Insertion of Unsaturated Organic Electrophiles into Molybdenum–Alkoxide and Rhenium–Alkoxide Bonds of Neutral, Stable Carbonyl Complexes

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract: Alkoxo complexes [Re(OR)(CO)$_3$(N-N)] (R = Me, Et, *t*Bu; N-N = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′bipyridine (bipy′), 1,10-phenanthroline (phen)) and [M(OMe)(η^3-allyl)(CO)$_2$(phen)] (M = Mo, W) have been synthesized in good yields and using mild conditions by the reaction of sodium alkoxides with [Re(OTf)(CO)$_3$(N-N)] and [MCl(η^3-allyl)(CO)$_2$(phen)] precursors. These have been characterized by IR and NMR spectroscopy as well as by X-ray diffraction for [W(OMe)(η^3-allyl)(CO)$_2$(phen)] (**10**). The reactions of the molybdenum and rhenium alkoxo complexes with isocyanates, R′NCO, yield [L$_n$M{N(R′)C(O)OR}] complexes; the carbamate ligand, which results from an R′NCO insertion into the M–OR bond, is monodentate through the nitrogen atom. The solid-state structures of Mo and Re examples have been determined by X-ray diffraction. The geometry around the carbamate nitrogen of these compounds is planar, and the distances indicate delocalization of the nitrogen lone pair involving mainly the carbonyl groups. Experiments carried out with the Re complexes showed that aryl isocyanates are more reactive than their alkyl counterparts, and that bulky R′ groups led to slow rates of insertion. Insertion reactions were also observed with isothiocyanates, although here it is the S–C bond that inserts into the M–OR bond, and the resulting ligand is bound to the metal by sulfur. Competition experiments with the Re compounds indicate that isocyanates are more reactive than isothiocyanates towards the Re–OR bonds. Tetracyanoethylene inserts into the Re–OMe bond of [Re(OMe)(CO)$_3$(bipy′)], forming a complex with a 2-methoxytetracyanoethyl ligand; the structure of which was determined by X-ray diffraction. The formation of the xanthato complex [Re(SC(S)O*t*Bu)(CO)$_3$(bipy)] (**20**) by reaction of [Re(OTf)(CO)$_3$(bipy)] with CS$_2$ and NaO*t*Bu, but not by the reaction of CS$_2$ and [Re(O*t*Bu)(CO)$_3$(bipy)] (**5a**), suggests that the insertion reactions do not take place by ionization of the alkoxo complexes to give the free alkoxide ion.

Keywords: alkoxides · insertion · molybdenum · rhenium

Introduction

The insertion of unsaturated molecules into transition metal–alkyl bonds, a prevalent step in catalytic processes, requires prior coordination of the substrate to a site adjacent to the bond that undergoes the insertion.[1] Therefore, a vacant site or a labile ligand must be present in the alkyl complex. Insertion into metal–alkoxide bonds can take place by a similar mechanism. However, the presence of lone pairs of electrons on the oxygen atom and the high polarity of the M–O bond open new mechanistic possibilities, such as nucleophilic attack on the uncoordinated substrate by either free alkoxide ions (resulting from heterolytic M–O bond cleavage) or the undissociated alkoxo ligand.[2]

Alkoxo complexes of low-valent, organometallic-type metal fragments are particularly attractive since the destabilizing interaction between the lone pairs of electrons of the alkoxo group and the metal d-electrons should enhance the reactivity of the M–O bond.[3] Thus, in a few instances, the reactions of these complexes with unsaturated organic electrophiles have been used to create new C–O bonds.[1] However, their high reactivity and the existence of facile decomposition pathways

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0947-6539/02/0819-4510 $ 20.00+.50/0

may hamper the isolation of low-valent alkoxo complexes.[4] Further complications may arise when the more general synthetic route, namely, the reaction of an alkaline alkoxide with a halocomplex, suffers from lack of selectivity. As a result, there is a paucity of alkoxo derivatives in some areas of the chemistry of transition metals in low oxidation states.

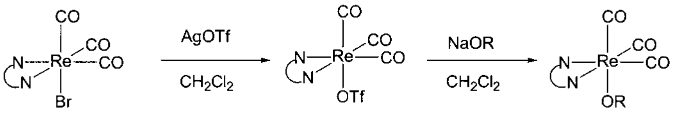
The $[Re(CO)_3(N\text{-}N)]$ fragments show little tendency to undergo loss of ligands or to otherwise be the center of reactivity, a fact that makes their complexes ideal candidates to study the processes taking place on the ligand that occupies the remaining sixth coordination site. $[Re(OR)(CO)_3L_2]$ (L_2 = two phosphines or a bidentate phosphine or arsine) complexes have been shown to insert CO, CO_2 and CS_2.[2d] Chelating diimines such as 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands are stronger electron donors than diphosphines or diarsines (see below). Since a more electron-rich metal center enhances the reactivity of alkoxo complexes towards electrophiles,[3b] diimine complexes of the type $[M(OR)(CO)_3(N\text{-}N)]$ are expected to be more reactive than their phosphine or arsine counterparts. The planarity and lack of bulky substituents on the diimine rings should contribute to a higher reactivity by facilitating the approach of the incoming electrophile to the alkoxo group. This is particularly important since the two nitrogen atoms of the N-N chelate and the anionic ligand X in $[ReX(CO)_3(N\text{-}N)]$ complexes are in a facial disposition.

We have recently found that $[MCl(\eta^3\text{-allyl})(CO)_2(N\text{-}N)]$ complexes (M = Mo, W; N-N = bipy, phen) react with carbanionic alkylating reagents to yield specifically the new alkyls $[M(R)(\eta^3\text{-allyl})(CO)_2(N\text{-}N)]$.[5] We hoped that an analogous route could be used to synthesize new alkoxo complexes $[M(OR)(\eta^3\text{-allyl})(CO)_2(N\text{-}N)]$, and that these species could share the interesting attributes mentioned above for the rhenium compounds.

The present paper deals with the synthesis of the alkoxo complexes $[Re(OR)(CO)_3(N\text{-}N)]$ and $[M(OR)(\eta^3\text{-allyl})(CO)_2(N\text{-}N)]$ (M = Mo, W) and their reactivity towards several unsaturated organic electrophiles.[6]

Results and Discussion

The reactions of $[Re(OTf)(CO)_3(N\text{-}N)]$ (N-N = bipy, phen, or 4,4′-dimethyl-2,2′bipyridine (bipy′)) compounds with a slight excess of sodium alkoxides in dichloromethane have been found to be an effective synthetic approach to the alkoxo complexes $[Re(OR)(CO)_3(N\text{-}N)]$. The starting triflato complexes could be prepared in virtually quantitative yield by the reaction of equimolar amounts of the corresponding bromo complexes and silver triflate in dichloromethane in the absence of light,[7] see Scheme 1.



	N-N
1a	bipy
1b	phen
1c	bipy′

	N-N
2a	bipy
2b	phen
2c	bipy′

	N-N	R
3a	bipy	Me
3b	phen	Me
3c	bipy′	Me
4	bipy′	Et
5a	bipy	*t*Bu
5b	bipy′	*t*Bu

Scheme 1. Synthesis of the alkoxo complexes. Preparation of the triflato-complex starting materials is possible in almost quantitative yields from the bromo precursors.

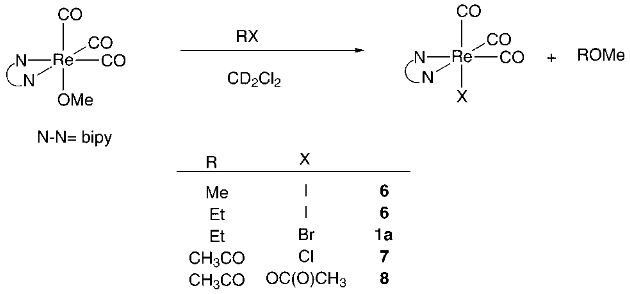
The entire preparation of the methoxo complexes could be carried out in less than one hour with good yields from the bromoprecursors, as detailed in the Experimental Section. Previous preparations of $[Re(OCH_3)(CO)_3(bipy)]$ involve the reaction of $[Re(NCMe)(CO)_3(bipy)]PF_6$ (in turn prepared by refluxing $[ReCl(CO)_3(bipy)]$ with $AgPF_6$ in CH_3CN for eight hours) with two equivalents of sodium methoxide in methanol (reaction time: 17 hours, yield: 42%)[8] and the photolysis in methanol of $[Re(CH_2OH)(CO)_3(bipy)]$ (obtained by reaction of $[Re(CO)_4(bipy)]OTf$ with $NaBH_4$ in methanol).[9]

Good yields of the ethoxo and *tert*-butoxo complexes were obtained using similar routes, although two and five equivalents, respectively, of the corresponding sodium alkoxide had to be used in order to keep reaction times short. Notably the $[Re(OTf)(CO)_3(L\text{-}L)]$ complexes (L-L = 1,2-(dimethylarsino)benzene or 1,2-bis(diethylphosphino)ethane) do not react with sodium *tert*-butoxide;[10] a difference that can be attributed to a destabilizing steric interaction between the substituent on the donor atoms of the chelates and the bulky *tert*-butyl group.

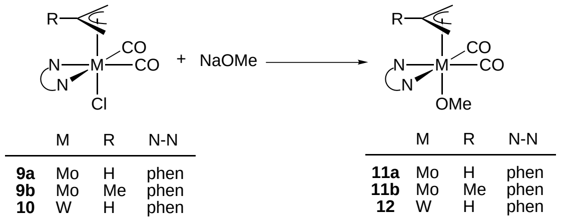
The new alkoxo complexes have been characterized by IR and NMR spectroscopy (see Experimental Section) and were found to be quite thermally stable; no appreciable decomposition was detected after a 20 hour refluxing period in THF. This is an important difference with regard to the zero-valent group 6 anionic alkoxo carbonyl complexes studied by Darensbourg: In this case the π-donor alkoxo ligand causes a strong CO-labilization,[11] that may result in the formation of bimetallic or cluster compounds in which the alkoxo groups act as bridging ligands. Another feature of those zero-valent complexes, not shared by the alkoxo derivatives reported here, is their tendency to undergo β-elimination reactions unless electron-withdrawing substituents are present at the alkoxo group.[12]

The alkoxide ligand in $[Re(OR)(CO)_3(N\text{-}N)]$compounds is a nucleophilic center. Thus, $[Re(OCH_3)(CO)_3(bipy)]$ (**3a**) reacted with methyl iodide, ethyl iodide and ethyl bromide to give the corresponding $[ReX(CO)_3(bipy)]$ (X = I or Br)[13] complex and $(CH_3)_2O$ or $CH_3OCH_2CH_3$. Analogous reactions with acetyl chloride or acetic anhydride yielded $[ReCl(CO)_3(bipy)]$ (**7**) or $[Re(OC(O)CH_3)(CO)_3\ (bipy)]$ (**8**) (independently prepared, see Experimental Section), respectively, and methyl acetate,[14] as shown in Scheme 2

Molybdenum and tungsten(II) alkoxo complexes could be prepared by means of similar straightforward procedures. The complex $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(phen)]$ (**9a**) reacted with sodium methoxide to yield, as indicated by the spectroscopic data, a single product. The product displayed, as did complex **9a**, two bands of similar intensity, indicatives of a *cis*-dicarbonyl geometry. A decrease of some 20 cm^{-1} relative to **9a** in the position of these bands is consistent with the substitution of Cl by the strongly electron-donating methoxo group, as displayed in Scheme 3.



Scheme 2. The reactions of complex **3a** with RX.



Scheme 3. Preparation of Mo and W (II) alkoxo complexes whereby the Cl ligand of the precursor is substituted by the strongly electron-donating methoxo group.

The product was isolated (see Experimental Section) in good yield as a microcrystalline garnet solid for which spectroscopic and analytic data support a [Mo(OMe)(η^3-C_3H_5)$(CO)_2$(phen)] (**11a**) formulation. The methoxo group appears as a sharp three-hydrogen singlet at 4.45 ppm in the ^{1}H NMR spectroscopy. The presence of phenanthroline (as a set of four signals) and of a static and symmetric η^3-C_3H_5 ligand is evident in the same spectrum (see Experimental Section) and indicates that the metal has been the site of the methoxide attack. Specific attack at the metal was also found in the reaction of **9a** with simple alkyl anions, in contrast with the allylic alkylation observed with stabilized carbanions.[15] The symmetric phen and allyl ^{1}H NMR patterns indicate that a mirror plane is present in **11a**, which, therefore, should have a pseudo-octahedral structure with *trans* OMe and allyl groups.

Polymetallic complexes having alkoxo-bridged {Mo(η^3-methallyl)$(CO)_2$} fragments, which result from the reaction of alkaline alkoxides with [MoCl(η^3-methallyl)$(CO)_2$$(NCMe)_2$] and [Mo($\eta^3$-methallyl)$(CO)_2$$(NCMe)_2$(THF)] complexes, have been reported recently by Limberg.[16]

Given that very few low-valent molybdenum alkoxo complexes are known, a crystallographic structural determination of **11a** was sought. However, repeated attempts failed to yield suitable crystals. The similar complex [Mo(OMe)(η^3-methallyl)$(CO)_2$(phen)] (**11b**), for which preparative details and characterization are given in the Experimental Section, was equally reluctant to afford X-ray quality single crystals. The tungsten methoxo complex [W(OMe)(η^3-C_3H_5)$(CO)_2$(phen)] (**12**) was prepared in a manner analogous to **11a–b**, and its spectroscopic data indicate a similar structure. A red crystal of **12**, obtained by hexane diffusion into a CH_2Cl_2 solution, could be used for the X-ray determination of the structure. The results are displayed in Figure 1 and Table 1.

Table 1. Selected bond lenghts [Å] and angles [°] for complex **12**.

W(1)–C(1)	1.972(7)	W(1)–N(1)	2.253(5)
W(1)–C(2)	1.959(7)	W(1)–N(2)	2.259(5)
W(1)–C(4)	2.332(6)	C(1)–O(1)	1.147(7)
W(1)–C(5)	2.218(6)	C(2)–O(2)	1.150(8)
W(1)–C(6)	2.343(6)	O(3)–C(3)	1.371(8)
W(1)–O(3)	2.031(4)		
C(2)-W(1)-C(1)	77.9(3)	C(2)-W(1)-O(3)	94.9(2)
C(1)-W(1)-N(2)	171.3(2)	O(3)-W(1)-N(1)	78.60(17)
C(2)-W(1)-N(1)	171.9(2)	O(3)-W(1)-N(2)	79.93(16)
C(1)-W(1)-O(3)	91.5(2)	C(3)-O(3)-W(1)	125.4(4)
N(1)-W(1)-N(2)	72.97(17)		

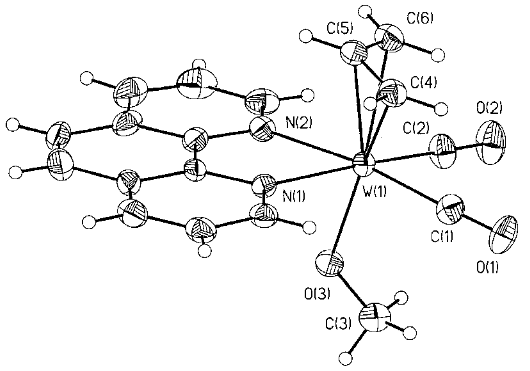


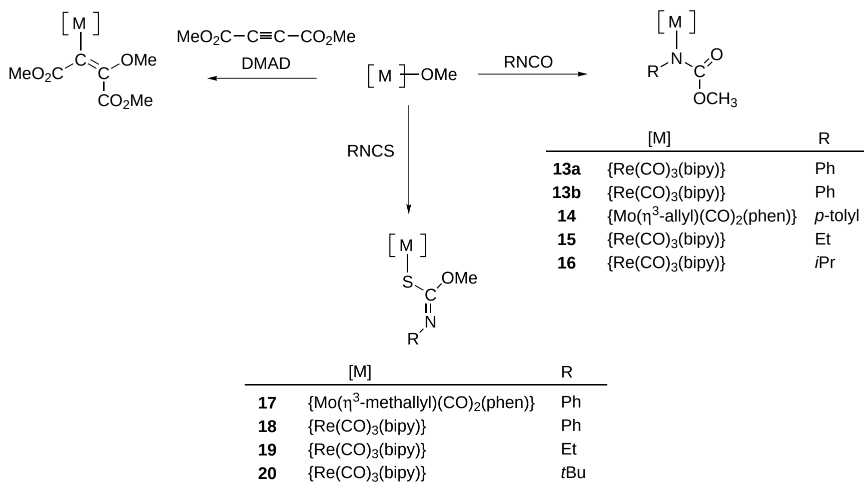
Figure 1. Molecular structure and numbering scheme of **12**.

The solid-state structure corresponds with the one deduced from the spectroscopic data in solution (see above). The W–O distance (2.031(4) Å) in **12** is slightly longer than in the other tungsten neutral alkoxo complexes structurally characterized, and shorter than in the anionic aryloxo complexes [W(O-2,6-Ph_2-C_6H_3)$(CO)_5$]$^-$ (2.175(9) Å)[17] and [W(OPh)$(CO)_4$$(PMePh_2)$]$^-$ (2.191(6) Å),[17] in which π-donation from oxygen to tungsten must be less than in **12** due to the negative charge, the lower oxidation state and the reduced electron releasing ability (compared with CH_3) of aryl groups. The W-O-C angle in **12** (125.4(4)°) is lower than in other neutral tungsten compounds with terminal alkoxo ligands (132.5(2)° for [W(η^5-C_5Me_5)(η^2-C{$NCMe_3$}CH_2CMe_3)$(OCMe_3)$(NO)],[18] and 128.4(6)° to 136.8(7)° values for [W$(OCH_2t\mathrm{Bu})_4$(py)(η^2-$OCPh_2$)][19]), which is likely to be due to the low steric profile of **12**.

The single, terminal alkoxo ligand and the lack of labile ligands in our rhenium and molybdenum alkoxo complexes make them good candidates to study the non-associative reactivity of a metal-alkoxide bond.

Reactions with isocyanates:[20] The complex [Re$(OCH_3)$$(CO)_3$(bipy)] (**3a**) reacts instantaneously at room temperature with phenyl isocyanate affording the new compound [Re(N(Ph)C(O)OCH_3)$(CO)_3$(bipy)] (**13a**) (see Scheme 4), which was characterized spectroscopically. The most informative features are the three-hydrogen singlet at 3.32 ppm in the ^{1}H NMR and the weak singlet at 162.31 ppm in the ^{13}C NMR spectrum assigned to the methoxo group and the carbonyl carbon of the N-phenyl-O-methylcarbamate ligand, respectively.[21]

Since our attempts to grow single crystals of **13a** were unsuccessful, we scanned similar derivatives and found that



	[M]	R
13a	{Re(CO)$_3$(bipy)}	Ph
13b	{Re(CO)$_3$(bipy)}	Ph
14	{Mo(η^3-allyl)(CO)$_2$(phen)}	*p*-tolyl
15	{Re(CO)$_3$(bipy)}	Et
16	{Re(CO)$_3$(bipy)}	*i*Pr

	[M]	R
17	{Mo(η^3-methallyl)(CO)$_2$(phen)}	Ph
18	{Re(CO)$_3$(bipy)}	Ph
19	{Re(CO)$_3$(bipy)}	Et
20	{Re(CO)$_3$(bipy)}	*t*Bu

Scheme 4. Reactions with DMAD, isocyanates and isothiocyanates.

[Re(OCH$_3$)(CO)$_3$(phen)] (**3b**) inserts PhNCO to give, in an identical manner, [Re(N(Ph)C(O)OCH$_3$)(CO)$_3$(phen)] (**13b**), for which single crystals suitable for X-ray diffraction could be obtained. The results of the structural determination are shown in Figure 2 and Table 2.

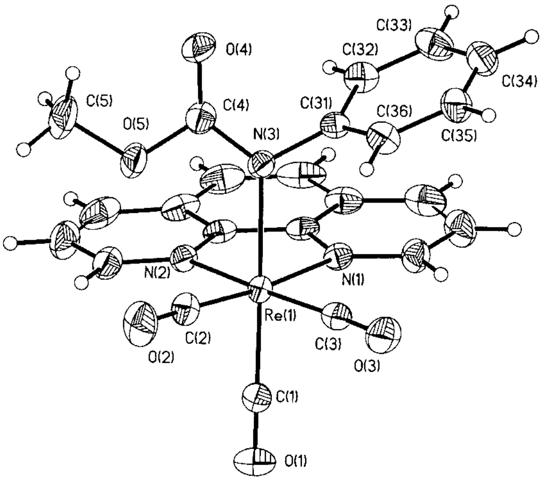


Figure 2. Molecular structure and numbering scheme of **13b**.

Table 2. Selected bond lengths [Å] and angles [°] for complex **13b**.

Re(1)–C(1)	1.916(6)	N(3)–C(31)	1.436(7)
Re(1)–C(2)	1.908(6)	C(4)–O(4)	1.220(8)
Re(1)–C(3)	1.904(6)	C(4)–O(5)	1.379(8)
Re(1)–N(1)	2.173(4)	C(1)–O(1)	1.149(7)
Re(1)–N(2)	2.194(4)	C(2)–O(2)	1.150(8)
Re(1)–N(3)	2.195(5)	C(3)–O(3)	1.161(7)
N(3)–C(4)	1.332(7)		
C(2)-Re(1)-C(1)	89.4(2)	C(2)-Re(1)-N(3)	93.2(2)
C(3)-Re(1)-C(2)	86.6(3)	C(1)-Re(1)-N(3)	175.35(19)
C(3)-Re(1)-C(1)	88.0(2)	N(1)-Re(1)-N(3)	82.71(17)
C(1)-Re(1)-N(1)	94.45(19)	N(2)-Re(1)-N(3)	84.77(16)
C(2)-Re(1)-N(1)	174.1(2)	C(4)-N(3)-Re(1)	127.2(4)
C(3)-Re(1)-N(1)	98.0(2)	C(31)-N(3)-Re(1)	118.7(3)
C(2)-Re(1)-N(2)	100.0(2)	C(4)-N(3)-C(31)	114.1(5)
C(1)-Re(1)-N(2)	90.9(2)	O(4)-C(4)-N(3)	129.3(6)
C(3)-Re(1)-N(2)	173.3(2)	O(4)-C(4)-O(5)	120.2(6)
N(1)-Re(1)-N(2)	75.44(17)	N(3)-C(4)-O(5)	110.5(3)
C(3)-Re(1)-N(3)	96.0(2)		

The carbamate ligand in **13b**, formed by isocyanate insertion into the Re–O bond is N-bonded to rhenium, with a Re–N distance (2.195(5) Å) slightly longer than that found in the amido complex [Re(NHPh)(CO)$_3$(P-P)] (P-P = 1,2-bis(diethylphosphino)ethane) (2.170(7) Å).[2c] However, the N–C(ipso) distance in **13b** (1.436(7) Å) is significantly longer than the corresponding distance in the amido complex (1.375(11) Å); this indicates that the phenyl ring does not participate appreciably in the delocalization of the nitrogen lone pair. On the other hand, the N(3)–C(4) distance (1.332(7) Å) is virtually identical to the corresponding distance in the complex [Ni(mesityl){N(Ph)C(O)CHPh$_2$}(PMe$_3$)$_2$] (1.339(3) Å) which was considered to imply significant electronic delocalization involving the carbonyl group.[22] For complex **13b**, this delocalization is further substantiated by the planarity around the nitrogen atom of the carbamate ligand.

Analogously, the reaction of [Mo(OR)(η^3-allyl)(CO)$_2$(phen)] (**11a**) with *p*-tolylisocyanate led to the quantitative transformation of **11a** into the complex [Mo{N(R)C(O)OCH$_3$}(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (R = *p*-tolyl) (**14**), as shown in Scheme 4. The most relevant spectroscopic data of **14** are a three-hydrogen singlet at 1.69 ppm in ^{1}H NMR, attributable to the methoxo group, and a weak signal at 162.8 ppm in ^{13}C NMR, corresponding to the carbonyl carbon of the N-*p*-tolyl-O-methylcarbamate ligand. The structure of **14** was also determined by X-ray diffraction (Figure 3 and Table 3). The carbamate ligand, resulting from isocyanate insertion into the Mo–O bond, is again N-bound to the metal.

Isocyanate insertion into M–O bonds of alkoxo complexes has some precedents.[21] However, so far, the crystallograph-

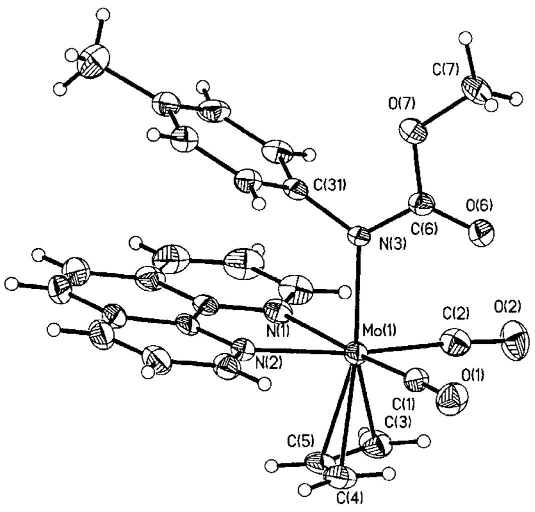


Figure 3. Molecular structure and numbering scheme of **14**.

Table 3. Selected bond lengths [Å] and angles [°] for complex **14**.

Mo(1)–C(1)	1.955(5)	C(1)–O(1)	1.151(5)
Mo(1)–C(2)	1.975(5)	C(2)–O(2)	1.149(5)
Mo(1)–C(3)	2.352(4)	N(3)–C(31)	1.448(5)
Mo(1)–C(4)	2.234(4)	N(3)–C(6)	1.348(5)
Mo(1)–C(5)	2.347(4)	C(6)–O(6)	1.227(5)
Mo(1)–N(1)	2.279(4)	C(6)–O(7)	1.367(5)
Mo(1)–N(2)	2.250(3)	O(7)–C(7)	1.438(5)
Mo(1)–N(3)	2.216(3)		
C(1)-Mo(1)-C(2)	78.64(19)	C(6)-N(3)-Mo(1)	121.9(3)
C(1)-Mo(1)-N(1)	172.53(16)	C(31)-N(3)-Mo(1)	122.7(3)
C(2)-Mo(1)-N(2)	172.57(16)	N(3)-C(6)-O(7)	112.7(4)
C(1)-Mo(1)-N(3)	89.88(16)	O(6)-C(6)-N(3)	126.8(4)
C(2)-Mo(1)-N(3)	89.25(16)	C(6)-O(7)-C(7)	117.5(4)
N(1)-Mo(1)-N(3)	84.20(12)	N(2)-Mo(1)-N(1)	73.29(14)
N(2)-Mo(1)-N(3)	83.33(12)	C(31)-N(3)-C(6)	115.3(3)

ically characterized insertion products have been N,O-bidentate carbamate ligands,[21a,d,f] due to the existence of vacant sites *cis* to the alkoxo group in the precursor complex. The sum of angles around N(3) in **14** is 360°. This planar geometry indicates a delocalization of the nitrogen lone pair that, given the bond lengths, involves mainly the bond N(3)–C(6). This distance (1.348(5) Å) is nearly identical to that mentioned above for the complex **13b**. An important consequence of this electronic delocalization is that **13b** and **14** do not react with a second equivalent of RNCO, whereas amido complexes usually insert isocyanates.[23]

To determine a relative order of reactivity, a competition experiment for the rhenium complexes was conducted. The reaction of **3a** with EtNCO is instantaneous at room temperature, giving an insertion product (**15**) analogous to **13a**–**b**, which was spectroscopically characterized. Thus, **3a** was added to a CD_2Cl_2 solution of equimolar amounts of PhNCO and EtNCO in an NMR tube. Compound **13a** was the only product detected by ^1H NMR, which indicates that PhNCO is significantly more reactive than EtNCO. As a Ph unit is less electron releasing than Et, the aryl isocyanate should be as stronger electrophile than EtNCO. This order of reactivity is consistent with the isocyanate being the electrophilic counterpart in the reaction with the nucleophilic alkoxo group.

The reaction of **3a** with *i*PrNCO to afford the insertion product **16** takes one hour at room temperature; no reaction was observed with *t*BuNCO, probably reflecting a combination of less electrophilic character (as a consequence of a more electron-donating alkyl chain) and an increase in steric hindrance of the isocyanate. The bulkier alkoxo group of [Re(O*t*Bu)$(CO)_3$(bipy′)] (**5b**) inserted only the more reactive PhNCO (30 min, room temperature). Since the *t*BuO ligand is more basic (and, therefore, considering electronic factors, should be more reactive) than OMe, this reflects the importance of the steric bulk on the nucleophilic oxygen.[24]

Reactions with isothiocyanates:[25] The insertion of isothiocyanates into Re–OR and Mo–OR bonds was also studied. The reaction of phenylisothiocyanate with [Mo(OMe)(η^3-methallyl)$(CO)_2$(phen)] (**11b**)[26] afforded the insertion product [Mo{SC(NPh)OCH_3}(η^3-$C_3H_4(CH_3)$)$(CO)_2$(phen)] (**17**) (see Scheme 4). The ^1H NMR spectra showed the incorporation of the isothiocyanate (aromatic multiplets at 6.95 and 6.68 ppm), as well as a signal at 3.88 ppm corresponding to the methoxo group. The results of an X-ray structural determination of **17** are showed in Figure 4 and Table 4.

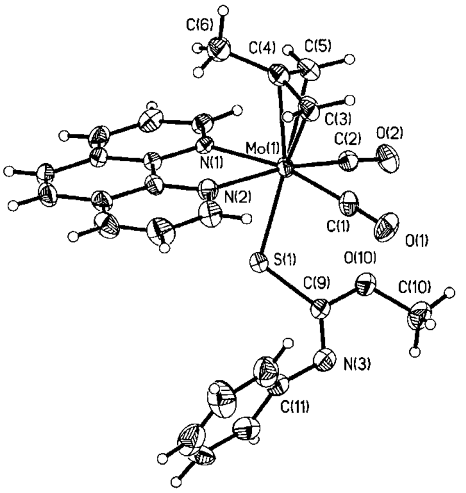


Figure 4. Molecular structure and numbering scheme of **17**.

Table 4. Selected bond lengths [Å] and angles [°] for complex **17**.

Mo(1)–C(1)	1.949(8)	C(1)–O(1)	1.154(9)
Mo(1)–C(2)	1.951(8)	C(2)–O(2)	1.166(9)
Mo(1)–C(3)	2.337(8)	S(1)–C(9)	1.766(8)
Mo(1)–C(4)	2.284(9)	C(9)–N(3)	1.264(10)
Mo(1)–C(5)	2.329(9)	C(9)–O(10)	1.334(9)
Mo(1)–N(1)	2.253(5)	O(10)–C(10)	1.429(10)
Mo(1)–N(2)	2.261(6)	N(3)–C(11)	1.405(11)
Mo(1)–S(1)	2.493(2)		
C(1)-Mo(1)-C(2)	79.2(3)	N(2)-Mo(1)-S(1)	79.20(18)
N(1)-Mo(1)-N(2)	72.8(2)	C(9)-S(1)-Mo(1)	110.2(3)
C(1)-Mo(1)-N(1)	167.1(3)	O(10)-C(9)-S(1)	112.5(6)
C(2)-Mo(1)-N(2)	168.7(3)	N(3)-C(9)-S(1)	112.7(4)
C(1)-Mo(1)-S(1)	89.0(3)	C(9)-O(10)-C(10)	117.4(7)
C(2)-Mo(1)-S(1)	89.6(2)	C(9)-N(3))-C(11)	120.7(7)
N(1)-Mo(1)-S(1)	78.57(16)		

The regiochemistry is different to the one found for the insertion of *p*-tolylisocyanate described before. In **17** the S–C bond rather than the N–C bond was inserted into the molybdenum–alkoxo bond. The resulting ligand is coordinated through the sulfur atom. The bond distances N(3)–C(9) (1.246(6) Å) and C(9)–S(1) (1.766(8) Å) are consistent with double and single bonds, respectively. A simple rationale for the different coordination mode of the ligands resulting from the insertion in complexes **14** and **17** is that the softer sulfur would be preferred for the coordination to an organometallic fragment. However, it should be noted that the isothiocyanate ligand is N-bound in the complexes [Mo(NCS)(η^3-allyl)-$(CO)_2$(N-N)] (N-N = bipy, phen), for which structures have been determined by X-ray diffraction.[27]

The methoxo complex **3a** was found to react with PhNCS, EtNCS, and *t*BuNCS (Scheme 4). While the reactions with phenyl and ethyl isothiocyanates took place in 15 minutes at room temperature, the reaction with the bulkier *tert*-butylisothiocyanate needed one day to reach completion. Competition experiments between PhNCO and PhNCS, and between EtNCO and EtNCS, established that isocyanates are more reactive towards **3a** than related isothiocyanates (see Experimental Section), a result reminiscent of the relative reactivities of RNCO and RNCS towards alcohols.[28] Therefore, the reaction of *t*BuNCS with **3a** is surprising given the lack of reaction between this complex and *t*BuNCO (see above). Aiming to obtain information that could clarify this point, complex [Re{SC(NEt)OCH$_3$}(CO)$_3$(bipy)] (**18**) was structurally characterized by X-ray diffraction.

The results (Figure 5 and Table 5) indicate the presence of the SC(NEt)OMe group (resulting from ethylisothiocyanate insertion into the Re–O bond) S-bonded to rhenium. The N(3)–C(4) (1.255(7) Å) and C(4)–S(1) (1.773(5) Å) distances are consistent with double and single bonds respectively, as depicted in Scheme 4. The different coordination modes found for the products of the reactions with isocyanates and isothiocyanates account for the fact that **3a** reacts with *t*BuNCS but does not with *t*BuNCO. Thus, S-coordination to Re of the resulting organic group keeps the bulky *tert*-butyl group away from the metal, whereas the unobserved product of *t*BuNCO insertion, with a structure such as **13**–**16** (see Schemes 4 and 5) would have the *tert*-butyl group on the nitrogen coordinated to rhenium, and therefore would suffer a destabilizing interaction between the {Re(CO)$_3$(bipy)} and *t*Bu groups.

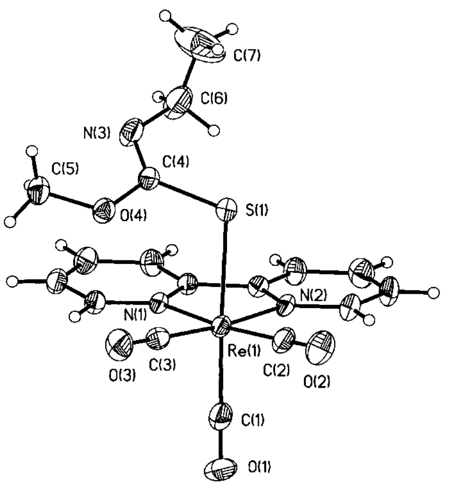
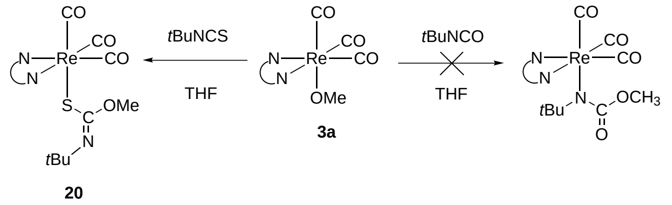


Figure 5. Molecular structure and numbering scheme of **18**.

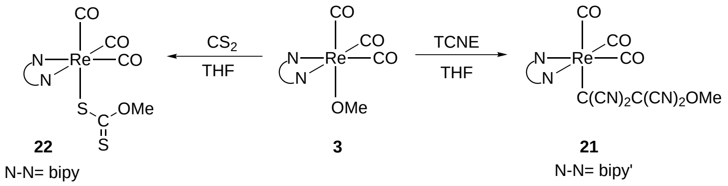
Table 5. Selected bond lengths [Å] and angles [°] for complex **18**.

Re(1)–C(1)	1.921(7)	N(3)–C(4)	1.255(7)
Re(1)–C(2)	1.925(6)	C(4)–O(4)	1.358(6)
Re(1)–C(3)	1.911(6)	O(4)–C(5)	1.432(6)
Re(1)–N(1)	2.176(4)	C(1)–O(1)	1.147(8)
Re(1)–N(2)	2.181(4)	C(2)–O(2)	1.143(7)
Re(1)–S(1)	2.5131(14)	C(3)–O(3)	1.155(7)
S(1)–C(4)	1.773(5)		
C(1)-Re(1)-C(2)	89.2(3)	C(1)-Re(1)-S(1)	176.8(2)
C(3)-Re(1)-C(2)	86.5(2)	C(2)-Re(1)-S(1)	90.95(18)
C(3)-Re(1)-C(1)	89.5(3)	C(3)-Re(1)-S(1)	93.69(17)
C(1)-Re(1)-N(1)	94.6(2)	N(1)-Re(1)-S(1)	84.97(11)
C(2)-Re(1)-N(1)	173.4(2)	N(2)-Re(1)-S(1)	82.95(11)
C(3)-Re(1)-N(1)	99.0(2)	C(4)-S(1)-Re(1)	107.93(18)
C(2)-Re(1)-N(2)	99.5(2)	N(3)-C(4)-O(4)	118.9(5)
C(1)-Re(1)-N(2)	93.9(2)	N(3)-C(4)-S(1)	128.6(4)
C(3)-Re(1)-N(2)	173.21(19)	O(4)-C(4)-S(1)	112.6(4)
N(1)-Re(1)-N(2)	74.87(15)	C(4)-O(4)-C(5)	116.1(4)



Scheme 5. The different coordination modes found for the products of the reactions with isocyanates and isothiocyanates account for the fact that complex **3a** reacts with *t*BuNCS to give compound **20** but does not react with *t*BuNCO.

Reactions with tetracyanoethylene (TCNE):[29] A significant shift to higher wavenumbers occurred in the IR $\tilde{\nu}_{CO}$ values when TCNE was added to a THF solution of **3c**. The single product of the reaction, [Re{C(CN)$_2$C(CN)$_2$(OMe)}(CO)$_3$(bipy')] (**21**) (see Scheme 6), was isolated as a thermally unstable crystalline solid and structurally characterized by X-ray diffraction (Figure 6 and Table 6).



Scheme 6. The formation of complexes **21** and **22** from THF solutions of **3**.

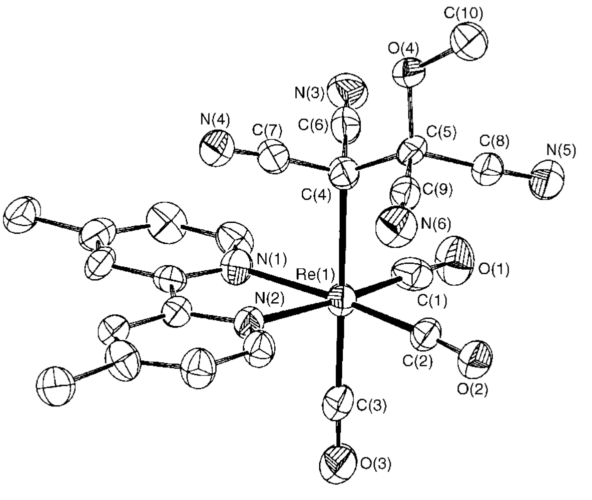


Figure 6. Molecular structure and numbering scheme of **21**.

The molecule of **21** consists of a *fac*-{Re(CO)$_3$(bipy')} fragment bound to a 2-methoxytetracyanoethyl group resulting from TCNE insertion into the Re–OMe bond. The Re–C distance (2.339(9) Å) is somewhat longer than the values found in rhenium complexes with simple alkyl groups,[30] in line with what is found for other metals.[31] Insertion reactions of TCNE with transition metal alkyls are well documented;[32] in contrast, this is, to our knowledge, the first TCNE insertion

Table 6. Selected bond lengths [Å] and angles [°] for complex **21**.

Re(1)–C(1)	1.903(9)	Re(1)–C(4)	2.339(9)
Re(1)–C(2)	1.915(7)	C(4)–C(5)	1.533(10)
Re(1)–C(3)	1.930(8)	C(1)–O(1)	1.162(10)
Re(1)–N(1)	2.183(6)	C(2)–O(2)	1.153(9)
Re(1)–N(2)	2.185(6)	C(3)–O(3)	1.142(10)
C(1)-Re(1)-C(2)	89.3(3)	C(2)-Re(1)-C(4)	96.2(3)
C(2)-Re(1)-C(3)	86.1(3)	C(3)-Re(1)-C(4)	177.3(3)
C(1)-Re(1)-C(3)	88.3(4)	N(1)-Re(1)-C(4)	85.0(2)
C(1)-Re(1)-N(1)	97.8(3)	N(2)-Re(1)-C(4)	88.4(3)
C(2)-Re(1)-N(1)	172.8(3)	C(5)-C(4)-Re(1)	116.1(5)
C(3)-Re(1)-N(1)	92.9(3)	C(7)-C(4)-Re(1)	110.0(5)
C(2)-Re(1)-N(2)	98.2(3)	C(6)-C(4)-Re(1)	105.4(5)
C(1)-Re(1)-N(2)	172.5(3)	C(7)-C(4)-C(6)	108.0(6)
C(3)-Re(1)-N(2)	92.6(3)	C(7)-C(4)-C(5)	108.5(7)
N(1)-Re(1)-N(2)	74.7(2)	C(6)-C(4)-C(5)	108.5(7)
C(1)-Re(1)-C(4)	90.4(3)		

Table 7. Selected bond lengths [Å] and angles [°] for complex **22**.

Re(1)–C(1)	1.920(8)	S(2)–C(4)	1.652(6)
Re(1)–C(2)	1.900(8)	C(4)–O(4)	1.315(7)
Re(1)–C(3)	1.924(7)	O(4)–C(5)	1.471(8)
Re(1)–N(1)	2.168(4)	C(1)–O(1)	1.146(8)
Re(1)–N(2)	2.168(5)	C(2)–O(2)	1.170(9)
Re(1)–S(1)	2.5059(15)	C(3)–O(3)	1.142(8)
S(1)–C(4)	1.729(6)		
C(2)-Re(1)-C(1)	89.9(3)	C(1)-Re(1)-S(1)	177.40(19)
C(2)-Re(1)-C(3)	87.2(3)	C(2)-Re(1)-S(1)	91.0(3)
C(1)-Re(1)-C(3)	88.8(3)	C(3)-Re(1)-S(1)	93.7(2)
C(1)-Re(1)-N(1)	94.7(2)	N(1)-Re(1)-S(1)	82.77(12)
C(2)-Re(1)-N(1)	97.3(2)	N(2)-Re(1)-S(1)	85.29(12)
C(3)-Re(1)-N(1)	174.4(2)	C(4)-S(1)-Re(1)	111.9(2)
C(2)-Re(1)-N(2)	171.6(2)	O(4)-C(4)-S(2)	124.3(2)
C(1)-Re(1)-N(2)	93.5(2)	O(4)-C(4)-S(1)	113.5(4)
C(3)-Re(1)-N(2)	100.6(2)	S(2)-C(4)-S(1)	122.2(3)
N(1)-Re(1)-N(2)	74.78(15)	C(4)-O(4)-C(5)	118.9(5)

into a transition metal–alkoxide bond. As noted for the products of isocyanate insertion, **21** is deactivated with respect to insertion of a second molecule of TCNE.

The reaction of the molybdenum alkoxo complex **11b** with TCNE in CH_2Cl_2 afforded a solution with IR bands suggestive of an insertion similar to that described above.[33] However, the scantly informative NMR spectra and our failure to obtain X-ray quality crystals preclude further discussion.

Reactions with carbon disulfide:[34] The complex [Re(OCH_3)$(CO)_3$(bipy)] (**3a**) reacts instantaneously with carbon disulfide to afford the xanthato complex [Re{SC(S)OCH_3}$(CO)_3$(bipy)] (**22**) (Scheme 6), which was characterized by IR and NMR spectroscopy and by X-ray diffraction (see Figure 7 and Table 7).

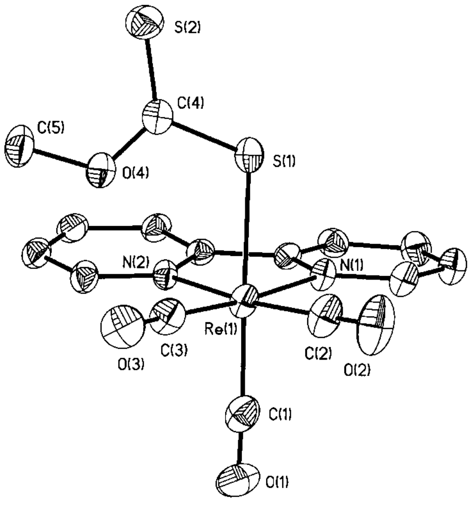


Figure 7. Molecular structure and numbering scheme of **22**.

Similar complexes were obtained by reaction of [Re(OCH_3)$(CO)_3$(L-L)] (L-L = $(PMe_3)_2$; 1,2-(dimethylarsino)-benzene) with CS_2, although **22** seems to be the only crystallographically characterized rhenium derivative with a monodentate xanthato ligand.[35] The Re–S distance (2.5059(15) Å) is slightly longer than the Re–S distances found in the bidentate xanthato ligand of [Re(η^5-C_5Me_5)Cl_3(S_2CO-cC_6H_{11})] (2.457(2) and 2.488(2) Å).[33] The S–C distances for the coordinated and uncoordinated sulfur atoms of the xanthato ligand (1.729(6) and 1.652(6) Å, respectively) are almost identical to the distances found in other neutral transition metal complexes with monodentate xanthato groups.[36]

The complex [Re(O*t*Bu)$(CO)_3$(bipy)] (**5a**) does not react with CS_2. This is not surprising given the importance of the steric bulk of the substituent at the oxygen atom (see above). However, the reaction of [Re(OTf)$(CO)_3$(bipy)] (**2a**) with a mixture of sodium *tert*-butoxide and CS_2 gives the xanthato complex [Re(SC(S)O*t*Bu)$(CO)_3$(bipy)] (**23**), which has been spectroscopically characterized. Therefore, the lack of reaction between **5a** and CS_2 can be taken as a strong indication that **5a** does not undergo significant ionization in solution otherwise dissociated *tert*-butoxide anion would, in the presence of CS_2, react to give **23** as it does when the separate components of the xanthate anion are added to **5a**. Since dissociation would be more favored for the much bulkier *tert*-butoxide group, one can assume that insertion reactions of [Re(OR)$(CO)_3$(N-N)] complexes occur by means of a non-dissociative mechanism.[37]

The reaction of [Mo(OMe)(η^3-methallyl)$(CO)_2$(phen)] (**11b**) with CS_2 afforded a new *cis*-dicarbonyl species with IR $\tilde{\nu}_{CO}$ bands at 1944 and 1858 cm^{-1}. However, further characterization was impossible due to its extreme insolubility.

To conclude, straightforward routes to [Re(OR)$(CO)_3$(N-N)] (N-N = bipy, phen) and [M(OR)(η^3-allyl)$(CO)_2$(phen)] (M = Mo, W) (previously unknown) complexes have been developed. These alkoxo derivatives, which are thermally stable towards both β-elimination of the alkoxo group and towards CO labilization, react in mild conditions with several organic unsaturated electrophiles, affording the products of single insertion of the organic molecule into the M–OR bond. The relative reactivities indicate that the alkoxo complexes act as nucleophiles towards the organic substrates. Insertion reactions are most likely initiated by the bimolecular attack of the undissociated alkoxo ligand to the organic substrate. The products of these insertions are inert towards further reactions with the organic electrophiles. Six insertion products have been fully characterized, including single-crystal X-ray structure determinations.

Experimental Section

General procedures: All reactions were carried out under dinitrogen using standard Schlenk techniques. Solvents were distilled from Na (hexanes), Na/benzophenone (tetrahydrofuran) and CaH_2 (CH_2Cl_2, CH_3OH, CH_3CH_2OH). CD_2Cl_2 and CD_3COCD_3 were dried over 4 Å molecular sieves and CD_2Cl_2 was stored in the dark over Na_2CO_3. Elemental analyses were obtained using a Perkin–Elmer 240-B microanalyzer. The IR and ^1H, ^{19}F and $^{13}C\{^1H\}$ NMR spectra were recorded on Perkin–Elmer FT 1720-X (over the range 2200–1600 cm^{-1}), and Bruker AC-200 (or AC-300 or DPX-300) spectrometers, respectively.

The complexes $[ReBr(CO)_3(N\text{-}N)]$[38] were prepared in quantitative yield by refluxing the equimolar quantities of $[ReBr(CO)_5]$[39] and the N-N ligand in toluene for 4 h.

The complexes $[MCl(\eta^3\text{-allyl})(CO)_2(phen)]$ (M = Mo, W) were synthesized according to the literature procedures.[40]

Crystal structure determination for compounds 12, 13b, 14, 17, 18 and 22: A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized $Mo_{K\alpha}$ X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[41] program. The structure was solved by direct methods with SHELXTL.[42] A semiempirical absorption correction was applied with the program SADABS.[43] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL. Crystal and refinement data are presented in Tables 8 and 9.

Crystal structure determination for compound 21: The crystal structure was solved by Patterson Methods using the program Dirdif.[44] Anisotropic least-squares refinement was carried out with SHELXL-97.[45] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and refined riding on their parent atoms. An empirical absorption correction was applied using XABS2.[46] Geometrical calculations were made with PARST.[47] The crystallographic plots were made with PLATON.[48] All calculations were carried out at the University of Oviedo using the Scientific Computer Center and X-Ray group computers. Crystal and refinement data are presented in Table 9.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 179604 (**12**), 179606 (**13b**), 179605 (**14**), 179607 (**17**), 179608 (**18**), 179609 (**21**) and 179610 (**22**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

Preparation of [Re(OTf)(CO)$_3$(bipy)] (2a):[4] AgOTf (0.257 g, 1 mmol) was added to a solution of $[ReBr(CO)_3(bipy)]$ (**1a**) (0.506 g, 1 mmol) in CH_2Cl_2 (20 mL), and the mixture stirred in the dark for 40 minutes. The solution was filtered through Celite. The solvent was evaporated under vacuum, hexane added and the complex **2a** precipitated as a pale yellow solid which was dried under vacuum to yield the title compound (0.545 g, 95%). Elemental analysis calcd (%) for $C_{14}H_8F_3N_2O_6ReS$: C 29.21, H 1.40, N 4.86; found: C 29.87, H 1.52, N 4.71; IR (CH_2Cl_2): $\nu = 2035$, 1935, 1914 cm^{-1}; ^1H NMR (CD_3COCD_3): $\delta = 9.22$, 8.79, 8.48, 7.92 (m, 2H each; bipy); ^{19}F NMR (CD_3COCD_3): $\delta = -77.6$.

Table 8. Crystal data and refinement details for complexes **12**, **13b**, **14** and **17**.

	12	**13b**	**14**	**17**
formula	$C_{36}H_{32}N_4O_6W_2$	$C_{24}H_{18}Cl_2N_3O_5Re$	$C_{26}H_{23}MoN_3O_4$	$C_{27}H_{23}MoN_3O_4S$
F_W	984.36	685.51	537.41	581.48
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a [Å]	11.0572(15)	9.0202(6)	9.0687(17)	10.2817(19)
b [Å]	11.6774(16)	16.2213(12)	10.918(2)	10.955(2)
c [Å]	14.0048(19)	17.4774(12)	23.867(4)	13.172(3)
α [°]	101.195(3)	90	90	73.908(4)
β [°]	106.646(2)	99.4060(10)	94.889(4)	89.367(4)
γ [°]	102.577(2)	90	90	66.664(4)
V [Å^3]	1626.14	2522.9(3)	2354.6(7)	1300.8(4)
Z	4	4	4	2
T [K]	293(2)	295(2)	295(2	295(2)
ρ_{calcd} [g cm^{-3}]	4.021	1.805	1.516	1.485
$F(000)$	1888	1328	1069	592
λ ($Mo_{K\alpha}$) [Å]	0.71073	0.71073	0.71073	0.71073
crystal size [mm]	0.26 × 0.12 × 0.12	0.11 × 0.13 × 0.21	0.07 × 0.11 × 0.19	0.03 × 0.15 × 0.30
μ [mm^{-1}]	14.245	5.068	0.595	0.622
scan range [°]	1.58 θ 23.31	1.72 θ 23.28	1.71 θ 23.30	1.62 θ 23.44
no refls measured	7427	11116	10176	5930
no independent refls	4622	3622	3390	3740
data/restraints/parameters	4622/0/436	3622/0/318	3390/0/309	3740/0/327
goodness-of-fit on F^2	1.043	1.006	1.000	1.059
R_1/R_{w2} [$I > 2\sigma(I)$]	0.0298	0.0268/0.0743	0.0378/0.0797	0.0546/0.1501
R_1/R_{w2} (all data)	0.0335	0.0310/0.0761	0.0614/0.0860	0.0732/0.1663

Table 9. Crystal data and refinement details for complexes **18**, **21** and **22**.

	18	**21**	**22**
formula	$C_{17}H_{16}N_3O_4ReS$	$C_{27}H_{27}N_6O_4Re$	$C_{15}H_{10}N_2O_4ReS_2$
F_W	544.59	685.75	522.49
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$Pcab$	$P2_1/c$
a [Å]	14.1351(15)	13.1706(2)	7.5200(4)
b [Å]	8.3436(9)	20.1255(3)	13.6333(7)
c [Å]	17.5543(18)	20.8107(3)	17.4955(9)
α [°]	90	90	90
β [°]	113.087(2)	90	100.9810(10)
γ [°]	90	90	90
V [Å^3]	1904.5(3)	5516.19(14)	1760.84(16)
Z	4	8	4
T [K]	295(2)	120(2)	293(2)
ρ_{calcd} [g cm^{-3}]	1.899	1.651	1.971
$F(000)$	1048	2704	972
λ($Mo_{K\alpha}$) [Å]	0.71073	0.71073	0.71073
crystal size [mm]	0.14 × 0.27 × 0.39	0.40 × 0.20 × 0.18	0.10 × 0.12 × 0.21
μ [mm^{-1}]	6.516	8.993	7.157
scan range [°]	1.57 θ 23.32	4.39 θ 69.87	1.91 θ 23.28
no refls measured	8147	47658	7840
no independent refls	2736	5184	2541
data/restraints/parameters	2736/0/238	5184/11/319	2541/0/218
goodness-of-fit on F^2	1.188	1.193	1.088
R_1/R_{w2} [$I > 2\sigma(I)$]	0.0252/0.0627	0.0494/0.1613	0.0254/0.0724
R_1/R_{w2} (all data)	0.0266/0.0633	0.0594/0.2250	0.0291/0.0746

Preparation of [Re(OTf)(CO)$_3$(phen)] (2b): The procedure was similar to that described above for **2a**, starting from [ReBr(CO)$_3$(phen)] (**1b**) (0.530 g, 1 mmol) and AgOTf (0.257 g, 1 mmol) to yield the title compund (0.515 g, 85 %). Elemental analysis calcd (%) for $C_{16}H_8F_3N_2O_6ReS$: C 32.05, H 1.34, N 4.67; found: C 32.17, H 1.42, N 4.71; IR (CH_2Cl_2): $\nu = 2035$, 1934, 1914 cm^{-1}; ^{1}H NMR (CD_3COCD_3): $\delta = 9.62$, 9.09, 8.39, 8.26 (m, 2H each; phen); ^{19}F NMR (CD_3COCD_3): $\delta = -77.8$.

Preparation of [Re(OTf)(CO)$_3$(bipy′)] (2c): Following the procedure described for **2a–b**, AgOTf (0.257 g, 1 mmol) was added to a solution of [ReBr(CO)$_3$(bipy′)] (**1c**) (0.534 g, 1 mmol) in CH_2Cl_2 (20 mL). Subsequent workup afforded complex **2c** (0.579 g, 96 %). Elemental analysis calcd (%) for $C_{16}H_{12}F_3N_2O_6ReS$: C 31.84, H 2.00, N 4.64; found: C 31.61, H 2.15, N 4.51; IR (CH_2Cl_2): $\nu = 2033$, 1933, 1913 cm^{-1}; ^{1}H NMR (CD_3COCD_3): $\delta = 9.10$ (d, $J = 5.65$ Hz, 2H; bipy′) 8.10 (s, 2H; bipy′), 7.52 (d, $J = 5.65$ Hz, 2H; bipy′), 2.71 (s, 6H; CH_3, bipy′); ^{19}F NMR (CD_3COCD_3): $\delta = -77.2$.

Preparation of [Re(OMe)(CO)$_3$(bipy)] (3a): Sodium (0.230 g, 10 mmol) was added to methanol (10 mL) at 0°C and stirred for 20 minutes to give a 1.0 M solution of NaOMe in methanol.

NaOMe (0.095 mL of the 1.0 M in methanol solution, 0.095 mmol) was added to a solution of **2a** (0.050 g, 0.087 mmol) in CH_2Cl_2 (15 mL). The color of the mixture changed from yellow to red and after 15 minutes the solvent was evaporated under vacuum. The solid residue was extracted with CH_2Cl_2 (10 mL) and the solution was filtered with a cannula tipped with filter paper. The solvent was removed to give **3a** (0.034 g, 87 %). Elemental analysis calcd (%) for $C_{14}H_{11}N_2O_4Re$: C 36.75, H 2.42, N 6.12; found: C 36.49, H 2.15, N 6.25; IR (THF): $\nu = 2001$, 1894, 1876 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.02$, 8.07, 7.57, 7.53 (m, 2H each; bipy), 3.73 (s, 3H; OMe). Complexes **3b** and **3c** were prepared similarly.

Preparation of [Re(OMe)(CO)$_3$(phen)] (3b): This was done from **2b** (0.050 g, 0.083 mmol) in CH_2Cl_2 and NaOMe (0.091 mL of a 1.0 M solution of MeOH) to yield the title compound (0.032 g, 80 %). Elemental analysis calcd (%) for $C_{16}H_{11}N_2O_4Re$: C 39.91, H 2.30, N 5.81; found: C 39.75, H 2.51, N 5.37; IR (THF): $\nu = 2001$, 1895, 1876 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.42$, 9.07, 8.27, 7.93 (m, 2H each; phen), 3.70 (s, 3H; OMe).

Preparation of [Re(OMe)(CO)$_3$(bipy′)] (3c): A 1.0 M solution of NaOMe in methanol (0.091 mL) was added to a solution of **2c** (0.050 g, 0.083 mmol) in CH_2Cl_2. The resulting red solution was stirred for 15 minutes. Subsequent workup was done as described for **3a** to yield the title compound (0.036 g, 90 %). Elemental analysis calcd (%) for $C_{16}H_{15}N_2O_4Re$: C 39.58, H 3.11, N 5.76; found: C 39.12, H 3.58, N 5.21; IR (THF): $\nu = 2000$, 1892, 1876 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.82$ (d, $J = 5.65$ Hz, 2H; bipy′), 7.99 (s, 2H; bipy′), 7.32 (d, $J = 5.65$ Hz, 2H; bipy′), 3.77 (s, 3H; OCH_3), 2.53 (s, 6H; CH_3, bipy′).

Preparation of [Re(OEt)(CO)$_3$(bipy′)] (4): Sodium (0.230 g, 10 mmol) was added to ethanol (10 mL) at 0°C and stirred for 20 minutes to afford a 1.0 M solution of NaOEt in ethanol.

NaOEt (0.248 mL of a 1.0 M solution in ethanol, 0.248 mmol) was added to a solution of [Re(OTf)(CO)$_3$(bipy′)] (0.050 g, 0.082 mmol) in CH_2Cl_2 (15 mL). The color of the mixture changed from yellow to red and after 30 minutes. The solvent was evaporated under vacuum. The workup was as described for **3a**, affording the title compound (0.037 g, 91 %). Elemental analysis calcd (%) for $C_{17}H_{17}N_2O_4Re$: C 40.87, H 3.43, N 5.60; found: C 40.76, H 3.72, N 5.29; IR (THF): $\nu = 1999$, 1889, 1872 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.79$ (d, $J = 5.69$ Hz, 2H; bipy′), 7.98 (s, 2H; bipy′), 7.29 (d, $J = 5.69$ Hz, 2H; bipy′), 3.78 (q, $J = 6.84$ Hz, 2H; OCH_2CH_3), 2.55 (s, 6H; bipy′), 0.83 (t, $J = 6.84$ Hz, 3H; OCH_2CH_3).

Preparation of [Re(O*t*Bu)(CO)$_3$(bipy)] (5a): NaO*t*Bu (0.042 g, 0.437 mmol) was added to a solution of **2a** (0.050 g, 0.087 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred in the dark for 5 h. The solution was filtered with a cannula tipped with filter paper. The solvent was removed under vacuum to give **5a** (0.034 g, 78 %). Elemental analysis calcd (%) for $C_{17}H_{17}N_2O_4Re$: C 40.87, H 3.43, N 5.66; found: C 40.61, H 3.72, N 5.85; IR (THF): $\nu = 1998$, 1888, 1870 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.64$, 8.35, 8.07, 7.37 (m, 2H each; bipy), 0.82 (s, 9H; $OC(CH_3)_3$).

Preparation of [Re(O*t*Bu)(CO)$_3$(bipy′)] (5b): Following the procedure described above, **5b** was prepared by reaction of **2c** (0.050 g, 0.083 mmol) and NaO*t*Bu (0.040 g, 0.415 mmol) in CH_2Cl_2 to yield the title compound (0.039 g, 90 %). Elemental analysis calcd (%) for $C_{19}H_{21}N_2O_4Re$: C 43.25, H 4.01, N 5.30; found: C 43.47, H 4.39, N 5.71; IR (THF): $\nu = 1998$, 1888, 1870 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.73$ (d, $J = 5.69$ Hz, 2H; bipy′), 7.95 (s, 2H; bipy′), 7.25 (d, $J = 5.69$ Hz, 2H; bipy′), 2.52 (s, 6H; CH_3, bipy′), 0.83 (s, 9H; $OC(CH_3)_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 201.60$ (2CO), 194.55 (CO), 156.05, 152.18, 151.39, 127.25, 123.80 (bipy′), 71.25 ($OC(CH_3)_3$), 34.28 ($OC(CH_3)_3$), 21.79 (CH_3, bipy′).

Reaction of 3a with methyl iodide: A 5 mm NMR tube was charged with a solution of **3a** (0.015 g, 0.032 mmol) in CD_2Cl_2 (0.5 mL) and then capped with a rubber septum. MeI (2 μL, 0.032 mmol) was injected. The reaction was monitored by ^{1}H NMR. After 7 hours at room temperature the color of the solution changed from red to yellow and the ^{1}H NMR spectrum showed the signals of Me_2O ($\delta = 3.25$; s, 6H) and of the [ReI(CO)$_3$(bipy)] (**6**) complex.

Reaction of 3a with ethyl iodide: Compound **3a** (0.015 g, 0.032 mmol) was dissolved in CD_2Cl_2 (0.5 mL) in a 5 mm NMR tube which was capped with a rubber septum. EtI (1.9 μL, 0.032 mmol) was injected and the reaction monitored by ^{1}H NMR. After 10 hours at room temperature the color of the solution changed from red to yellow and the ^{1}H NMR spectrum showed signals due to MeOEt (3.26 [s, 3H; OCH_3], 3.40 [q, $J = 7.11$ Hz, 2H; OCH_2], 1.15 [t, $J = 7.11$ Hz, 3H; CH_3CH_2O]) and the complex **6**.

Independent preparation of [ReI(CO)$_3$(bipy)] (6): [ReCl(CO)$_3$(bipy)] (0.150 g, 0.296 mmol) was dissolved in CH_2Cl_2 (15 mL) and KI (0.049 g, 0.296 mmol) was added. The solution was stirred for 2 h and filtered through Celite. The solvent was evaporated under vacuum, hexane added and **6** was obtained as a yellow solid (0.146 g, 89 %). Elemental analysis calcd (%) for $C_{13}H_8IN_2O_3Re$: C 28.21, H 1.45, N 5.06; found: C 28.75, H 1.67, N 5.29; IR (CH_2Cl_2): $\nu = 2024$, 1920, 1899 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.07$, 8.22, 8.05, 7.53 (m, 2H each; bipy).

Reaction of 3a with ethyl bromide: A 5 mm NMR tube was charged with a solution of **3a** (0.015 g, 0.032 mmol) in CD_2Cl_2 (0.5 mL), EtBr (2.4 μL, 0.032 mmol) was added with a syringe and then the tube was stoppered. The reaction was monitored by ^{1}H NMR. After 48 h the ^{1}H NMR spectrum showed the signals of MeOEt and [ReBr(CO)$_3$(bipy)] (**1a**) ($\delta = 9.02$, 8.22, 8.06, 7.54; m, 2H each; bipy).

Reaction of 3a with acetyl chloride: An NMR tube was charged with **3a** (0.015 g, 0.032 mmol) and CD_2Cl_2 (0.5 mL) and fitted with a rubber septum. CH_3COCl (2.3 μL, 0.032 mmol) was injected. When CH_3COCl reached the solution, a yellow color immediately developed. A ^{1}H NMR spectrum taken 10 minutes after the addition showed the complete conversion of **3a** to [ReCl(CO)$_3$(bipy)] (**7**)[26] and $CH_3C(O)OCH_3$ ($\delta = 3.62$ (s, 3H; OCH_3), 2.02 (s, 3H; CH_3)).

Reaction of 3a with acetic anhydride: In a 5 mm NMR tube was placed a solution of **3a** (0.015 g, 0.032 mmol) in CD_2Cl_2 (0.5 mL). The tube was capped with a rubber septum and $CH_3COOCOCH_3$ (3 μL, 0.032 mmol) was injected. The color of the solution changed from red to yellow. The ^{1}H NMR spectrum taken 10 minutes after the addition showed the conversion of **3a** into the complex [Re(OC(O)CH$_3$)(CO)$_3$(bipy)] (**8**) and CH_3COOCH_3.

Independent preparation of [Re(OC(O)CH$_3$)(CO)$_3$(bipy)] (8): Potassium acetate (0.018 g, 0.183 mmol) was added to a solution of [Re(OTf)(CO)$_3$(bipy)] (**2a**)(0.100 g, 0.173 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 2 h. The solution was filtered with a cannula tipped with filter paper and the solvent evaporated under vacuum to give **8** (0.067 g, 78 %). Elemental analysis calcd (%) for $C_{15}H_{11}N_2O_5Re$: C 37.11, H 2.28, N 5.77; found: C 37.60, H 2.13, N 5.51; IR (CH_2Cl_2): $\nu = 2018$, 1916, 1889; 1631 cm^{-1} (C=O ester); ^{1}H NMR (CD_2Cl_2): $\delta = 9.12$, 8.19, 8.11, 7.55 (m, 2H each; bipy), 1.51 (s, 3H; CH_3CO).

Preparation of [Mo(OMe)(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (11a): NaOMe (0.25 mL of a 1 M solution in MeOH, 0.25 mmol) was added to a solution of [MoCl(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (0.100 g, 0.24 mmol) in CH_2Cl_2 (20 mL). After stirring for 30 min the solvent was evaporated under vacuum. The residue was extracted with CH_2Cl_2 and filtered through Celite. The solvent was evaporated under reduced pressure, hexane was added and the complex **11a** was obtained as a dark red microcrystalline solid (0.082 g, 83 %). Elemental analysis calcd (%) for $C_{18}H_{16}MoN_2O_3$: C 53.48, H 3.99, N 6.93; found: C 53.71, H 3.81, N 7.06; IR (CH_2Cl_2): $\nu = 1927$, 1837 cm^{-1} ($\tilde{\nu}_{CO}$); ^{1}H NMR (CD_2Cl_2): $\delta = 9.12$ (dd, $J_{H2,3} = J_{H9,8} = 5.0$ Hz, $J_{H2,4} = J_{H7,9} = 1.5$ Hz, 2H; $H_{2,9}$), 8.45 (dd, $J_{H4,3} = J_{H7,8} = 8.2$ Hz, 2H; $H_{4,7}$), 7.92 (s, 2H; $H_{5,6}$), 7.79 (dd, 2H; $H_{3,8}$), 4.45 (s, 3H; OMe), 3.15 (d, $J_{Hs,c} = 6.7$ Hz, 2H; H_{syn}), 3.03 (m, 1H; CH of η^3-C$_3$H$_5$), 1.17 (d, $J_{Ha,Hc} = 9.1$ Hz, 2H; H_{anti}).

Preparation of [Mo(OMe)(η^3-C$_3$H$_4$(CH$_3$))(CO)$_2$(phen)] (11b): Following the procedure described above, **11b** was prepared by the reaction of **9b**

(0.10 g, 0.24 mmol) and NaOMe (0.24 mL of a 1 M solution in MeOH, 0.20 mmol) in CH_2Cl_2 to yield the title compound (0.089 g, 90%). Elemental analysis calcd (%) for $C_{19}H_{18}MoN_2O_3$: C 54.56, H 4.34, N 6.70; found: C 54.27, H 4.39, N 6.61; IR (CH_2Cl_2): $\nu = 1931, 1843$ cm^{-1} ($\tilde{\nu}_{CO}$); ^{1}H NMR (CD_2Cl_2): $\delta = 9.09$ (dd, $J_{H2,3} = J_{H9,8} = 5.0$ Hz, $J_{H2,4} = J_{H7,9} = 1.5$ Hz, 2H; $H_{2,9}$), 8.42 (dd, $J_{H4,3} = J_{H7,8} = 8.2$ Hz, 2H; $H_{4,7}$), 7.89 (s, 2H; $H_{5,6}$), 7.77 (dd, 2H; $H_{3,8}$), 4.34 (s, 3H; OMe), 2.95 (s, 2H; H_{syn}), 1.20 (s, 2H; H_{anti}), 0.72 (s, 3H; $C_3H_4(CH_3)$).

Preparation of [W(OMe)(η^3-C_3H_5)(CO)$_2$(phen)] (12): A procedure similar to that described for **11a**, using [WCl(η^3-C_3H_5)(CO)$_2$(phen)] (0.100 g, 0.20 mmol) and NaOMe (0.20 mL of a 1 M solution in MeOH, 0.20 mmol) gave complex **12** as a dark red solid (0.078 g, 79%). Elemental analysis calcd (%) for $C_{18}H_{16}N_2O_3W$: C 43.93, H 3.28, N 5.69; found: C 44.12, H 3.53, N 5.56; IR (CH_2Cl_2): $\nu = 1916, 1822$ cm^{-1} ($\tilde{\nu}_{CO}$); ^{1}H NMR (CD_2Cl_2): $\delta =$ 9.19 (dd, $J_{H2,3} = J_{H9,8} = 5.0$ Hz, $J_{H2,4} = J_{H7,9} = 1.5$ Hz, 2H; $H_{2,9}$), 8.49 (dd, $J_{H4,3} = J_{H7,8} = 8.3$ Hz, 2H; $H_{4,7}$), 7.94 (s, 2H; $H_{5,6}$), 7.81 (dd, 2H; $H_{3,8}$), 4.52 (s, 3H; OMe), 2.99 (d, $J_{Hs,c} = 6.2$ Hz, 2H; H_{syn}), 2.13 (m, 1H; CH of η^3-C_3H_5), 1.38 (d, $J_{Ha,c} = 8.9$ Hz, 2H; H_{anti}); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 224.59$ (CO), 153.05, 152.28, 138.70, 138.39, 128.44, 128.26 (phen), 67.34 (C^2 of η^3-C_3H_5), 53.35 (C^1, C^3 of η^3-C_3H_5), 46.44 (OCH_3).

Reaction of 3a with PhNCO: PhNCO (12 µL, 0.109 mmol) was added to a solution of **3a** (0.050 g, 0.109 mmol) in THF (15 mL). The color of the solution changed from red to orange immediately. The solvent was removed under vacuum to give the complex **13a** (0.051 g, 81%). Elemental analysis calcd (%) for $C_{21}H_{16}N_3O_5Re$: C 43.74, H 2.79, N 7.28; found: C 43.19, H 2.45, N 7.59; IR (THF): $\nu = 2018, 1914, 1899$ cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.67, 8.09, 7.95, 7.25$ (m, 2H each; bipy), 6.82 (m, 2H; Ph), 6.72 (m, 2H; Ph), 6.28 (m, 1H; Ph), 3.32 (s, 3H; OCH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 198.95$ (2CO), 193.41 (CO), 162.31 (O=C), 155.81, 154.17 (bipy), 151.75 (N$-C_{ipso}$), 139.18, 128.20 (bipy), 127.76, 126.63 (Ph), 122.99 (bipy), 122.83 (Ph), 51.55 (OCH_3).

Reaction of 3b with PhNCO: The procedure is as described for the reaction of **3a** and PhNCO, using [Re(OMe)(CO)$_3$(phen)] (**3b**) (0.050 g, 0.103 mmol) and PhNCO (11 µL, 0.103 mmol). Slow diffusion of hexanes into a CH_2Cl_2 solution of **13b** at −20°C afforded orange crystals (0.046 g, 74%), one of which was suitable for an X-ray experiment. Elemental analysis calcd (%) for $C_{23}H_{22}N_3O_5Re$: C 45.96, H 2.68, N 6.99; found: C 45.41, H 2.59, N 6.75; IR (THF): $\nu = 2018, 1914, 1899$ cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.37, 9.01, 8.35, 7.95$ (m, 2H each; phen), 6.78 (m, 2H; Ph), 6.69 (m, 2H; Ph), 6.29 (m, 1H; Ph), 3.32 (s, 3H; OCH_3).

Reaction of 11a with (*p*-tolyl)NCO: RNCO (R = *p*-tolyl) (22 µL, 0.17 mmol) was added to a solution of **11a** (0.060 g, 0.14 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 2 h and the solvent evaporated under vacuum. Slow difusion of hexanes into a CH_2Cl_2 solution of **14** at −20°C afforded red crystals (0.062 g, 82%). Elemental analysis calcd (%) for $C_{26}H_{23}MoN_3O_4$: C 58.11, H 4.31, N 7.82; found: C 57.91, H 4.42, N 7.87; IR (CH_2Cl_2): $\nu = 1945, 1862$; ^{1}H NMR (CD_2Cl_2): $\delta = 9.03$ (dd, $J_{H2,3} = J_{H9,8} =$ 5.0 Hz, $J_{H2,4} = J_{H7,9} = 1.3$ Hz, 2H; $H_{2,9}$), 8.29 (dd, $J_{H4,3} = J_{H7,8} = 8.2$ Hz, 2H; $H_{4,7}$), 7.70 (s, 2H; $H_{5,6}$), 7.68 (dd, 2H; $H_{3,8}$), 5.69, 5.11 (qAB, $J_{HA,B} = 8.0$ Hz, 4H; C_6H_4), 3.54 (s, 3H; OMe), 3.05 (d, $J_{Hs,c} = 6.2$ Hz, 2H; H_{syn}), 2.27 (m, 1H; CH of η^3-C_3H_5), 1.19 (s, 3H; C_6H_4-CH_3), 1.36 (d, $J_{Ha,c} = 9.2$ Hz, 2H; H_{anti}).

Reaction of 3a with EtNCO: EtNCO (8.7 µL, 0.109 mmol) was added to a solution of **3a** (0,050 g, 0.109 mmol) in THF (15 mL). The color of the solution changed from red to dark orange. Subsequent workup afforded the complex **15** (0.046 g, 80%). Elemental analysis calcd (%) for $C_{17}H_{16}N_3O_5Re$: C 38.63, H 3.05, N 7.95; found: C 38.42, H 3.16, N 7.85; IR (THF): $\nu = 2012, 1909, 1887$ cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.09$, 8.17, 8.08, 7.53 (m, 2H each; bipy), 3.21 (s, 3H; OMe), 2.75 (q, $J = 6.99$ Hz, 2H; NCH_2CH_3), 0.44 (t, $J = 6.99$ Hz, 3H; NCH_2CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 198.98$ (2CO), 193.63 (CO), 163.62 (O=C), 156.28, 154.19, 139.38, 126.47, 123.14 (bipy), 50.33 (OCH_3), 46.73 (NCH_2CH_3), 15.48 (NCH_2CH_3).

Reaction of 3a with *i*PrNCO: *i*PrNCO (0.011 µL, 0.109 mmol) was added to a solution of **3a** (0.050 g, 0.109 mmol) in THF (15 mL). The solution was stirred at room temperature for 1 h, resulting in complete conversion of **3a** into **16** (0.049 g, 83%). Elemental analysis calcd (%) for $C_{18}H_{18}N_3O_5Re$: C 39.84, H 3.34, N 7.74; found: C 39.61, H 3.21, N 7.65; IR (THF): $\nu = 2012$, 1909, 1887 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.01, 8.21, 8.11, 7.53$ (m, 2H each; bipy), 3.13 (s, 3H; OMe), 2.97 (m, $J = 6.45$ Hz, 1H; $NCH(CH_3)_2$), 0.77 (d, $J = 6.45$ Hz, 6H; $NCH(CH_3)_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 198.98$ (2CO), 193.76 (CO), 161.69 (O=C), 156.30, 154.34, 139.35, 126.36, 122.96 (bipy), 55.35 (OCH_3), 49.80 ($NCH(CH_3)_2$), 20.19 ($NCH(CH_3)_2$).

Competition experiment between PhNCO and EtNCO: A 5 mm NMR tube was charged with a solution **3a** (0.015 g, 0.032 mmol) in CD_2Cl_2 (0.3 mL) and fitted with a rubber septum. A solution of EtNCO (2.5 µL, 0.032 mmol) and PhNCO (3.5 µL, 0.032 mmol) in CD_2Cl_2 (0.3 mL) was injected. A ^{1}H NMR spectrum taken 10 minutes after the addition showed the complete conversion of **3a** into **13a** and EtNCO.

Reaction of 5b with PhNCO: PhNCO (10 µL, 0.095 mmol) was added to a solution of [Re(O*t*Bu)(CO)$_3$(bipy′)] (**5b**) (0.050 g, 0.095 mmol) in THF (15 mL) and the mixture was stirred for 30 minutes. The solvent was removed under vacuum to give **16** (0.046 g, 75%). Elemental analysis calcd (%) for $C_{26}H_{26}N_3O_5Re$: C 48.28, H 4.05, N 6.49; found: C 48.59, H 4.19, N 6.75; IR (THF): $\nu = 2013, 1910, 1885$ cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.51$ (d, $J = 5.69$ Hz, 2H, bipy′), 7.85 (s, 2H; bipy′), 7.02 (d, $J = 5.69$ Hz, 2H; bipy′), 6.74 (m, 2H; Ph), 6.66 (m, 2H; Ph), 6.26 (m, 1H; Ph), 2.48 (s, 6H; CH_3 bipy′), 1.22 (s, 9H; $OC(CH_3)_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 199.38$ (2CO), 194.06 (CO), 160.14 (O=C), 155.50, 153.74, 151.38 (bipy′), 152.31 (N$-C_{ipso}$), 128.12,(Ph), 127.66 (bipy′), 126.66 (Ph), 123.88 (bipy′), 122.05 (Ph), 58.15 ($OC(CH_3)_3$), 28.76 ($OC(CH_3)_3$), 21.65 (CH_3, bipy′).

Reaction of 11b with PhNCS: PhNCS (18 µL, 0.15 mmol) was added to a solution of **11b** (0.055 g, 0.13 mmol) in CH_2Cl_2 (25 mL). The solution was stirred for 2 h and then the solvent was evaporated under reduced pressure. Slow diffusion of hexanes into a CH_2Cl_2 solution of **17** at room temperature afforded red crystals (0.062 g, 85%), one of which was suitable for an X-ray experiment. Elemental analysis calcd (%) for $C_{26}H_{23}MoN_3O_3S$: C 56.42, H 4.18, N 7.59; found: C 56.34, H 4.27, N 7.51; IR (CH_2Cl_2): $\nu = 1941$, 1858 cm^{-1} ($\tilde{\nu}_{CO}$); ^{1}H NMR (CD_2Cl_2): $\delta = 8.96$ (dd, $J_{H2,3} = J_{H9,8} = 5.1$ Hz, $J_{H2,4} = J_{H7,9} = 1.3$ Hz, 2H; $H_{2,9}$), 8.36 (dd, $J_{H4,3} = J_{H7,8} = 8.1$ Hz, 2H; $H_{4,7}$), 7.83 (s, 2H; $H_{5,6}$), 7.73 (dd, 2H; $H_{3,8}$), 6.95 (m, 2H; Ph), 6.68 (m, 3H; Ph), 3.88 (s, 3H; OCH_3), 2.87 (s, 2H; H_{syn}), 1.54 (s, 2H; H_{anti}), 0.50 (s, 3H; $C_3H_4(CH_3)$).

Reaction of 3a with PhNCS: [Re(OMe)(CO)$_3$(bipy)] (**3a**) (0.050 g, 0.109 mmol) was dissolved in THF (15 mL) and PhNCS (13 µL, 0.109 mmol) was added. After 15 minutes of stirring, the color of the solution changed from red to orange. The solvent was removed to afford **18** (0.052 g, 81%). Elemental analysis calcd (%) for $C_{21}H_{16}N_3O_4ReS$: C 42.56, H 2.72, N 7.09; found: C 42.17, H 2.69, N 7.25; IR (THF): $\nu = 2015, 1913$, 1889 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.00, 8.16, 8.05, 7.50$ (m, 2H each; bipy), 7.10, 6.84, 6.57 (m, 5H; Ph), 3.68 (s, 3H; OCH_3).

Reaction of 3a with EtNCS: The procedure was similar to that described for **18**, using **3a** (0.050 g, 0.109 mmol) and EtNCS (9.5 µL, 0.109 mmol) in THF (15 mL). Slow diffusion of hexanes into a solution of **19** in THF afforded orange crystals (0.047 g, 79%), one of which was used for an X-ray experiment. Elemental analysis calcd (%) for $C_{17}H_{16}N_3O_4ReS$: C 37.49, H 2.96, N 7.71; found: C 37.17, H 2.75, N 7.25; IR (THF): $\nu = 2016, 1917$, 1896 cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.00, 8.21, 8.05, 7.51$ (m, 2H each; bipy), 3.42 (s, 3H; OCH_3), 2.98 (q, $J = 7.29$ Hz, 2H; NCH_2CH_3), 0.88 (t, $J =$ 7.29 Hz, 3H; NCH_2CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 198.54$ (2CO), 190.85 (CO), 164.72 (N=C), 155.88, 153.72, 139.09, 127.00, 123.48 (bipy), 53.35 (OCH_3), 46.39 (NCH_2CH_3), 16.30 (NCH_2CH_3).

Reaction of 3a with *t*BuNCS: Following the procedure described above for **18**–**19**, **3a** (0.050 g, 0.109 mmol) and *t*BuNCS (13.8 µL, 0.109 mmol) were allowed to react in THF (15 mL). The solution was stirred 24 h and the solvent removed under vacuum to give **20** (0.048 g, 77%). Elemental analysis calcd (%) for $C_{19}H_{20}N_3O_4ReS$: C 39.85, H 3.52, N 7.33; found: C 39.17, H 3.41, N 7.16; IR (THF): $\nu = 2015, 1916, 1895$ cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.98, 8.19, 8.02, 7.48$ (m, 2H each; bipy), 3.32 (s, 3H; OCH_3), 1.04 (s, 9H; $NC(CH_3)_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 198.81$ (2CO), 191.16 (CO), 159.39 (N=C), 156.00, 153.75, 138.93, 126.80, 123.75 (bipy), 52.89 (OCH_3), 52.17 ($NC(CH_3)_3$), 29.63 ($NC(CH_3)_3$).

Competition experiment between PhNCO and PhNCS: A 5 mm NMR tube was charged with a solution **3a** (0.015 g, 0.032 mmol) in CD_2Cl_2 (0.3 mL) and capped with a rubber septum. A solution of PhNCS (3.8 µL, 0.032 mmol) and PhNCO (3.5 µL, 0.032 mmol) in CD_2Cl_2 (0.3 mL) was added using a syringe. A ^{1}H NMR spectrum taken 10 minutes after the addition showed the complete conversion of **3a** into complex **13a** along with unreacted PhNCS.

Competition experiment between EtNCO and EtNCS: Following the procedure described above, the complex **3a** (0.015 g, 0.032 mmol) was dissolved in CD_2Cl_2 (0.3 mL). A mixture of EtNCO (2.5 µL, 0.032 mmol) and EtNCS (2.8 µL, 0.032 mmol) in CD_2Cl_2 (0.3 mL) was injected. A ^1H NMR spectrum taken 10 minutes after the addition showed the complete conversion of **3a** into **15** and unreacted EtNCS.

Reaction of 3c with tetracyanoethylene: Tetracyanoethylene (0.026 g, 0.205 mmol) was added to a solution of $[Re(OMe)(CO)_3(bipy')]$ (**3c**) (0.100 g, 0.205 mmol) in THF (15 mL). The color of the solution changed immediately from red to pale yellow. Slow diffusion of hexanes into a THF solution of **21** at −20°C afforded yellow crystals (0.107 g, 85%). One of these crystals was used for an X-ray experiment. Elemental analysis calcd (%) for $C_{22}H_{15}N_6O_4Re$: C 43.06, H 2.46, N 13.69; found: C 43.55, H 2.17, N 13.51; IR (THF): $\nu = 2219$ (CN), 2029, 1927, 1920 cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 8.83$ (d, $J = 5.70$ Hz, 2H; bipy'), 8.11 (s, 2H; bipy'), 7.42 (d, $J = 5.70$ Hz, 2H; bipy'), 3.75 (s, 3H; OCH_3), 2.59 (s, 6H; bipy').

Reaction of 3a with CS_2: CS_2 (0.041 mL, 0.545 mmol) was added to a solution of $[Re(OCH_3)(CO)_3(bipy)]$ (**3a**) (0.050 g, 0.109 mmol) in THF (10 mL). A change of color was seen immediately in the solution, from red to orange. The solvent and the excess of CS_2 were removed under vacuum to afford **22**. Orange crystals of **22** (0.052 g, 90%) were obtained from slow diffusion of hexanes into a THF solution at room temperature. A single crystal obtained in this way was used for an X-ray experiment. Elemental analysis calcd (%) for $C_{15}H_{11}N_2O_4ReS_2$: C 33.76, H 2.07, N 5.24; found: C 33.51, H 2.29, N 5.31; IR (THF): $\nu = 2018$, 1920, 1904 cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 9.00$, 8.22, 8.06, 7.51 (m, 2H each; bipy), 3.95 (s, 3H; OCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 224.72$ (C=S), 197.84 (2CO), 191.23 (CO), 155.84, 153.86, 139.41, 127.35, 123.79 (bipy), 59.76 (OCH_3).

Preparation of $[Re(SC(S)O\textit{t}Bu)(CO)_3(bipy)]$ (20): A solution prepared by reaction of NaO*t*Bu (0.017 g, 0.180 mmol) and CS_2 (0.042 mL, 0.900 mmol) in THF (10 mL) was added using a cannula over solution of **2a** (0.100 g, 0.173 mmol) in THF (10 mL). The mixture was stirred for 2 h, the solvent was removed under reduced pressure. The solid residue was extracted with CH_2Cl_2 (10 mL) and the solution filtered through Celite. The solvent was evaporated under vacuum to afford **20** (0.089 g,89%). Elemental analysis calcd (%) for $C_{18}H_{17}N_2O_4ReS_2$: C 37.55, H 2.97, N 4.86; found: C 37.40, H 2.79, N 4.67; IR (THF): $\nu = 2015$, 1916, 1901 cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta =$ 9.03, 8.21, 8.07, 7.54 (m, 2H each; bipy), 1.74 (s, 9H; $OC(CH_3)_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 221.54$ (C=S), 198.15 (2CO), 192.21 (CO), 155.46, 153.88, 139.29, 127.66, 123.65 (bipy), 89.49 ($OC(CH_3)_3$), 28.11 ($OC(CH_3)_3$).

Acknowledgement

We thank Ministerio de Ciencia y Tecnología and Ministerio de Educación, Cultura y Deporte for support of this work (Projects MCT-00-BQU-0220, PB97-0470-C02-01 and PR-01-GE-7) and predoctoral fellowships (to E.H. and L.R.)

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Received: February 28, 2002 [F3911]