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Reactivity of the Amido Complex [Re(NH*p*Tol)(CO)$_3$(bipy)] toward Neutral Organic Electrophiles

Eva Hevia, Julio Pérez,* and Víctor Riera

Departamento de Química Orgánica e Inorgánica /IUQOEM, Facultad de Química, Universidad de Oviedo-CSIC, 33071 Oviedo, Spain

Daniel Miguel

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

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The amido complex [Re(NH*p*Tol)(CO)$_3$(bipy)] (**1**) reacts with *p*TolNCS and with Ph$_2$CCO giving the products of the insertion of these heterocumulenes into the Re−N and N−H bonds, the complexes [Re{SC(N*p*Tol)(NH*p*Tol)}(CO)$_3$(bipy)] (**2**) and [Re{N(*p*Tol)C(O)CHPh$_2$}(CO)$_3$(bipy)] (**3**), respectively. The reaction of **1** with activated acetylenes containing at least one alkoxycarbonyl group afforded the compounds [Re{N(*p*Tol)C(R′)C(R)C(OH)}(CO)$_3$(bipy)] (**4a**−**c**). The formation of the metallacycle present in these compounds involves the activation of one of the carbonyl ligands of **1**. The structures of the complexes **2**, **3**, and **4b** have been determined by single-crystal X-ray diffraction. ^{13}C NMR and crystallographic data indicate that the metal-bonded carbon atom of the metallacycle possesses carbene character.

Introduction

Low-valent transition metal amido complexes display a high nucleophilicity at nitrogen as a result of destabilizing interactions between the amido lone electron pair and filled metal d orbitals.[1] As a consequence, these complexes react with different organic electrophiles, including unsaturated molecules such as CO$_2$, CS$_2$, and isocyanates, with formation of C−N bonds. Most of these studies have been conducted with transition metals of groups 8−10.[2] Bergman reported the synthesis of [Re(NHPh)(CO)$_3$(PR$_3$)$_2$] amido complexes and their reactivity toward CO$_2$.[3] We have recently reported the synthesis of [Re(N(R)Ar)(CO)$_3$(bipy)] (R = H, Me, aryl; bipy = 2,2′-bipyridine) amido complexes[4] and their reactivity with isocyanates.[5]

We wondered if our rhenium amido complexes can be used to form C−N bonds with the organic substrates that were found to react with the previously known amido complexes of the group 8−10 metals. Our findings are the matter of this paper.

Results and Discussion

We have previously found (a) that the amido complex [Re(NH*p*Tol)(CO)$_3$(bipy)] (*p*Tol = *para*-tolyl) (**1**) reacts with isocyanates[5] and (b) that isothiocyanates are less reactive substrates than isocyanates toward the rhenium methoxo complex [Re(OMe)(CO)$_3$(bipy)].[6] Therefore, we wanted to know whether the amido complex **1** would react with isothiocyanates. While the reactivity of isocyanates with transition metal organometallic complexes has been the subject of a number of studies,[7] the related isothiocyanate chemistry has been much less explored.[8]

The reaction of equimolar amounts of **1** and *p*TolNCS (see Scheme 1) in THF takes place instantaneously and is accompanied by a change in the color of the solution from emerald green to orange. The resulting solution displayed three ν(CO) bands (the one at higher frequency being much more acute than the other two) in the IR spectrum, indicative of the retention of a *fac*-tricarbonyl moiety. Their frequencies were some 15 cm^{-1} higher than those of the precursor amido complex, as expected for the addition of an electrophile. The ^{1}H NMR

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* Correspondence author. E-mail: japm@sauron.quimica.uniovi.es.

[1] (a) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125. (b) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25. (c) Jayaprakash, K. N.; Conner, D.; Gunnoe, T. B. *Organometallics* **2001**, *20*, 5254. (d) Conner, D.; Jayaprakash, K. N.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2002**, *41*, 3042. (e) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44.

[2] (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6499. (c) Glueck, D. J.; Newman Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. (d) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2963. (e) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1994**, *13*, 569. (f) Boncella, J. M.; Villanueva, L. A. *J. Organomet. Chem.* **1994**, *465*, 297. (g) Vanderlende, D. D.; Abboud, K. A. Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319. (h) Boncella, J. M.; Eve, T. M.; Rickman, B.; Abboud, K. A. *Polyhedron* **1998**, *5*, 725.

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[4] Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1966.

[5] Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. *Chem. Commun.* **2002**, 1814.

[6] Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D.; del Río, I.; García-Granda, S. *Chem., Eur. J.* **2002**, *8*, 4510.

[7] For a review of transition metal mediated reactions of isocyanates, see: Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927. See also refs 2b, c, e, f, and g.

[8] The reactivity of lanthanocene diphenylamido complexes toward PhNCS has been recently reported: Li, H.; Yao, Y.; Shen, Q.; Weng, L. *Organometallics* **2002**, *21*, 2529.

10.1021/om020667p CCC: $25.00

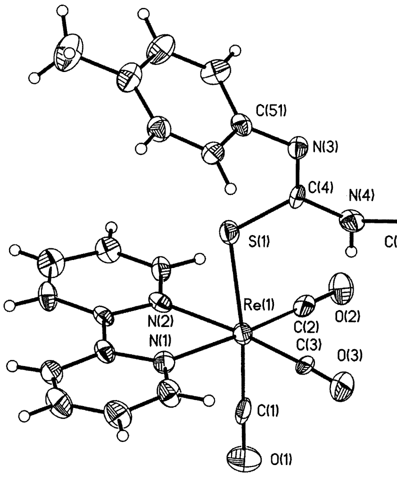
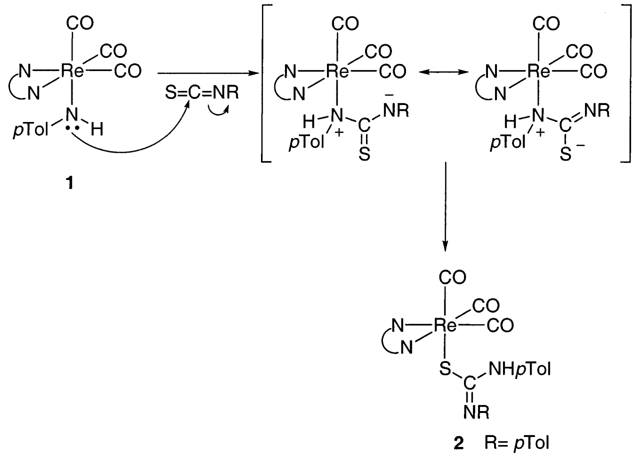


Figure 1. Plot of [Re{SC(N*p*Tol)(NH*p*Tol)}(CO)$_3$(bipy)] (**2**) showing the atom-numbering scheme (30% probability ellipsoids).

Scheme 1



spectrum of the crude product showed the presence of a single species **2** with four bipy signals, indicating the presence of a mirror plane. This was confirmed by the five bipy signals in the ^{13}C NMR spectrum. Both spectra contained only one set of *para*-tolyl signals, although their integration against the signals of the bipy ligand in the ^{1}H NMR spectrum indicated the existence of two *para*-tolyl groups, as expected for the addition of a *p*TolNCS molecule to the *p*-tolylamido complex. Thus, the two *para*-tolyl groups are equivalent. A broad signal at 2.16 ppm in ^{1}H NMR is assigned to the nitrogen-bonded hydrogen atom. The limited solubility of **2** precluded the observation of more signals than those of bipy and *p*-tolyl groups in the ^{13}C NMR.

Complex **2** was isolated as an analytically and spectroscopically pure solid by crystallization of the crude product in 81% yield (see Experimental Section).

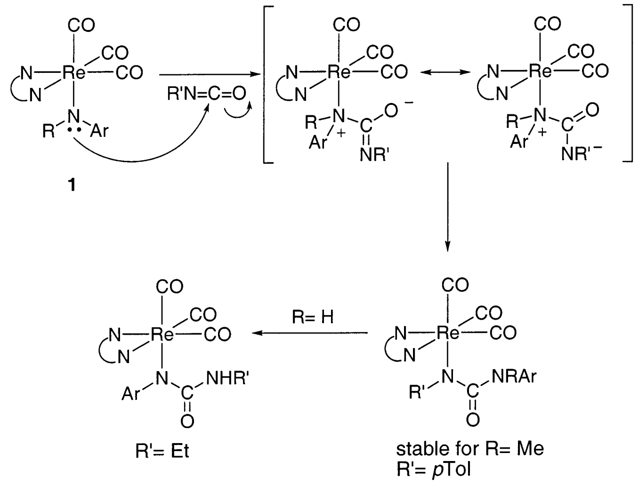
The structure of **2** was determined by means of X-ray diffraction on a single crystal of **2**·CH$_2$Cl$_2$ obtained by slow diffusion of diethyl ether into a CH$_2$Cl$_2$ solution of the complex. A representation of the molecular structure of **2** is shown in Figure 1, and selected distances and angles are given in Table 1.

The molecule of **2** consists of a {Re(CO)$_3$(bipy)} fragment bonded to the sulfur atom of a SC(N*p*Tol)(N(H)*p*Tol) thioureato ligand resulting from the formal insertion of the C−S bond of *p*-tolylisothiocyanate into the Re−N bond of the amido complex **1**. The Re−S distance, 2.498(2) Å, is close to those found for the complexes [Re{SC(=NEt)OMe}(CO)$_3$(bipy)] (2.5131(14) Å) and [Re{SC(=S)OMe}(CO)$_3$(bipy)] (2.5059(15) Å), obtained by the reactions of [Re(OMe)(CO)$_3$(bipy)] with EtNCS and with CS$_2$ respectively.[6] The S−C distance in **2**, 1.755(8) Å, also close to those found in the above complexes (1.729(6) and 1.755(5) Å respectively), is within the range of single C−S bonds.[9] The distances C(4)−N(3) (1.302(9) Å) and C(4)−N(4) (1.359(10) Å) are intermediate between single and double bonds, indicating some degree of delocalization. In view of the structure, the equivalence of the two *para*-tolyl groups in the NMR spectrum can be ascribed to the fast exchange of the hydrogen atom between the two nitrogens.

Table 1. Selected Bond Distances and Angles for Complex 2

Bond Distances (Å)			
Re(1)−C(1)	1.872(11)	Re(1)−S(1)	2.498(2)
Re(1)−C(2)	1.888(11)	S(1)−C(4)	1.755(8)
Re(1)−C(3)	1.898(9)	C(4)−N(3)	1.302(9)
Re(1)−N(1)	2.180(6)	C(4)−N(4)	1.359(10)
Re(1)−N(2)	2.156(7)		
Bond Angles (deg)			
C(1)−Re(1)−C(2)	87.4(3)	C(1)−Re(1)−N(2)	92.6(3)
C(3)−Re(1)−C(2)	89.8(4)	C(2)−Re(1)−S(1)	96.8(2)
C(1)−Re(1)−C(3)	88.6(4)	C(1)−Re(1)−S(1)	173.7(3)
C(2)−Re(1)−N(1)	173.8(3)	C(3)−Re(1)−S(1)	96.0(3)
C(1)−Re(1)−N(1)	92.2(3)	N(1)−Re(1)−S(1)	83.11(17)
C(3)−Re(1)−N(1)	96.3(3)	N(2)−Re(1)−S(1)	82.94(14)
C(2)−Re(1)−N(2)	99.6(3)	C(4)−S(1)−Re(1)	116.1(3)
C(3)−Re(1)−N(2)	170.5(3)	C(4)−N(4)−C(41)	133.1(8)
N(1)−Re(1)−N(2)	74.2(3)	C(4)−N(3)−C(51)	119.2(7)

Scheme 2



We have previously studied the reactivity of the amido complex **1** with isocyanates.[5] Our observations, as well as those of previous workers,[2f,g] can be accounted for assuming initial nucleophilic attack by the undissociated amido ligand to the central carbon of the isocyanate and rearrangement of the resulting zwitterionic species through a displacement of the amino end of the resulting ligand by the better donor amido end (see Scheme 2). Then, for R = H, H and {Re(CO)$_3$(bipy)} would exchange sites due to the different acidity of the two nitrogens. For isothiocyanate insertion, the putative zwitterionic

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[9] Carmona, E.; Contreras, L.; Sánchez, L. J.; Gutiérrez-Puebla, E.; Monge, A. *J. Chem. Soc., Dalton Trans.* **1989**, 2003.

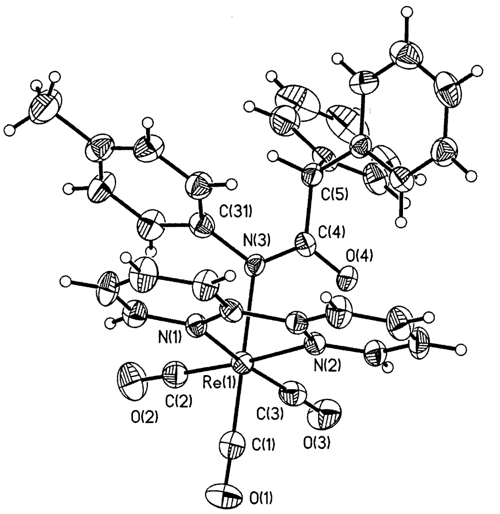
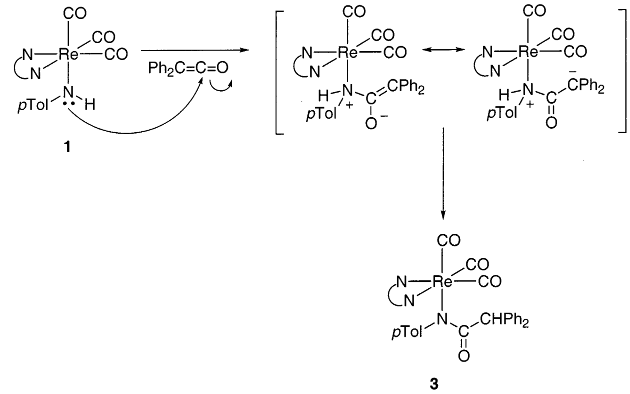


Figure 2. Plot of [Re{N(*p*Tol)C(O)CHPh$_2$}(CO)$_3$(bipy)] (**3**) showing the atom-numbering scheme (30% probability ellipsoids).

Scheme 3



intermediate would rearrange to the observed S-bound product. The softer nature of sulfur should be an important factor of this difference. A similar structural difference (Re−N versus Re−S) was found for the reactivity of [Re(OMe)(CO)$_3$(bipy)] with isocyanates and isothiocyanates.[6] A final step of exchange between H and the metal fragment, like the one in the proposed mechanism of RNCO insertion,[5] does not occur with isothiocyanate due to the higher acidity of S−H compared with N−H.

The amido complex **1** reacted instantaneously with diphenylketene, as indicated by a change in the color of the THF solution from green to orange and a shift to higher wavenumbers in the IR ν(CO) bands (See Scheme 3). The single product **3** was isolated in a 87% yield and was characterized by spectroscopy and single-crystal X-ray diffraction. The IR ν(CO) bands and the ^{1}H NMR bipy signals are consistent with the presence in solution of an octahedral molecule with a facial disposition of the three carbonyl ligands and a mirror plane, as was found for **2** (see above). In addition, for **3**, further support for this type of structure is lent by the observation of two signals with an approximate 1:2 intensity ratio in the carbonyl region of the ^{13}C NMR spectrum. The results of the structural determination (Figure 2 and Table 2) showed that the molecule of **3** consists of a {Re(CO)$_3$(bipy)} fragment bonded to the nitrogen atom of a (N-*p*Tolyl)diphenylacetamidato group. The central C−H unit of the diphenylmethyl group appears as signals at 54.99 and 4.58 ppm in the ^{13}C and ^{1}H NMR spectra, respectively, and the carbonyl group within the amidato ligand resonates at 174.29 in ^{13}C NMR.

Table 2. Selected Bond Distances and Angles for Complex 3

Bond Distances (Å)			
Re(1)−C(1)	1.889(10)	Re(1)−N(3)	2.184(6)
Re(1)−C(2)	1.880(10)	N(3)−C(4)	1.333(8)
Re(1)−C(3)	1.907(10)	N(3)−C(31)	1.432(9)
Re(1)−N(1)	2.172(6)	C(4)−O(4)	1.228(8)
Re(1)−N(2)	2.192(6)		
Bond Angles (deg)			
C(2)−Re(1)−C(1)	88.4(4)	C(1)−Re(1)−N(2)	93.2(3)
C(2)−Re(1)−C(3)	87.0(3)	C(2)−Re(1)−N(3)	94.3(3)
C(1)−Re(1)−C(3)	88.8(3)	C(1)−Re(1)−N(3)	175.7(3)
C(2)−Re(1)−N(1)	100.3(3)	C(3)−Re(1)−N(3)	94.7(3)
C(1)−Re(1)−N(1)	92.2(3)	N(1)−Re(1)−N(3)	84.0(2)
C(3)−Re(1)−N(1)	172.6(3)	N(3)−Re(1)−N(2)	83.7(2)
C(2)−Re(1)−N(2)	174.1(3)	C(4)−N(3)−Re(1)	122.6(5)
C(3)−Re(1)−N(2)	98.7(3)	C(4)−N(3)−C(31)	120.6(6)
N(1)−Re(1)−N(2)	73.9(2)	C(31)−N(3)−Re(1)	116.6(5)

The amidato ligand present in **3** corresponds to a formal insertion of the C=C bond of the ketene into the amido N−H bond of complex **1**. A similar insertion of diphenylketene was reported by Boncella for a square-planar nickel(II) anilido complex.[2g] The reaction resembles those of secondary amines with ketenes to give *N*,*N*-disubstituted amides.[10] The different regiochemistry (insertion into N−H versus Re−N) encountered for the formation of **3** with respect to that of **2** can be rationalized assuming proton transfer from the ammonium nitrogen of the zwitterionic intermediate (resulting from amido attack to the ketene carbonyl carbon) to the less acidic carbon atom, as depicted in Scheme 3. Nucleophilic attack by nitrogen at the carbonyl group is considered to be the first step in the reactions of amines with ketenes,[11] and a zwitterionic species such as the one depicted in Scheme 3 has been spectroscopically detected in recent studies of the reaction between diphenylketene and pyridine.[11] The instantaneous reaction of **1** with diphenylketene at room temperature contrasts with the slower reactions of diphenylketene with anilines.[12] This difference can be rationalized taking into account that the repulsive interaction between metal filled d orbitals and the electron pair on the nitrogen increases the nucleophilicity of the latter.

The molecule of **3** is planar at nitrogen (sum of the angles around N(3) = 359.8°), mainly due to the delocalization of the amido nitrogen lone pair involving the carbonyl group. Evidence of this interaction is provided by the short N(3)−C(4) distance (1.333(8) Å). A similar feature was found in the complex [Re{N(*p*Tol)C(O)NHEt}(CO)$_3$(bipy)], obtained by the reaction of the amido complex **1** with ethylisocyanate,[5] as well as in the nickel complex mentioned above.[2g] The N−C(ipso) distance, 1.462(9), Å is longer than that found in the anilido complex [Re(NHPh)(CO)$_3$(bipy)] (1.360(5) Å),[4] analogous to **1**, in which the nitrogen lone pair delocalizes through the phenyl group.[13] The Re−N(3) distance

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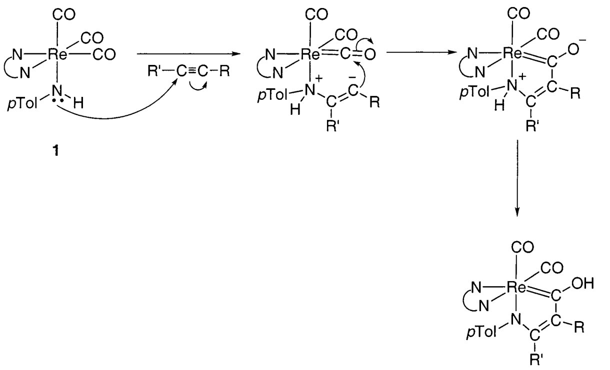
(10) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1992; p 799.

(11) Wagner, B. D.; Arnold, B. R.; Brown, G. S.; Lusztyk, J. *J. Am. Chem. Soc.* **1998**, *120*, 1827.

(12) Briody, J. M.; Satchell, D. P. N. *Tetrahedron* **1966**, *22*, 2649.

(13) The N−C(ipso) distance in **3** is similar to that found in [Re(NH$_2$*p*Tol)(CO)$_3$(bipy)]OTf (1.448(6) Å); see ref 4.

Scheme 4



R	R'	
CO_2Me	CO_2Me	**4a**
CO_2Et	CO_2Et	**4b**
CO_2Me	H	**4c**

(2.184(6) Å) is very close to the corresponding Re–N distance in [Re{N(*p*Tol)C(O)NHEt}$(CO)_3$(bipy)] (2.182(4) Å), mentioned above. A consequence of the amido pair delocalization is that the Re-bonded nitrogen is no longer nucleophilic; thus, **3** does not further react with diphenylketene.

The amido complex **1** reacted instantaneously with dimethylacetylenedicarboxylate, DMAD (Scheme 4). As in the previous reactions of **1** with electrophiles, the color of the solution changed from green to red. To our surprise, the IR spectrum of the resulting solution contained two ν(CO) bands of similar intensity and width at 1921 and 1852 cm^{-1}. This pattern is diagnostic of a *cis*-$Re(CO)_2$ moiety. This was unexpected since *fac*-$Re(CO)_3$ fragments are very reluctant to undergo CO substitution processes.[14] The ^1H NMR of the reaction crude showed the formation of a single product, **4a**, which could be isolated in the form of red needle-shaped crystals, whose IR and ^1H NMR were identical to those of the crude solutions. The incorporation of DMAD was indicated by the two CO_2Me singlets at 3.66 and 3.37 ppm in the ^1H NMR. Unlike in complexes **2** and **3**, an asymmetric bipy pattern was found in the ^1H NMR of **4a**, indicating the absence of a molecular mirror plane. As a result, the two carbonyl ligands appeared as two separate resonances of similar intensity at 205.08 and 199.58 ppm in the ^{13}C NMR spectrum.

A single crystal of **4a** suitable to determine its structure by means of X-ray diffraction could not be obtained. Therefore, we prepared the analogous complex **4b**, resulting from reaction of **1** with diethylacetylenedicarboxylate. The spectroscopic data of **4b**, given in the Experimental Section, showed it to be isostructural with **4a**. A single crystal of **4b** was used for an X-ray structural determination, the results of which are displayed in Figure 3 and Table 3.

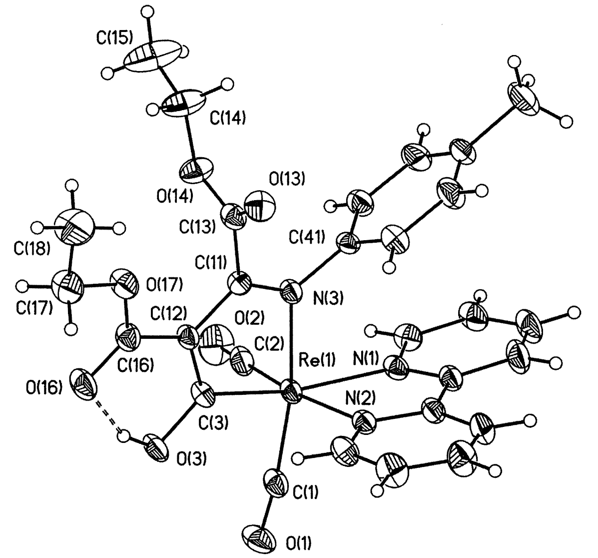


Figure 3. Plot of [Re{N(*p*Tol)C(CO_2Et)C(CO_2Et)C(OH)}$(CO)_3$(bipy)] (**4b**) showing the atom-numbering scheme (30% probability ellipsoids).

Table 3. Selected Bond Distances and Angles for Complex 4b

	Bond Distances (Å)		
Re(1)–C(1)	1.869(6)	Re(1)–N(3)	2.189(4)
Re(1)–C(2)	1.897(6)	N(3)–C(11)	1.304(6)
Re(1)–C(3)	2.024(5)	C(11)–C(12)	1.435(6)
Re(1)–N(1)	2.200(4)	C(12)–C(3)	1.425(7)
Re(1)–N(2)	2.177(4)	C(3)–O(3)	1.354(6)
	Bond Angles (deg)		
C(1)–Re(1)–C(2)	87.0(2)	C(1)–Re(1)–N(3)	165.75(18)
C(2)–Re(1)–C(3)	91.8(2)	C(3)–Re(1)–N(3)	75.78(17)
C(1)–Re(1)–C(3)	90.8(2)	N(3)–Re(1)–N(1)	90.06(14)
C(2)–Re(1)–N(1)	96.21(19)	N(2)–Re(1)–N(3)	83.11(15)
C(1)–Re(1)–N(1)	102.75(19)	C(41)–N(3)–Re(1)	123.6(3)
C(3)–Re(1)–N(1)	164.59(17)	C(11)–N(3)–C(41)	120.7(4)
C(2)–Re(1)–N(2)	170.03(18)	C(11)–N(3)–Re(1)	115.1(3)
C(3)–Re(1)–N(2)	98.04(17)	O(3)–C(3)–Re(1)	124.7(4)
N(2)–Re(1)–N(1)	73.85(15)	O(3)–C(3)–C(12)	116.5(4)
C(1)–Re(1)–N(2)	94.4(2)	C(12)–C(3)–Re(1)	118.9(3)
C(2)–Re(1)–N(3)	97.9(2)		

The molecule of **4b** consists of a rhenium atom in a distorted octahedral environment. Two coordination positions are occupied by the two carbonyl ligands, which are in mutual *cis* disposition (C(1)–Re–C(2) = 87.0(2)°), and two are occupied by the bipy nitrogens. The remaining two positions belong to the carbon and nitrogen ends of a five-membered Re–N–C–C–C metallacycle. The cycle is essentially planar, the major deviation affecting N(3), 0.0173 Å out of plane. Aside from the typical small bite angle of the bipy chelate (N(1)–Re–N(2) = 73.85(15)°), the main deviations from an idealized octahedral geometry are imposed by the metallacycle (for instance, C(3)–Re–N(3) = 75.78(17)°, and C(1)–Re–N(3) = 165.75(18)°). The four atoms that, in addition to rhenium, form the metallacycle are the nitrogen from the amido group, the two acetylenic carbons from $EtO_2CC{\equiv}CCO_2Et$, and one carbon atom from a carbonyl ligand. The Re–C(3) distance, 2.024(5) Å, is quite short, suggesting some multiple character. Thus, for instance, Re–C distances of 2.071(8) and 2.078(10) Å were found for the carbene carbons of the octahedral $L_nM{=}C(OEt)Me$ and $L_nM{=}C(OMe)C(H){=}C(H)Me$ (L_nM = $Re(CO)_2$(triphos)) complexes,[15] and a Re–C distance of 2.198(8) Å was found for the single bond in [Re{C(CO_2Me)=C(CO_2Me)OMe}$(CO)_3$(bipy)].[16]

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[14] Koike, K.; Tanabe, J.; Toyama, S.; Tsubaki, H.; Sakamoto, K.; Westwell, J. R.; Johnson, F. P. A.; Hori, H.; Saitoh, H.; Ishitani, O. *Inorg. Chem.* **2000**, *39*, 277, and references therein.

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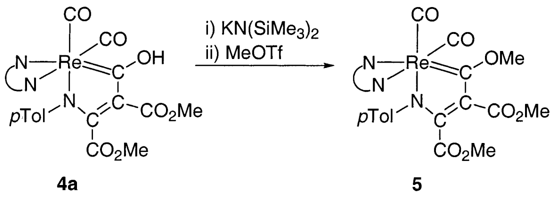
[16] Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1750.

Scheme 5



In agreement with this short distance, the corresponding carbon appears at 269.07 ppm in the ^{13}C NMR, a chemical shift close to those found for the carbene complexes mentioned above. Also close are the chemical shift values reported by Casey for rhenium cyclic hydroxycarbenes.[17]

The Re−N(3) distance (2.189(4) Å) is similar to that found for complex **3**, and C−C and C−N distances within the metallacycle have values between those expected for single and double bonds, suggesting significant delocalization, in agreement with the planarity of the cycle noted above. The presence of a hydroxy group is supported by the results of the X-ray structure determination. Thus, the C(3)−O(3) distance (1.354(6) Å) corresponds to a single bond,[18] and the hydrogen atom bonded to O(3) was located and refined with the distance fixed at 0.923 Å, but it was allowed to rotate freely. Furthermore, the hydrogen resonates at 13.85 ppm in the ^{1}H NMR spectrum, a value similar to previously reported hydroxycarbenes.[17] A hydrogen bond interaction between this hydrogen and O(16) (d(O−H) = 1.684 Å and d(O(3)−O(16)) = 2.561(7) Å) completes a six-membered cycle, as represented in Figure 3 by the dashed line. The two cycles are virtually coplanar.

A reaction like those leading to **4a**,**b** was observed to occur between **1** and methyl propiolate (Scheme 4). The longer reaction time (30 min at room temperature) is attributed to the lower electrophilic character of the acetylene.[19] Complexes **4a**−**c** were isolated in yields around 80% (see Experimental Section). No reaction was observed between **1** and PhC≡CCO$_2$Me.

Complex **4a** did not react with trimethylphosphine (3 equiv, 4 h, refluxing THF), a fact that indicates that the opening of the metallacycle is not facile. Treatment of **4a** with the stoichiometric amount of either ^{n}BuLi or KN(SiMe$_3$)$_2$ led to solutions with lower values of ν(CO) IR bands, suggesting deprotonation of the OH group. Addition of methyl triflate afforded the neutral complex **5** (see Scheme 5), spectroscopically characterized (see Experimental Section).

A rationale for the formation of the metallacycles in **4a**−**c**, depicted in Scheme 4, assumes nucleophilic amido attack (as discussed for the formation of **2** and **3**) to the activated acetylene, attack by the resulting carbanion to one of the proximal CO groups, and proton transfer from nitrogen to oxygen.

The formation of the metallacycles **4a**−**c** contrasts with the reactivity of DMAD toward ruthenium, nickel, and palladium amides to give the products of acetylene insertion into the M−N bond, previously reported by Boncella,[2f−h] and with our recently reported insertion of DMAD into the Re−O bond of alkoxo complexes [Re(OR)(CO)$_3$(bipy)] to afford tricarbonyl bipyridine complexes with a *Z*-alkenyl ligand.[16] {Re(CO)$_3$(bipy)} fragments are very robust,[20] and a CO activation at these systems is rare.

In addition to the amido complexes mentioned above, the recent preparation by Templeton of a five-membered metallacycle containing a carbene carbon from acetylene carbons and a carbonyl ligand is pertinent to the present work.[21] Insertion of acetylenes into metal−nitrogen bonds has few precedents,[22] and, recently, such a reaction allowed Odom to obtain a four-membered metallacycle in a Mo(IV) complex.[23]

In conclusion, we have found that the amido complex **1** reacts with three different organic electrophiles to form new C−N bonds. The nucleophilicity of **1** is comparable to those exhibited by previously known amido compounds of the groups 8−10.

Experimental Section

General procedures and preparation of **1** are given elsewhere.[4]

Crystal Structure Determination for Compounds 2, 3, and 4b. A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized Mo Kα 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[24] program. The structure was solved by direct methods with SHELXTL.[25] A semiempirical absorption correction was applied with the program SADABS.[26] 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 Table 4.

Reaction of 1 with *p*-Tolylisothiocyanate. *p*TolNCS (0.013 g, 0.083 mmol) was added to a solution of **1** (0.050 g, 0.083 mmol) in THF (15 mL). The color of the solution changed instantaneously from green to orange. Solvent was removed under vacuum, and the red solid was redisolved in CH$_2$Cl$_2$ (5 mL). Slow diffusion of diethyl ether into this solution at room temperature afforded orange crystals of **2**·CH$_2$Cl$_2$, one of which was employed for an X-ray structure determination. Yield: 81% (0.051 g). IR (CH$_2$Cl$_2$): 2021, 1919, 1900. ^{1}H NMR(CD$_2$Cl$_2$): 8.85 [m, 2H, bipy], 8.01 [m, 4H, bipy], 7.39 [m, 2H, bipy], 6.91−6.59 [m, 8H, *p*Tol], 2.25 [s, 6H, C*H*$_3$, *p*Tol], 2.16 [s, 1H, br, N*H*]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 155.48, 153.45 [bipy], 147.65 [*p*Tol], 138.93 [bipy],130.85, 128.91, 128.18 [*p*Tol], 127.33, 123.55 [bipy], 20.84 [CH$_3$, *p*Tol]. Anal. Calcd for C$_{28}$H$_{23}$N$_4$O$_3$-

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(17) Casey, C. P.; Czerwinski, C. J.; Fusie, K. A.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 3971.

(18) C(16)−O(16) = 1.234(6) Å and C(13)−O(13) = 1.199(6) Å distances are indicative of C=O double bonds.

(19) The methoxo complex [Re(OMe)(CO)$_3$(bipy)] reacts with DMAD, but not with methyl propiolate.

(20) Thus, for instance, CO substitution at these complexes requires drastic conditions; see ref 14.

(21) Gunnoe, T. B.; Caldarelli, J. L.; White, P. S.; Templeton, J. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2093.

(22) (a) Kemmitt, R. D. W.; Mason, S.; Moore, M. R.; Fawcett, J.; Russell, D. R. *Chem. Commun.* **1990**, 1535. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Organomet. Chem.* **1992**, *428*, 13. (c) Cabeza, J. A.; del Río, I.; Grepioni, F.; Moreno, M.; Riera, V. *Organometallics* **2001**, *20*, 4190.

(23) Katayev, E.; Li, Y.; Odom, A. L. *Chem. Commun.* **2002**, 836.

(24) *SAINT+*. SAX area detector integration program, Version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

(25) Sheldrick, G. M. *SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data*, Version 5.1*;* Bruker AXS, Inc.: Madison, WI, 1998.

(26) Sheldrick, G. M. *SADABS*, *Empirical Absorption Correction Program;* University of Göttingen: Göttingen, Germany, 1997.

Table 4. Crystal Data and Refinement Details for Complexes 2, 3, and 4b

	2	**3**	**4b**
formula	$C_{28}H_{23}N_4O_3ReS{\cdot}CH_2Cl_2$	$C_{38}H_{34}N_3O_5Re$	$C_{32}H_{34}N_3O_8Re$
fw	766.69	798.88	774.78
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	15.275(3)	8.7734(17)	8.895(2)
b, Å	17.059(3)	11.721(2)	13.262(3)
c, Å	12.377(2)	16.512(3)	15.644(4)
α, deg	90	101.297(4)	65.453(4)
β, deg	109.805(4)	90.510(4)	81.655(4)
γ, deg	90	99.202(4)	80.031(4)
V, Å^3	3034.2(9)	1642.2(6)	1647.8(7)
Z	4	2	2
T, K	295(2)	293(2)	293(2)
D_c, g cm^{-3}	1.678	1.616	1.562
F(000)	1504	796	772
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst size, mm	0.03 × 0.10 × 0.11	0.04 × 0.08 × 0.19	0.04 × 0.07 × 0.25
μ, mm^{-1}	5.209	3.749	3.739
scan range, deg	$1.11 \leq \theta \leq 23.26$	$1.26 \leq \theta \leq 23.32$	$1.70 \leq \theta \leq 23.45$
no. of reflns measd	13 402	10 760	10 588
no. of ind reflns	4357	4725	4774
no. of data/restraints/params	4357/0/367	4725/0/425	4774/0/379
goodness-of-fit on F^2	0.929	1.004	1.020
R_1/R_{w2} [$I>2\sigma(I)$]	0.0389/0.0546	0.0324/0.0657	0.0282/0.0637
R_1/R_{w2} (all data)	0.0755/0.0591	0.0464/0.0875	0.0341/0.0652

$ReS{\cdot}CH_2Cl_2$: C, 45.43; H, 3.28; N, 7.30. Found: C, 45.55; H, 3.31; N, 7.43.

Reaction of 1 with Diphenylketene. $Ph_2C{=}C{=}O$[27] (13 μL, 0.083 mmol) was added to a solution of **1** (0.050 g, 0.083 mmol) in THF (15 mL). The color of the solution changed instantaneously from green to orange. Slow diffusion of hexane into this solution at room temperature afforded orange crystals of **3**·THF, one of which was employed for an X-ray structure determination. Yield: 87% (0.057 g). IR (THF): 2014, 1914, 1887. ^{1}H NMR(CD_2Cl_2): 8.86 [m, 2H, bipy], 8.04 [m, 4H, bipy], 7.34 [m, 2H, bipy], 7.05 [m, 6H, Ph], 6.73 [m, 4H, Ph], 6.63, 6.59, 5.93, 5.91 [AA′BB′, 4H, *p*Tol], 4.58 [s, 1H, C*H*], 2.18 [s, 3H, CH_3, *p*Tol]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 199.39 [2CO], 193.68 [CO], 174.29 [O═C], 155.66, 155.08 [bipy], 149.10, [*p*Tol], 143.32 [Ph], 139.46 [bipy], 133.04 [*p*Tol], 129.31 [Ph], 128.97 [bipy], 127.97 [Ph], 126.90, 126.52, 125.99 [Ph, *p*Tol], 122.60 [bipy], 54.99 [*C*H], 20.80 [CH_3, *p*Tol]. Anal. Calcd for $C_{38}H_{34}N_3O_5$-Re: C, 57.13; H, 4.28; N, 5.25. Found: C, 57.18; H, 4.19; N, 5.33.

Reaction of 1 with Dimethylacetylenedicarboxylate. $MeO_2CC{\equiv}CCO_2Me$ (10 μL, 0.083 mmol) was added to a solution of **1** (0.050 g, 0.083 mmol) in THF (10 mL). The color of the solution changed instantaneously from green to red. Volatiles were removed under vacuum, and the solid was redissolved in CH_2Cl_2 (10 mL). Slow diffusion of hexanes into this solution at room temperature afforded red crystals of **4a**. Yield: 0.047 g, 84%. IR (THF): 1921, 1852. ^{1}H NMR (CD_2Cl_2): 13.91 [s, br, 1H, OH], 8.86 [m, 1H, bipy], 8.46 [m, 1H, bipy], 7.94 [m, 2H, bipy], 7.48 [m, 3H, bipy], 7.17 [m, 1H, bipy], 6.48 [m, 4H, *p*Tol], 3.66 [s, 3H, OC*H*$_3$], 3.37 [s, 3H, OC*H*$_3$], 2.06 [s, 3H, CH_3, *p*Tol]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 269.10 [Re═C], 205.08 [CO], 199.58 [CO], 171.40 [C═O], 168.29 [NC═*C*], 165.71 [C═O], 156.66, 154.07, 153.78, 152.36 [bipy], 143.13 [C(OH)*C*(CO_2Me)], 138.18, 135.66 [bipy], 134.88, 128.95 [*p*Tol], 126.91, 126.45 [bipy], 124.48 [*p*Tol], 122.44, 122.28 [bipy], 113.55 [*p*Tol], 51.89 [OCH_3], 51.08 [OCH_3], 25.94 [CH_3, *p*Tol]. Anal. Calcd for $C_{26}H_{22}N_3O_7Re$: C, 46.28; H, 3.28; N, 6.22. Found: C, 46.37; H, 3.19; N, 6.35.

Reaction of 1 with Diethylacetylenedicarboxylate. Following the procedure described for **4a**, the reaction of **1** (0.050 g, 0.083 mmol) with $EtO_2CC{\equiv}CCO_2Et$ (13 μL, 0.083 mmol) afforded red crystals of **4b**, one of which was suitable for an X-ray experiment. Yield: 0.046 g, 79%. IR (THF): 1920, 1851. ^{1}H NMR(CD_2Cl_2): 13.85 [s, br, 1H, OH], 8.89 [m, 1H, bipy], 8.50 [m, 1H, bipy], 7.96 [m, 2H, bipy], 7.60 [m, 3H, bipy], 7.46 [m, 1H, bipy], 6.48 [m, 4H, *p*Tol], 4.16 [q (6.98 Hz), 2H, OC*H*$_2$CH$_3$], 3.82 [q (6.98 Hz), 2H, OC*H*$_2$CH$_3$], 2.07 [s, 3H, CH_3, *p*Tol], 1.81 [t (6.98 Hz), 3H, OCH$_2$C*H*$_3$], 1.20 [t (6.98 Hz), 3H, OCH$_2$C*H*$_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 269.07 [Re═C], 205.45 [CO], 199.84 [CO], 171.90 [C═O], 168.12 [NC═*C*], 165.06 [C═O], 156.68, 154.13, 153.73, 152.34 [bipy], 143.11 [C(OH)*C*(CO_2-Me)], 138.32, 135.79 [bipy], 134.87, 129.21 [*p*Tol], 126.94, 126.46 [bipy], 123.21 [*p*Tol], 122.60, 122.44 [bipy], 113.44 [*p*Tol], 61.20 [O*C*H$_2$CH$_3$], 59.9 [O*C*H$_2$CH$_3$], 25.94 [CH_3, *p*Tol], 14.36 [OCH$_2$*C*H$_3$], 13.74 [OCH$_2$*C*H$_3$]. Anal. Calcd for $C_{24}H_{20}N_3O_5$-Re: C, 47.85; H, 3.72; N, 5.97. Found: C, 47.90; H, 3.75; N, 5.84.

Reaction of 1 with Methyl Propiolate. $HC{\equiv}CCO_2Me$ (7.5 μL, 0.083 mmol) was added to a solution of **1** (0.050 g, 0.083 mmol) in THF (10 mL). After 30 min stirring, the solvent was removed under vacuum and the red solid was redissolved in CH_2Cl_2 (10 mL). Slow diffusion of hexanes into this solution at room temperature afforded red crystals of **4c**. Yield: 0.041 g, 81%. IR (THF): 1918, 1848. ^{1}H NMR (CD_2Cl_2): 13.60 [s, br, 1H, OH], 9.13 [m, 1H, bipy], 8.37 [m, 1H, bipy], 7.88 [m, 2H, bipy], 7.63 [m, 3H, bipy], 7.27 [m, 1H, bipy], 6.60, 6.56, 5.98, 5.94 [AA′BB′, 4H, *p*Tol], 3.70 [s, 3H, OC*H*$_3$], 2.10 [s, 3H, CH_3, *p*Tol]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 269.34 [Re═C], 204.93 [CO], 200.21 [CO], 169.78 [N*C*H═C], 169.07, 165.01 [C═O], 156.37, 154.20, 153.94, 151.83 [bipy], 146.74 [C(OH)*C*(CO_2-Me)], 139.75, 138.02 [bipy], 134.36, 129.03 [*p*Tol], 126.83, 126.61 [bipy], 122.55 [*p*Tol], 122.49, 122.11 [bipy], 115.77 [*p*Tol], 50.59 [OCH_3], 20.77 [CH_3, *p*Tol]. Anal. Calcd for $C_{24}H_{20}N_3O_5Re$: C, 46.74; H, 3.26; N, 6.81 Found: C, 46.64; H, 3.29; N, 6.69.

Reaction by Deprotonation/Methylation of 4a. KN-($SiMe_3$)$_2$ (0.150 mL of a 0.5 M solution in toluene, 0.074 mmol) was added to a solution of **4a** (0.050 g, 0.074 mmol) in THF (15 mL) previously cooled at −78 °C. The color of the solution darkened inmediately. MeOTf (8.4 μL, 0.074 mmol) was added at −78 °C, and the mixture was stirred and allowed to reach room temperature. The solvent was removed under vacuum. The red residue was extracted with CH_2Cl_2 (2 × 10 mL). The resulting solution was concentrated to 5 mL. Slow diffusion of hexanes into this solution at room temperature afforded **5** as a red microcrystaline solid. Yield: 0.037 g, 74%. IR (THF):

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1914, 1841. ^{1}H NMR (CD$_2$Cl$_2$): 8.92 [m, 1H, bipy], 8.57 [m, 1H, bipy], 8.03 [m, 2H, bipy], 7.60 [m, 3H, bipy], 7.17 [m, 1H, bipy], 6.57 [m, 4H, *p*Tol], 4.42 [s, 3H, Re═COC*H*$_3$], 3.65 [s, 3H, OC*H*$_3$], 3.36 [s, 3H, OC*H*$_3$], 2.10 [s, 3H, CH$_3$, *p*Tol]. ^{13}C-{^{1}H} NMR(CD$_2$Cl$_2$): 272.65 [Re═C], 205.63 [CO], 197.61 [CO], 173.24 [C═O], 166.04 [N*C*═C], 165.01 [C═O], 156.66, 154.27, 152.44, 151.23 [bipy], 143.98 [C(OMe)═*C*(CO$_2$Me)], 138.83, 136.32 [bipy], 134.37, 129.11 [*p*Tol], 127.17, 126.72 [bipy], 122.85 [*p*Tol], 122.71, 122.26 [bipy], 118.68 [*p*Tol], 66.74 [Re═CO*C*H$_3$], 51.69 [OCH$_3$], 50.72 [OCH$_3$], 20.71 [CH$_3$, *p*Tol]. Anal. Calcd for C$_{27}$H$_{24}$N$_3$O$_7$Re: C, 47.08; H, 3.51; N, 6.10 Found: C, 47.14; H, 3.58; N, 6.09.

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Supporting Information Available: Tables giving positional and thermal parameters, bond distances, and bond angles for **2**, **3**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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