentration of an aqueous solution obtained in the washing process afforded pale yellow crystals of what X-ray crystallography showed to be *fac*-[Re(pyz^B)(CO)$_3$(H$_2$O)] (**4b**). Mp: 165 °C (dec). IR data (KBr, cm^{-1}): 3426 m ν(O−H); 3110 m,b, 2931 w ν(N−H); 2024 vs, 1919 vs, 1907 vs ν(CO); 1620 s ν(C═O); 1506 s, 1411 s ν(ring); 763 w ν(C═S). ^{1}H NMR data (acetone-d_6, ppm): 11.75 s, 9.35 s (2H) δ(NH$_2$); 6.2 s (1H) δ(H$_2$O); 2.35 s (3H) δ-(C(3)−CH$_3$); 1.75 s (3H) δ(C(2)−CH$_3$). The crystals obtained were too few for elemental analysis or meaningful estimation of yield.

***x* = a, b, c.** These reactions were performed by the same general procedure as above and likewise yielded impure **3a** or **3b**, but we were unable to obtain single crystals.

Studies of Cyclization-Elimination Reactions. NMR tubes containing solutions of **1** (ca. 10 mg) in acetone-d_6 (0.75 mL) were kept at 50 ± 3 °C and examined periodically by ^{1}H NMR spectroscopy at 20 °C. Initially all the signals of the thiosemicarbazone ligand were observed, but after 7 h the signals due to N(1)-H$_2$, N(2)H, and C(3)H (see Scheme 1) disappeared through deuteration. After 30 h (**1a**), 41 h (**1b**), 76 h (**1c**), or 80 h (**1d**), the integral of the signal due to released alcohol was equal to that of the R^{2}O ligand group signal, showing that 50% of the complex had been cyclized.

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic data collection and refinement parameters are listed in Table 5. All crystallographic measurements were performed on a Bruker Smart CCD apparatus at CACTI (Universidade de Vigo). The data were corrected for absorption effects using the program SADABS.[25a]

Structure analyses were carried out by direct methods.[25b] Least-squares full-matrix refinements on F^2 were performed using the program SHELXL97. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from ref 25c. Reflection data for **1c**·$^1/_2C_7H_8$·$^1/_2H_2O$ and for the tetragonal form of **3a**·C_7H_8 were corrected for the diffuse scattering due to disordered toluene molecules by means of the program SQUEEZE.[8] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined as riders except those belonging to the hydrazinic nitrogen and water groups in **1c**, the enol group in **2d**, and the water in **4b**, which were refined isotropically in positions previously determined in the corresponding Fourier map. Graphics were obtained with PLATON[9] and SCHAKAL.[25d]

Acknowledgment. We thank the Secretariat General for Research and Development of the Xunta de Galicia (Spain) for financial support under Project PGIDT00PX120301PR.

Note Added after ASAP: Due to a production error, the version of this paper posted ASAP on August 30, 2003, contained an incorrect figure in place of Figure 2. The version posted on September 2, 2003, contains the correct Figure 2.

Supporting Information Available: X-ray crystallographic files (CIF format) for **1c**·$^1/_2C_7H_8$·$^1/_2H_2O$, **2d**, **3a**·C_7H_8 (monoclinic and tetragonal forms), and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC030154Q

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