# New Octahedral Rhenium(I) Tricarbonyl Amido Complexes

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Several new Re(I) octahedral amido complexes *fac*-[Re(NRR′)$(CO)_3$(N−N)] (R = aryl; R′ = H, aryl; N−N = 2,2′-bipyridine, bipy; 1,10-phenanthroline, phen) have been synthesized either by reaction of [Re(OTf)$(CO)_3$(N−N)] precursors with potassium amides or by deprotonation of [Re$(NH_2Ar)(CO)_3$(N−N)]OTf compounds, in turn obtained by reaction of [Re(OTf)$(CO)_3$-(N−N)] compounds with amines. The structure of the amido complexes [Re(NHPh)$(CO)_3$-(bipy)] (**5**) and [Re$(NPh_2)(CO)_3$(bipy)] (**6**) have been determined by single-crystal X-ray diffraction. The results, coupled with the solution NMR behavior of the complexes, indicate that the delocalization of the nitrogen lone pair of the amido group involves mainly the N−aryl bonds. Amido complexes [Re(NH*p*-Tol)$(CO)_3$(N−N)] (**4a**,**b**) (*p*-Tol = 4-methylphenyl) react with 4-ethylphenol, with ethanothiol, and with diphenylphosphine to give the complexes [Re$(OC_6H_4$-4-$C_2H_5)(CO)_3$(bipy)] (**8**), [Re$(SCH_2CH_3)(CO)_3$(bipy)] (**9**), and [Re$(PPh_2)(CO)_3$(N−N)] (**10a**,**b**). The structure of the diphenylphosphido complex [Re$(PPh_2)(CO)_3$(phen)] (**10b**), determined by X-ray diffraction, was compared with the structure of the homologous diphenylamido complex **6**. The different geometries (pyramidal phosphorus and planar amido nitrogen) correlate with the higher nucleophilicity of the phosphido complex.



## Introduction

Amido complexes of late transition metals in low oxidation states have been the subject of much research[1] due to (a) the earlier belief that these compounds would be inherently unstable as a result of the mismatch between the soft metal fragment and the hard amido ligand and (b) the interesting reactivity displayed by some of these species. Although it is now recognized that no thermodynamic instability is necessarily attached to this type of complex, their syntheses remain challenging due to undesirable side reactions brought about by the strongly basic or reducing character of the reagents.

In its simple description, the metal−amido bond can be considered to consist of (a) a $\sigma$ bond like the M−C bond in metal alkyls, and (b) a $\pi$ bond due to donation of an electron pair from the nitrogen atom into a suitable empty d orbital of the metal fragment. This second component is important in amido complexes of early transition metals of intermediate or high oxidation states. However, for 18-electron low-valent transition metal amido complexes, at least formally, this $\pi$ donation should not be possible and, therefore, the amido ligand should be pyramidal, and the metal−nitrogen distance should correspond to a single bond. In turn, this should have important consequences on the reactivity: the nitrogen atom should possess a high basicity and nucleophilicity, and the repulsion between the nitrogen lone pair and the metal filled orbitals should make the M−N bond very reactive. Actually, a meaningful discussion of the M−N distances requires the comparison between structures determined with a high accuracy, which are not always available. Furthermore, the relationship between the degree of multiplicity of the M−N bond and the M−N distance may be complicated by steric factors. This is of particular importance when a metal center has both a high coordination number and very bulky ligands, which are often used to stabilize the amido complexes. This situation is typically found in $d^6$ octahedral amido complexes, which are the most relevant to the work described here.[2−5]

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(1) (a) Chisholm, M. H. *Comprehensive Inorganic Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, pp 161−188. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188. (C) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1−40.

(2) Re(I) amido complexes: (a) Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1991**, 712−714. (b) Dewey, M. A.; Knight, D. A.; Arif, A.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815−824. (c) Dewey, M. A.; Stark, G. A.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4798−4807. (d) Simpson R. D.; Bergman, R. G. *Organometallics* **1992**, *11*, 3980−3993.

(3) Ru(II) amido complexes: (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444−1456. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717−2719. (c) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875−1887. (d) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781−2794. (e) Hsu, G. C.; Kosar, W. P.; Jones, W. D. *Organometallics* **1994**, *13*, 385−396. (f) Kaplan, A. W.; Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6828−6829. (g) Boncella, J. M.; Eve, T. M.; Rickman, B.; Abboud, K. A. *Polyhedron* **1998**, *17*, 725−736. (h) Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 8799−8800. (i) Jayaprakash, K. N.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2001**, *40*, 6481−6486.

(4) Os(II) amido complexes: Flood, T. C.; Lim, J. K.; Deming, M. A.; Keung, W. *Organometallics* **2000**, *19*, 1166−1174.

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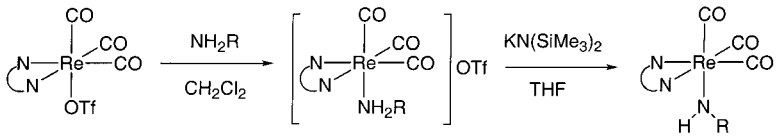
**Scheme 1**




| | N-N |
|---|---|
| **1a** | bipy |
| **1b** | phen |

| | N-N | R |
|---|---|---|
| **2a** | bipy | p-Tol |
| **2b** | phen | p-Tol |
| **3** | bipy | Ph |

| | N-N | R |
|---|---|---|
| **4a** | bipy | *p*-Tol |
| **4b** | phen | *p*-Tol |
| **5** | bipy | Ph |

With regard to the geometry of the amido ligand, most complexes of this sort are planar at the nitrogen,[6] a fact usually interpreted in terms of electron delocalization involving the R groups on the amido nitrogen, and that is most significant when R = aryl, C(O)R, and $SiR_3$.[1c] Nevertheless, these $d^6$ octahedral amido complexes display a rich reactivity. We have begun to explore the synthesis, structure, and reactivity of amido complexes of the metal fragment {$Re(CO)_3$(bipy)}, and here we report our first results.

Octahedral Re(I) derivatives *fac*-[$ReX(CO)_3$(bipy)] (X = anionic ligand) have been extensively studied within the fields of photophysics[7] and $CO_2$ activation,[8] whereas their application in other areas has been somewhat limited.[9] In particular, no amido derivatives of this kind were known. We felt that amido complexes [Re(NRR′)-$(CO)_3$(bipy)], if they could be prepared, would be attractive for several reasons: (a) {$Re(CO)_3$(bipy)} fragments are rather inert, thus eliminating possible side reactions, including facile descomposition pathways. (b) Given the very strong preference for a *fac* geometry and the planarity of the bipy ligand, steric hindrance would be, unlike in most isolable low-valent amido complexes, virtually absent, a feature that would simplify the analysis of the influence of the electronic properties and that, coupled with the fact that no N→Re $\pi$-donation would be possible for these 18-electron species, should enhance their reactivity.

## Results and Discussion

We have found that arylamido complexes [Re(NRAr)-$(CO)_3$(bipy)] (R = H, Ph, 4-$MeC_6H_4$ (*p*-Tol)) can be prepared by two methods. The first method is the reaction of the triflato complex [Re(OTf)$(CO)_3$(bipy)][10] (**1a**) with potassium amides. The employment of the more labile triflato complex as precursor was found to be necessary given that [$ReX(CO)_3$(bipy)][11] (X = Cl, Br) halo complexes are unreactive toward the amide reagent. Complex **1a** is rather thermally stable and can be stored under nitrogen several months. Alternatively, it can be generated by reaction of [$ReCl(CO)_3$(bipy)] with silver triflate and, once the AgBr byproduct was removed by filtration, used without isolation for the synthesis of the amido complexes. We initially employed lithium amides as reagents for the preparation of amido complexes. However, only oily materials could be obtained. Similar difficulties, attributed to the presence of lithium triflate, were experienced by Gladysz during the purification of [ReCp(NRR′)(NO)($PPh_3$)] complexes.[2b] The complete elimination of LiOTf is difficult due to its appreciable solubility in the solvents into which the amido complexes can be extracted. Hence, we turned our attention to potassium amides, generated by in situ deprotonation of amines with $KN(SiMe_3)_2$. The lower solubility of KOTf allowed the isolation of the amido complexes as microcrystalline solids. However, when this method was applied to the synthesis of the arylamido compounds [Re(NHAr)$(CO)_3$(bipy)] (Ar = *p*-Tol, Ph), the $^1H$ NMR of the products showed the contamination with traces of unidentified species. Therefore, we sought an alternative method.

The triflato complex **1a** reacts with arylamines $NH_2$*p*-Tol and $NH_2$Ph to give the salts [Re($NH_2$*p*-Tol)$(CO)_3$-(bipy)]OTf (**2a**) and [Re($NH_2$Ph)$(CO)_3$(bipy)]OTf (**3**). The facile substitution of the triflate group in **1a** using stoichiometric amounts of arylamine and mild conditions (1 h, room temperature) contrasts with the previously reported substitution using $PPh_3$, which required 100 equiv of triphenylphosphine.[11] This difference can be attributed to the higher basicity and lower steric bulk of the primary amines.

The treatment of **2a** and **3** with $KN(SiMe_3)_2$ in THF at −78 °C afforded the amido complexes [Re(NH*p*-Tol)-$(CO)_3$(bipy)] (**4a**) and [Re(NHPh)$(CO)_3$(bipy)] (**5**), respectively (see Scheme 1), which could be isolated as spectroscopically pure compounds. The deprotonation of coordinated amines in cationic complexes was previously used as a route to amido complexes and, in some instances, was found to be preferable to the employment of preformed alkaline amides.[12]

The IR spectra of **4a** and **5** displayed three $\nu_{CO}$ bands typical of *fac*-tricarbonyl compounds, with wavenumber values some 30 $cm^{-1}$ lower than the precursor amino complexes, reflecting the transformation of cationic species into neutral ones.

(5) Ir(III) amido complexes: (a) Glueck, D. S.; Winslow, L. J. N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462−1479. (b) Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479−1486. (c) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888−7889.

(6) We are aware of only two exceptions; see refs 2a−c and 3i.

(7) See for instance: (a) Stufkens, D. J.; Vlcek, A., Jr. *Coord. Chem. Rev.* **1998**, *177*, 127−179. (b) Farrell, I. R.; Vlcek, A., Jr. *Coord. Chem. Rev.* **2000**, *208*, 87−101. (c) Striplin, D. R.; Crosby, G. A. *Coord. Chem. Rev.* **2001**, *211*, 163−175.

(8) (a) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161−2166. (b) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500−1505. (c) Kutal, C.; Corbin, J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553−557. (d) Scheiring, T.; Klein, A.; Kaim, W. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2569−2571.

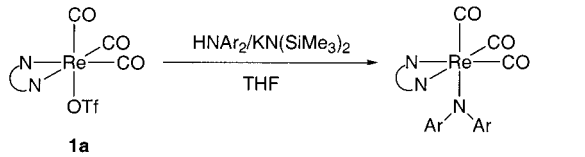
(9) Gibson, D. H.; Sleaad, B. A.; Yin, X.; Vij, A. *Organometallics* **1998**, *17*, 2689−2691.

(10) Triflato complexes of this kind have been previously prepared. See for instance: Guerrero, J.; Pino, O. E.; Wolcan, E.; Feliz, M. R.; Ferraudi, G.; Moya, S. A. *Organometallics* **2001**, *20*, 2842−2853.

(11) Klein, A.; Vogler, C.; Kaim, W. *Organometallics* **1996**, *15*, 236−244.

(12) Martin, G. C.; Palenik, G. J.; Boncella, J. M. *Inorg. Chem.* **1990**, *29*, 2027−2030.

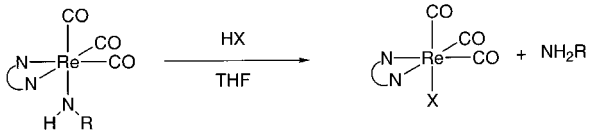
**Scheme 2**




**1a**

| | N-N | Ar |
|---|---|---|
| **6** | bipy | Ph |
| **7** | bipy | *p*-Tol |

**Scheme 3**




| | N-N | R |
|---|---|---|
| **4a** | bipy | *p*-Tol |
| **4b** | phen | *p*-Tol |

| | N-N | X |
|---|---|---|
| **8** | bipy | OAr |
| **9** | bipy | SEt |
| **10a** | bipy | $PPh_2$ |
| **10b** | phen | $PPh_2$ |

The most relevant features in the NMR spectra of the new compounds are the broad signals at 5.51 (**2a**) and 4.78 (**3**) ppm, and the broad singlets at 2.15 ppm (**4a**) and 2.11 ppm (**5**), assigned to the nitrogen-bonded hydrogens.[13]

Diarylamines $Ph_2NH$ and *p*-$Tol_2NH$ did not react with [Re(OTf)$(CO)_3$(bipy)] (**1a**) under the conditions used for the synthesis of the primary amine complexes, surely due to the lower basicity and larger bulk of the diarylamines. Fortunately, the reaction of **1a** with the potassium diarylamides yielded the diarylamido complexes [Re$(NPh_2)(CO)_3$(bipy)] (**6**) and [Re$(Np\text{-}Tol_2)(CO)_3$(bipy)] (**7**), which could be purified by filtration followed by crystallization.

We have begun to study the reactivity of the new amido complexes. The *p*-tolylamido complex **4a** does not react with an excess (10 equiv) of methanol or water (5 h, room temperature, THF). This contrasts with the reactivity toward methanol shown by Bergman's complex [Re(NHPh)$(CO)_3$(depe)].[2d] Complex **4a** reacted with 4-ethylphenol to yield the orange aryloxo complex [Re(OAr)$(CO)_3$(bipy)] (**8**) (Ar = 4-ethylphenyl) and with ethanethiol to give the red thiolato complex [Re(SEt)$(CO)_3$(bipy)] (**9**) (see Scheme 3 and Experimental Section). The reaction of **4a** with an equimolar amount of diphenylphosphine in THF at room temperature afforded the diphenylphosphido complex [Re$(PPh_2)(CO)_3$(bipy)] (**10a**). The reaction was accompanied by a color change from emerald green to deep blue. The $^{31}P$ NMR chemical shift of the singlet of **10a** (−43.09 ppm) is close to that of free diphenylphosphine (−40.55 ppm), in accordance with the data of previously reported rhenium terminal phosphido complexes.[14] When the reaction between **4a** and $HPPh_2$ was carried out in an NMR tube in $C_6D_6$, the $^1H$ NMR spectrum of the resulting solution showed the presence of free *p*-toluidine in addition to the signals of **10a**. Although bridging phosphido complexes are relatively abundant, only a few terminal examples have been fully characterized, including the rhenium(I) complex [ReCp$(PPh_2)(NO)(PPh_3)$].[14a−c] This preparation of phosphido complexes **10a**,**b** is reminiscent of the reaction between the methoxo complex [Re(OMe)$(CO)_3$(depe)] and $HPPh_2$ to afford the phosphido complex [Re$(PPh_2)(CO)_3$(depe)].[2d]

The structures of the amido complexes **5** and **6** were determined by single-crystal X-ray diffraction (Figures 1 and 3 and Tables 1 and 3). For comparative purposes,

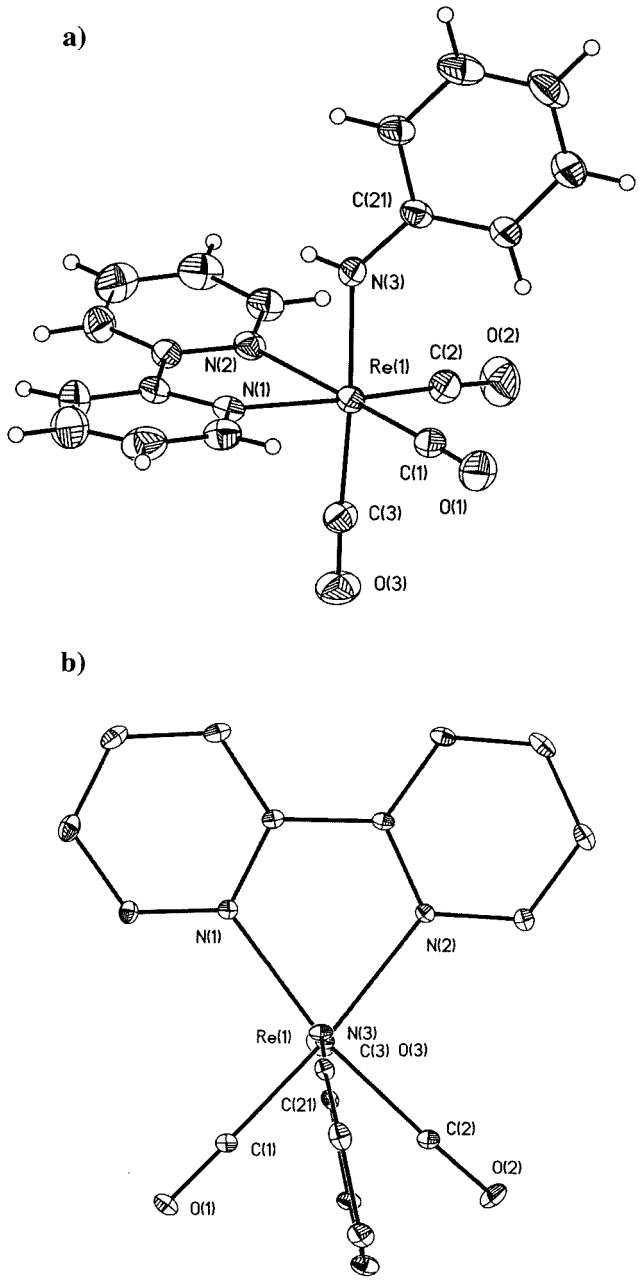



**Figure 1.** Thermal ellipsoid plot (ellipsoids at 30% probability level) of **5**.

(13) The chemical shift of N-H hydrogens of amido complexes has been reported to appear over a wide range of values; see for instance: (a) Powell, K. R.; Pérez, P. J.; Luan, L.; Feng, S. G., White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851−1864: 15.33 and 13.00 ppm for the major and minor rotational isomers of [WTp′(NHPh)$(CO)_2$]. (b) VanderLende, D. D.; Abboud, K. A., Boncella J. M. *Inorg. Chem.* **1995**, *34*, 5319−5326: 0.18 ppm for *trans*-[Ni(Ph)(NHPh)$(PMe_3)_2$].

(14) See ref 2d and: (a) Buhro, W. E.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3346−3348. (b) Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1985**, *24*, 3507−3508. (c) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427−2439, and references therein.

**Table 1. Selected Bond Distances and Angles for Complex 5**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Re(1)−C(1) | 1.901(5) | Re(1)−N(3) | 2.112(4) |
| Re(1)−C(2) | 1.898(5) | N(3)−C(21) | 1.360(5) |
| Re(1)−C(3) | 1.925(5) | C(1)−O(1) | 1.156(5) |
| Re(1)−N(1) | 2.182(3) | C(2)−O(2) | 1.152(5) |
| Re(1)−N(2) | 2.188(4) | C(3)−O(3) | 1.154(6) |
| **Bond Angles (deg)** | | | |
| C(1)−Re(1)−C(2) | 90.0(2) | C(1)−Re(1)−N(2) | 173.09(16) |
| C(2)−Re(1)−C(3) | 86.74(19) | C(2)−Re(1)−N(3) | 97.22(18) |
| C(1)−Re(1)−C(3) | 87.47(18) | C(1)−Re(1)−N(3) | 93.75(17) |
| C(2)−Re(1)−N(1) | 170.21(16) | C(3)−Re(1)−N(3) | 175.85(17) |
| C(1)−Re(1)−N(1) | 99.71(17) | N(3)−Re(1)−N(1) | 83.69(14) |
| C(3)−Re(1)−N(1) | 92.20(16) | N(3)−Re(1)−N(2) | 82.94(14) |
| C(2)−Re(1)−N(2) | 96.45(17) | Re(1)−N(3)−C(21) | 134.9 3) |
| C(3)−Re(1)−N(2) | 95.42(15) | H(3)−N(3)−C(21) | 111.1(9) |
| N(1)−Re(1)−N(2) | 73.95(13) | Re(1)−N(3)−H(3) | 114.1(7) |

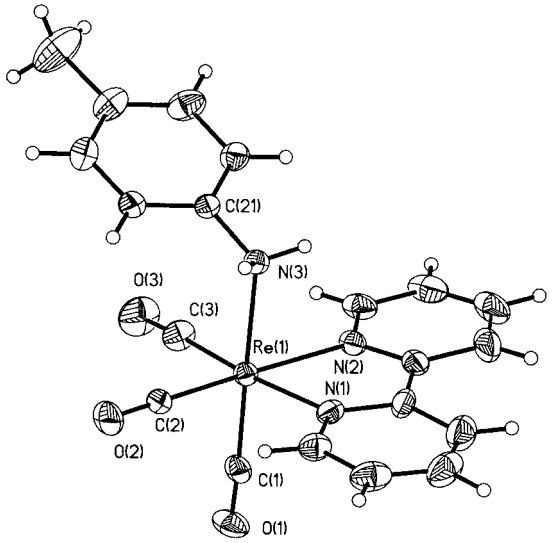



**Figure 2.** Thermal ellipsoid plot (ellipsoids at 30% probability level) of **2a**.

**Table 2. Selected Bond Distances and Angles for Complex 2a**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Re(1)−C(1) | 1.926(6) | Re(1)−N(3) | 2.250(3) |
| Re(1)−C(2) | 1.915(5) | N(3)−C(21) | 1.488(6) |
| Re(1)−C(3) | 1.934(6) | C(1)−O(1) | 1.141(6) |
| Re(1)−N(1) | 2.162(4) | C(2)−O(2) | 1.144(6) |
| Re(1)−N(2) | 2.163(4) | C(3)−O(3) | 1.132(7) |
| **Bond Angles (deg)** | | | |
| C(2)−Re(1)−C(1) | 89.0(2) | N(1)−Re(1)−N(2) | 74.96(16) |
| C(2)−Re(1)−C(3) | 88.6(2) | C(1)−Re(1)−N(2) | 94.72(17) |
| C(1)−Re(1)−C(3) | 85.8(2) | C(2)−Re(1)−N(3) | 92.18(18) |
| C(2)−Re(1)−N(1) | 97.27(19) | C(1)−Re(1)−N(3) | 178.83(16) |
| C(1)−Re(1)−N(1) | 95.19(17) | C(3)−Re(1)−N(3) | 94.16(19) |
| C(3)−Re(1)−N(1) | 174.1(2) | N(1)−Re(1)−N(3) | 84.78(14) |
| C(2)−Re(1)−N(2) | 171.64(19) | N(2)−Re(1)−N(3) | 84.14(15) |
| C(3)−Re(1)−N(2) | 99.1(2) | C(21)−N(3)−Re(1) | 111.9(3) |

the structure of the amino complex **2a** was also determined (Figure 2 and Table 2). The three derivatives have the expected octahedral geometry around the rhenium atom, the major deviation from an idealized octahedral geometry being the small (74−75°) angle subtended by Re and the bipy nitrogens, imposed by the rigid geometry of the chelate.

For complex **5**, the distance between rhenium and the carbon atom of the carbonyl ligand trans to the amido group (1.925(5) Å) is appreciably longer than the corresponding distances for the other two CO groups (1.898(5) and 1.901(5) Å). Since the comparison is between the Re−CO distances of the three carbonyl ligands each trans to a nitrogen atom, the difference reflects the larger trans influence of the amido group. The amido ligand of **5**, as in nearly all the previously known amido complexes structurally characterized, is planar at nitrogen[6] (the sum of the angles about N is 360.1°).

The Re−N(amido) distance (2.112(4) Å) in **5** is somewhat shorter than the Re−N(bipy) distances (2.182(3) and 2.188(4) Å) in the same complex and then the Re−N(amine) distance (2.250(3) Å) in **2a**. The Re−N(amido) bond has some degree of ionic component, which is known to shorten the bond lengths.[15] Moreover, a dative (as opossed to covalent) bond, like Re−N(bipy), usually gives larger bond lengths. Therefore, multiple character of the Re−N(amido) bond does not need to be invoked to account for the difference in Re−N bond lengths.

The $^1$H NMR spectra of [Re(NH*p*-Tol)(CO)$_3$(bipy)] (**4a**) and [Re(NHPh)(CO)$_3$(bipy)] (**5**) each show one set of four multiplets for the bipy ligand. Given that the $^1$H NMR spectrum of **4a** is more informative, variable-temperature experiments were carried out with this complex. The bipy signals in the $^1$H NMR of **4a** remain invariant between 25 and −80 °C. This is consistent with free rotation around the Re−N(amido) bond over this temperature range or with a static structure with the amido group lying in the mirror plane of the {Re(CO)$_3$(bipy)} fragment. Since there is neither steric hindrance nor $\pi$ donation from the amido lone pair to the metal dp orbitals (filled in these d$^6$ complexes), free rotation seems to be the more plausible explanation.

The Re−N(amido) distance in **5** (2.112(4) Å) is slightly shorter than in the structurally similar complex [Re(NHPh)(CO)$_3$(depe)][2d] (2.170(4) Å), a fact that can be attributed to the steric bulk of the diphosphine depe (1,2-diethylphosphinoethane), both P atoms of which are adjacent to the amido group in this complex. A slightly shorter Re−N(amido) distance was found in the complex [ReCp(NHPh)(NO)(PPh$_3$)][2a,b] (2.076(6) Å), which features a pyramidal amido ligand and for which, therefore, the lack of multiple character for the Re−N bond is well established. The longer Re−N distance of **5** should, at least in part, be due to the presence of a CO ligand (with a strong trans influence) in the position trans to the amido group in the octahedral molecule of **5**.

An interesting comparison can be made between the structures of the aminocomplex **2a** and the amido derivative **5**. The N−C(ipso) distance in **5** (1.360(5) Å) is significantly shorter than the corresponding distance in **2a** (1.488(6) Å), which in turn is similar to the value found for other structurally characterized rhenium aniline complexes (1.444(6) Å in [Re(NH$_2$Ph)(NPh)Cl$_3$]).[16] This indicates that substantial delocalization of the nitrogen lone pair takes place involving the phenyl group, a fact that explains why the amido group is planar at the nitrogen in this 18-electron compound. The lone pair delocalization involving the N−Ar bond is further substantiated by the variable-temperature $^1$H NMR behavior of complex **4a**. At room temperature, an

(15) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115−129.
(16) Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1988**, *142*, 23−25.

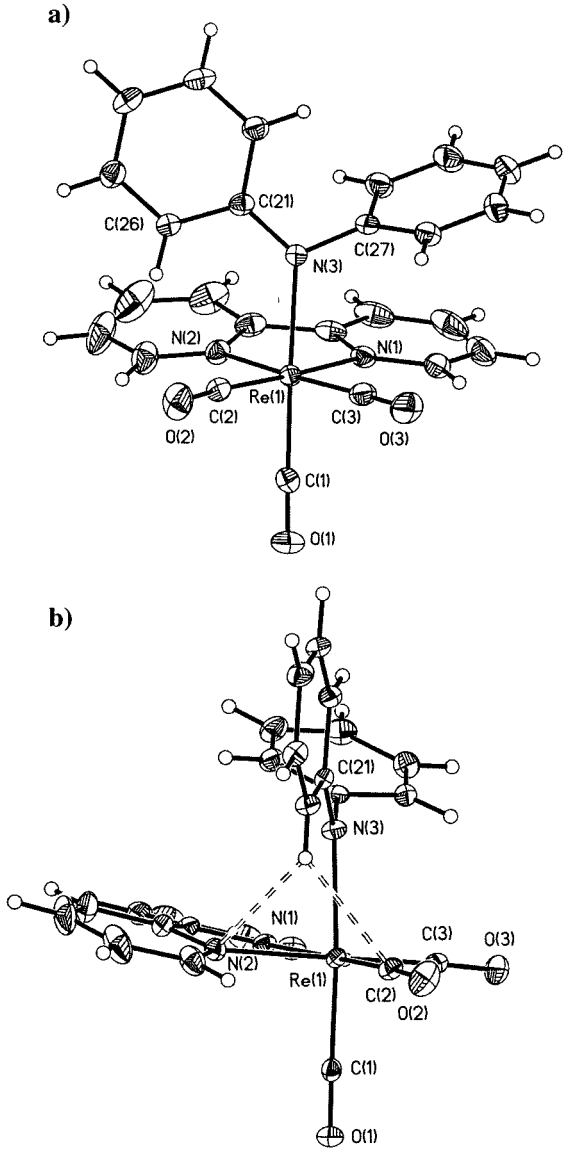



**Figure 3.** Thermal ellipsoid plot (ellipsoids at 30% probability level) of **6**.

AA′BB′ quartet in the $^1$H NMR spectrum is observed for the four aromatic hydrogen atoms of the *p*-tolyl group. This pattern changes when the temperature is lowered, indicating that the rotation around the N−C(ipso) bond is being frozen. At −80 °C the *p*-tolyl region of the spectrum displays three signals; one of them (6.72 ppm), integrating as two hydrogens, is assigned to one ortho and one meta hydrogen, whereas the two remaining hydrogens give two signals at 6.37 and 5.75 ppm.[17] This pattern is similar to the one found at intermediate temperatures for the amido complex *trans*-[PtCl{NH-(4-I-$C_6H_4$)}($PEt_3$)$_2$].[18]

In the solid-state structure of [Re($NPh_2$)($CO$)$_3$(bipy)] (**6**) (see Figure 3), the ortho hydrogen on C(26) is close to one of the bipy nitrogens (N(2)−H(26) = 2.851(9) Å) and to one of the carbonyl carbons (C(2)−H(26) = 2.549-(9) Å),[19] as shown in Figure 3. This weak interaction seems to affect the Re−N and Re−C distances, since

**Table 3. Selected Bond Distances and Angles for Complex 6**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Re(1)−C(1) | 1.920(3) | N(3)−C(21) | 1.384(4) |
| Re(1)−C(2) | 1.933(4) | N(3)−C(27) | 1.433(4) |
| Re(1)−C(3) | 1.905(3) | C(1)−O(1) | 1.153 (4) |
| Re(1)−N(1) | 2.178(3) | C(2)−O(2) | 1.142(4) |
| Re(1)−N(2) | 2.197(3) | C(3)−O(3) | 1.157(4) |
| Re(1)−N(3) | 2.201(2) | | |
| **Bond Angles (deg)** | | | |
| C(1)−Re(1)−C(2) | 88.57(13) | C(1)−Re(1)−N(2) | 92.37(11) |
| C(3)−Re(1)−C(2) | 86.11(14) | C(2)−Re(1)−N(3) | 95.69(12) |
| C(3)−Re(1)−C(1) | 87.98(13) | C(1)−Re(1)−N(3) | 175.46(11) |
| C(2)−Re(1)−N(1) | 174.80(12) | C(3)−Re(1)−N(3) | 93.90(12) |
| C(1)−Re(1)−N(1) | 92.12(11) | N(1)−Re(1)−N(3) | 83.50(9) |
| C(3)−Re(1)−N(1) | 99.06(12) | N(2)−Re(1)−N(3) | 85.30(10) |
| C(2)−Re(1)−N(2) | 100.47(12) | C(21)−N(3)−Re(1) | 129.8(2) |
| C(3)−Re(1)−N(2) | 173.41(12) | C(27)−N(3)−Re(1) | 114.81(18) |
| N(1)−Re(1)−N(2) | 74.35(10) | C(21)−N(3)−C(27) | 115.1(2) |

Re−C(2) (1.933(4) Å) and Re−N(2) (2.197(3) Å) are longer than the "equivalent" Re−C(3) (1.905(3) Å) and Re−N(1) (2.178(3) Å) (which are almost identical to the distances found in **5**).

The amido ligand in **6** is planar at the nitrogen, with a Re−N distance of 2.201(2) Å. The longer distance with respect to **5** is due to the lower basicity and larger bulk of the diphenylamido ligand, but given the planarity of the bipy ligand and the octahedral geometry of the complex, the steric factor must be of minor importance.

With regard to the basicity, it should be noted that for **6** two aromatic rings are available for the resonance delocalization of the nitrogen lone pair. As a result, the N−C(ipso) distance in complex **5**, with only one aromatic ring, (1.360(5) Å), is shorter than any of the N−C(ipso) distances in the diphenylamido complex **6** (1.384(4) and 1.433(4) Å). The difference found between the two N−C(ipso) distances in complex **6** can be interpreted as indicating that one of the phenyl rings (the one with the shorter N−C distance) is significantly more engaged in the delocalization. This ring lies in the plane defined by Re, N(amido), and C(ipso) (see Figure 3), thus maximizing the delocalization. The presence of four signals for the bipy hydrogens in $^1$H NMR, five singlets for the bipy carbons in the $^{13}$C{H} NMR, and only one $^{13}$C NMR signal for the two carbonyl ligands trans to the bipy nitrogens, maintained at −80 °C in complex **6**, is interpreted, reasoning as for complex **5** (see above), as due to free rotation around the Re−N(amido) bond. Variable-temperature $^1$H NMR of [Re(N*p*-$Tol_2$)($CO$)$_3$-(bipy)] (**7**) showed the presence of only one methyl singlet and only one AA′BB′ quartet at temperatures as low as −80 °C, indicating a similar behavior. In addition, between room temperature and −80 °C, the two phenyl groups of **6** appear as only four signals in the $^{13}$C{H} NMR, reflecting that the two ortho carbons and the two meta carbons of each ring are equivalent over this temperature range. Thus, free rotation around the N−C(ipso) bonds must be assumed.

(17) Variable-temperature $^1$H NMR spectra of **4a** are given as Supporting Information.

(18) Albéniz, A. C.; Calle, V.; Espinet, P.; Gómez, S. *Inorg. Chem.* **2001**, *40*, 4211−4216.

(19) Similar distances have been found in a search through the Cambridge Structural Database for three-center interactions between a nitrogen, a carbonyl ligand, and an ortho phenyl hydrogen; see, for instance: (a) Alonso, F. J. G.; Sanz, M. G.; Riera, V.; Abril, A. A.; Tiripicchio A.; Ugozzoli, U. *Organometallics* **1992**, *11*, 801−806. (b) Gargulak, J. D.; Gladefelter, W. L. *Inorg. Chem.* **1994**, *33*, 253−257. (c) Cook, J.; Davison, A.; Davis, W. M.; Jones, A. G. *Organometallics* **1995**, *14*, 650−654.

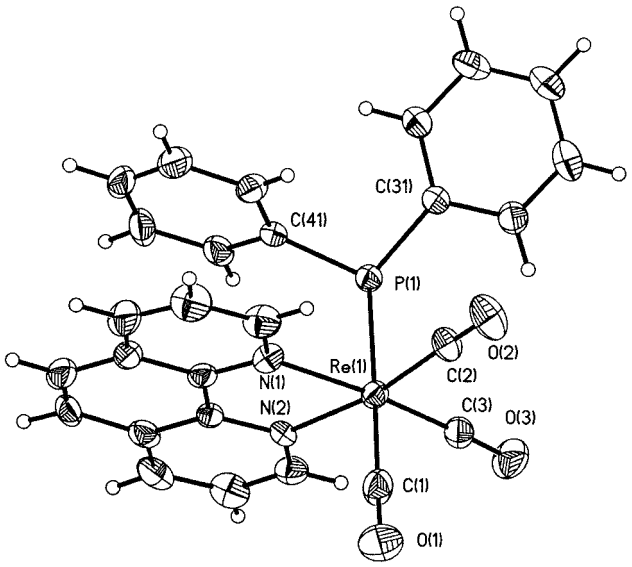



**Figure 4.** Thermal ellipsoid plot (ellipsoids at 30% probability level) of **10b**.

It was mentioned that, in the solid state, one of the aryl rings of complex **6** is more involved in the delocalization of the nitrogen lone pair. A good orbital overlap requires this ring to lie in the plane defined by the amido nitrogen and the two ipso carbons. Rotation of that ring around the N−C(ipso) bond, found to occur in solution, should result in loss of overlap and, therefore, of lone pair delocalization through this aryl group. However, the other ring is also rotating around the N−C(ipso) bond. At a given point, this second ring would lie in the $NC_2$ plane, achieving maximum overlap for the nitrogen lone pair delocalization. This process of concordant rotation explains that the two aryl rings are equivalent in solution, although the two N−C(ipso) distances of **6** are so different in the solid state (see above).

As few terminal phosphido compounds have been crystallographically characterized, we sought to carry out an X-ray analysis of complex **10a**. All our attempts to obtain single crystals of **10a** suitable for X-ray diffraction were unsuccessful. However, we found that the phenanthroline complex [$Re(PPh_2)(CO)_3$(phen)] (**10b**), prepared in a completely analogous manner and whose spectroscopic data are very similar to those of **10a** (see Experimental Section), afforded X-ray quality crystals, one of which was used for the determination of the structure (see Figure 4 and Table 4).

In contrast with the planar diphenylamido ligand of complex **6**, the diphenylphosphido group of **10b** is pyramidal: the sum of the angles about phosphorus is 323.5°, nearly identical to what was found in the complex [$ReCp(PPh_2)(NO)(PPh_3)$][14a−c] (323°); this sum would be 328.5° and 360° for idealized tetrahedral and planar phosphorus atoms, respectively. Planar amido and pyramidal phosphido ligands are the normally encountered situations, and a discussion of the factors leading to this difference has been given by Buhro.[20]

The Re−P distance (2.571(2) Å) is somewhat longer than the Re−P distances found for phosphine complexes,[2d] a fact that can be related to the repulsion between the lone pair on the phosphorus atom and the filled d orbitals of the metal fragment.[14a−c] Note that the opposite is true for amido complexes, which feature Re−N distances shorter than amino complexes, as exemplified by the structures of **5** and **6** versus that of **2a** (see above). An important consequence of this difference between homologous amido and phosphido compounds is that, whereas amines are more nucleophilic than phosphines, the phosphido complexes are more nucleophilic than the amido counterparts. Thus, whereas [$Re(NPh_2)(CO)_3$(bipy)] (**6**) does not react with methyl iodide (stoichiometric, room temperature, 24 h, $CD_2Cl_2$ or THF), the phosphido complex **10a** is instantaneously methylated by MeI (room temperature, THF) to yield the salt [$Re(PPh_2Me)(CO)_3$(bipy)]I (**11**-I) (see Scheme 4). With the stronger methylating agent MeOTf, **6** reacts (2 h in $CD_2Cl_2$ at room temperature) to give [Re(OTf)$(CO)_3$(bipy)] (**1a**) plus free methyldiphenylamine; on the other hand, **10a** reacts with MeOTf (instantaneous at −78 °C, THF) to afford the salt [Re-($PPh_2Me$)$(CO)_3$(bipy)]OTf (**11**-OTf) (see Scheme 4).

These results reflect, besides the more nucleophilic character of the phosphido complex, the better ability of phosphorus to accommodate a higher coordination number due to its larger size.[22] Other aspects of the reactivity of the new amido complexes are being studied and will be the subject of a forthcoming paper.

**Table 4. Selected Bond Distances and Angles for Complex 10b**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Re(1)−C(1) | 1.930(10) | P(1)−C(31) | 1.833(9) |
| Re(1)−C(2) | 1.924(10) | P(1)−C(41) | 1.830(9) |
| Re(1)−C(3) | 1.894 (10) | C(1)−O(1) | 1.164 (12) |
| Re(1)−N(1) | 2.190(7) | C(2)−O(2) | 1.125(11) |
| Re(1)−N(2) | 2.164(7) | C(3)−O(3) | 1.179(11) |
| Re(1)−P(1) | 2.571 (2) | | |

| Bond Angles (deg) | | | |
|---|---|---|---|
| C(2)−Re(1)−C(1) | 90.0(4) | C(1)−Re(1)−N(2) | 96.2(4) |
| C(3)−Re(1)−C(2) | 89.7(3) | C(2)−Re(1)−P(1) | 93.6(3) |
| C(3)−Re(1)−C(1) | 90.4(4) | C(1)−Re(1)−P(1) | 176.0(4) |
| C(2)−Re(1)−N(1) | 174.80(12) | C(3)−Re(1)−P(1) | 87.8(3) |
| C(1)−Re(1)−N(1) | 89.8(4) | N(1)−Re(1)−P(1) | 91.59(19) |
| C(3)−Re(1)−N(1) | 172.5(4) | N(2)−Re(1)−P(1) | 80.52(18) |
| C(2)−Re(1)−N(2) | 97.8(4) | C(41)−P(1)−Re(1) | 107.0(3) |
| C(3)−Re(1)−N(2) | 97.4(3) | C(31)−P(1)−Re(1) | 112.8(3) |
| N(1)−Re(1)−N(2) | 75.1(3) | C(41)−P(1)−C(31) | 103.7(4) |

## Experimental Section

**General Procedures.** All manipulations were carried out under dinitrogen using standard Schlenk techniques. Solvents were distilled from Na (hexanes), Na/benzophenone (tetrahydrofuran and diethyl ether), and $CaH_2$ ($CH_2Cl_2$). $CD_2Cl_2$ and $C_6D_6$ 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 $^1H$, $^{19}F$, $^{31}P$, and $^{13}C$ 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 [Re(OTf)$(CO)_3$(N−N)][10] (**1a**,**b**) were prepared in virtually quantitative yield by the reaction of equimolar amounts of the corresponding [$ReBr(CO)_3$(N−N)][11] compounds with AgOTf in $CH_2Cl_2$ in the dark, followed by filtration through diatomaceous earth to remove AgBr.

**Crystal Structure Determination for Compounds 2a, 5, 6, and 10b.** A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer

(20) Coel, S. C.; Chiang, M. Y.; Rauscher, D. J.; Buhro W. E. *J. Am. Chem. Soc.* **1993**, *115*, 160−169.

**Scheme 4**

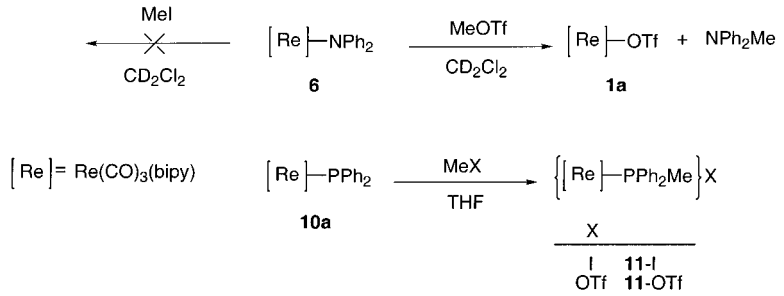



**Table 5. Crystal Data and Refinement Details for Complexes 2a, 5, 6, and 10b**

| | 2a | 5 | 6 | 10b |
|---|---|---|---|---|
| formula | $C_{21}H_{17}F_3N_3O_6ReS$ | $C_{23}H_{22}N_3O_4Re$ | $C_{25}H_{18}N_3O_3Re$ | $C_{29}H_{22}N_2O_3PRe\cdot 1/2C_4H_8O$ |
| fw | 682.64 | 590.64 | 594.62 | 671.66 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $C2/c$ | $P2_1/n$ | $P2_1/c$ |
| $a$, Å | 18.5006(9) | 24.903(3) | 10.4605(8) | 14.237(8) |
| $b$, Å | 9.9985(5) | 11.8285(13) | 13.1053(10) | 11.487(6) |
| $c$, Å | 13.0499(6) | 18.891(2) | 16.1229(12) | 19.161(11) |
| α, deg | 90 | 90 | 90 | 90 |
| $\beta$, deg | 95.4930(10) | 127.520(3) | 104.0680(10) | 111.749(10) |
| $\gamma$, deg | 90 | 90 | 90 | 90 |
| $V$, Å$^3$ | 2402.9(2) | 4413.5(9) | 2144.0(3) | 2911(3) |
| $Z$ | 4 | 8 | 4 | 4 |
| $T$, K | 293(2) | 293(2) | 293(2) | 295(2) |
| $D_c$, g cm$^{-3}$ | 1.887 | 1.778 | 1.842 | 1.533 |
| $F$(000) | 1320 | 2304 | 1152 | 1352 |
| $\lambda$(Mo Kα), Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| cryst size, mm | 0.32 × 0.21 × 0.11 | 0.45 × 0.22 × 0.18 | 0.27 × 0.28 × 0.36 | 0.22 × 0.31 × 0.45 |
| $\mu$, mm$^{-1}$ | 5.209 | 5.541 | 5.701 | 4.262 |
| scan range, deg | $1.11 \le \theta \le 23.26$ | $2.01 \le \theta \le 23.28$ | $2.03 \le \theta \le 23.32$ | $1.54 \le \theta \le 23.66$ |
| no of reflns measd | 10 312 | 13 742 | 9432 | 12 756 |
| no of ind reflns | 3458 | 3169 | 3095 | 4242 |
| data/restraints/params | 3458/0/318 | 3169/0/285 | 3095/0/290 | 4242/0/344 |
| goodness-of-fit on $F^2$ | 1.045 | 1.032 | 1.059 | 1.014 |
| $R_1/R_{w2}$ [$I>2\sigma(I)$] | 0.0256/0.0665 | 0.0228/0.0621 | 0.0156/0.0390 | 0.0468/0.1222 |
| $R_1/R_{w2}$ (all data) | 0.0279/0.0677 | 0.0268/0.0644 | 0.0175/0.0398 | 0.0624/0.1357 |



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[21] program. The structure was solved by direct methods with SHELXTL.[22] A semiempirical absorption correction was applied with the program SADABS.[23] 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 5.

**[Re(NH$_2$*p*-Tol)(CO)$_3$(bipy)]OTf (2a).** *p*-TolNH$_2$ (0.010 g, 0.095 mmol) was added to a solution of [Re(OTf)(CO)$_3$(bipy)] (**1a**) (0.050 g, 0.086 mmol) in $CH_2Cl_2$ (15 mL), and the mixture was stirred for 1 h. The solvent was removed under vacuum, and the yellow solid was washed with $Et_2O$ (2 × 5 mL) to give the complex **2a**. Slow diffusion of hexanes into a solution of **2a** in $CH_2Cl_2$ at −20 °C afforded yellow crystals, one of which was suitable for an X-ray analysis. Yield: 0.054 g, 92%. IR ($CH_2Cl_2$): 2034, 1925. $^1$H NMR ($CD_2Cl_2$): 8.84, 8.25, 8.14, and 7.55 [m, 2H each, bipy], 6.85, 6.81, 6.40, and 6.36 [AA′BB′, 4H, $C_6H_4$], 5.51 [s, 2H, $NH_2$], 2.23 [s, 3H, $CH_3$]. $^{13}$C{$^1$H} NMR($CD_2Cl_2$): 195.87 [2CO], 190.22 [CO], 156.32, 154.22, and 140.87 [bipy], 139.85 and 135.02 [*p*Tol], 129.95 [bipy], 128.45 [*p*Tol], 125.87 [q (361.78 Hz), $CF_3SO_3$], 124.16 [bipy], 120.09 [*p*Tol], 20.73 [$CH_3$]. $^{19}$F NMR($CD_2Cl_2$): −78.57. Anal. Calcd for $C_{21}H_{17}F_3N_3O_6ReS$: C, 36.94; H, 2.51; N, 6.85. Found: C, 36.47; H, 2.62; N, 6.68.

**[Re(NH$_2$*p*-Tol)(CO)$_3$(phen)]OTf (2b).** It was prepared as described for **2a**, starting from [Re(OTf)(CO)$_3$(phen)] (**2a**) (0.050 g, 0.083 mmol) and *p*-TolNH$_2$ (0.010 g, 0.095 mmol). Yield: 0.052 g, 88%, yellow. IR ($CH_2Cl_2$): 2033, 1923. $^1$H NMR ($CD_2Cl_2$): 9.36, 9.21, 8.63, and 8.17 [m, 2H each, phen], 6.62, 6.58, 6.09, and 6.04 [AA′BB′, 4H, $C_6H_4$], 5.78 [s, 2H, $NH_2$], 2.11 [s, 3H, $CH_3$]. $^{19}$F NMR ($CD_2Cl_2$): −79.02. Anal. Calcd for $C_{23}H_{17}F_3N_3O_6ReS$: C, 39.09; H, 2.42; N, 5.94. Found: C, 39.21; H, 2.50; N, 5.87.

**[Re(NH$_2$Ph)(CO)$_3$(bipy)]OTf (3).** The previous procedure was followed using [Re(OTf)(CO)$_3$(bipy)] (**1a**) (0.050 g, 0.086 mmol) in $CH_2Cl_2$ (15 mL) and $PhNH_2$ (9 μL, 0.090 mmol) to give the complex **3**. Yield: 0.049 g, 85%, yellow. IR ($CH_2Cl_2$): 2034, 1925. $^1$H NMR ($CD_2Cl_2$): 8.80, 8.20, 8.09, and 7.54 [m, 2H each, bipy], 6.97 [m, 3H, $C_6H_5$], 6.24 [m, 2H, $C_6H_5$], 4.78 [s, 2H, $NH_2$]. $^{19}$F NMR ($CD_2Cl_2$): −78.05. Anal. Calcd for $C_{20}H_{15}F_3N_3O_6ReS$: C, 35.98; H, 2.26; N, 6.28. Found: C, 35.48; H, 2.31; N, 6.49.

**[Re(NH*p*Tol)(CO)$_3$(bipy)] (4a).** [Re(NH$_2$*p*-Tol)(CO)$_3$(bipy)]-OTf (**2a**) (0.050 g, 0.073 mmol) was dissolved in THF (10 mL), and the solution was cooled to −70 °C. KN(SiMe$_3$)$_2$ (0.146 mL of a 0.5 M solution in toluene, 0.073 mmol) was added. The color of the solution changed from yellow to dark green. After stirring for 15 min at −70 °C, the solution was allowed to warm to room temperature. Volatiles were removed under vacuum, the green solid was extracted with $CH_2Cl_2$ (2 × 10 mL), and the solution was filtered using a cannula tipped with filter paper. $CH_2Cl_2$ was removed under vacuum to afford **4a** as an

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

(22) 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.

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

emerald green solid. Crystallization of **4a** was carried out in THF/hexane, affording green crystals of **4a**·THF. Yield: 0.033 g, 75%. IR (THF): 2003, 1899, 1884. $^1$H NMR ($CD_2Cl_2$): 9.01, 8.28, 8.12, and 7.55 [m, 2H each, bipy], 6.62, 6.58, 6.30, and 6.26 [AA′BB′, 4H, $C_6H_4$], 2.15 [s, 1H, NH], 2.05 [s, 3H, $CH_3$]. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): 200.37 [2CO], 195.45 [CO], 155.53, 153.45, and 139.48 [bipy]. 138.76 and 129.58 [*p*Tol], 127.58 [bipy], 127.10 [*p*Tol], 123.67 [bipy], 116.14 [*p*Tol], 20.23 [$CH_3$]. Anal. Calcd for $C_{24}H_{24}N_3O_4Re$: C, 47.67; H, 4.00; N, 6.94. Found: C, 47.29; H, 4.10; N, 6.79.

**[Re(NH*p*Tol)(CO)$_3$(phen)] (4b).** As described for **4a**, **4b** was obtained using **2b** (0.050 g, 0.070 mmol) and KN($SiMe_3$)$_2$ (0.141 mL of a solution 0.5 M in toluene, 0.070 mmol). Subsequent workup afforded **4b**. Yield: 0.029 g, 74%, emerald green. IR (THF): 2003, 1899, 1884. $^1$H NMR ($CD_2Cl_2$): 9.30, 8.55, 8.05, and 7.84 [m, 2H each, phen], 6.56, 6.53, 6.20, and 6.17 [AA′BB′, 4H, $C_6H_4$], 2.31 [s, 1H, NH], 2.22 [s, 3H, $CH_3$]. Anal. Calcd for $C_{22}H_{16}N_3O_3Re$: C, 47.47; H, 2.89; N, 7.54. Found: C, 47.09; H, 2.97; N, 7.41.

**[Re(NHPh)(CO)$_3$(bipy)] (5).** Following the procedure described for **4a**,**b** [Re($NH_2Ph$)(CO)$_3$(bipy)]OTf (**3**) (0.050 g, 0.075 mmol) was dissolved in THF (10 mL) and KN($SiMe_3$)$_2$ (0.150 mL of a solution 0.5 M in toluene, 0.075 mmol) was added at −70 °C. Subsequent workup gave **5**. Slow diffusion of hexanes into a solution of **5** in THF at room temperature afforded dark green crystals, one of which was used for X-ray analysis. Yield: 0.031 g, 70%. IR (THF): 2002, 1897 1887. $^1$H NMR ($CD_2Cl_2$): 8.96, 8.20, 8.06, and 7.51 [m, 2H each, bipy], 6.75 [m, 2H, $C_6H_5$], 6.32 [m, 2H, $C_6H_5$], 6.05 [m, 1H, $C_6H_5$], 2.11 [s, 1H, NH]. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): 200.54 [2CO], 195.65 [CO], 160.53 [Ph], 155.46, 153.48, 139.51, and 129.11 [bipy], 127.65, 115.92, and 110.84 [Ph]. Anal. Calcd for $C_{23}H_{22}N_3O_4Re$: C, 46.77; H, 3.75; N, 7.11. Found: C, 46.57; H, 3.63; N, 7.31.

**[Re(NPh$_2$)(CO)$_3$(bipy)] (6).** A solution of $KNPh_2$ (prepared by the reaction of $NHPh_2$ (0.016 g, 0.094 mmol) and KN($SiMe_3$)$_2$ (0.188 mL of a solution 0.5 M in toluene, 0.094 mmol) in THF (5 mL) at −70 °C) was added to a solution of [Re(OTf)(CO)$_3$(bipy)] (**1a**) (0.050 g, 0.086 mmol) cooled to −70 °C. The color of the solution changed from yellow to green. After 15 min stirring at low temperature, the mixture was allowed to reach room temperature. Volatiles were removed under vacuum, the green solid was extracted with $CH_2Cl_2$ (2 × 10 mL), and the solution was filtered using a cannula tipped with filter paper. Slow diffusion of hexanes into a solution of **6** in THF at −20 °C afforded green crystals, one of which was used for the X-ray analysis.Yield: 0.037 g, 72%. IR (THF): 2008, 1903, 1890. $^1$H NMR ($CD_2Cl_2$): 8.87 [m, 2H, bipy], 7.95 [m, 4H, bipy], 7.39 [m, 2H, bipy], 6.75 [m, 4H, Ph], 6.39 [m, 4H, Ph], 6.22 [m, 2H, Ph]. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): 200.02 [2CO], 193.22 [CO], 157.00 [Ph], 155.96, 153.39, and 138.99 [bipy], 128.85 [Ph], 127.04 [bipy], 123.25 [Ph], 123.07 [bipy], 116.52 [Ph]. Anal. Calcd for $C_{25}H_{18}N_3O_3Re$: C, 50.49; H, 3.05; N, 7.06. Found: C, 50.13; H, 3.29; N, 7.17.

**[Re(N*p*Tol$_2$)(CO)$_3$(bipy)] (7).** As described for **6**, **7** was obtained using [Re(OTf)(CO)$_3$(bipy)] (**1a**) (0.050 g, 0.086 mmol), NH*p*Tol$_2$ (0.018 g, 0.094 mmol), and KN($SiMe_3$)$_2$ (0.188 mL of a solution 0.5 M in toluene, 0.094 mmol). Yield: 0.045 g, 79%, green. IR (THF): 2007, 1902, 1887. $^1$H NMR ($CD_2Cl_2$): 8.81 [m, 2H, bipy], 7.89 [m, 4H, bipy], 7.32 [m, 2H, bipy], 6.55, 6.53, 6.10, and 6.08 [AA′BB′, 8H, *p*Tol], 2.06 [s, 6H, $CH_3$, *p*-Tol]. Anal. Calcd for $C_{27}H_{22}N_3O_3Re$: C, 52.07; H, 3.56; N, 6.74. Found: C, 52.13; H, 3.49; N, 6.47.

**Reaction of 4a with 4-Ethlyphenol.** 4-Ethylphenol (0.008 g, 0.067 mmol) was added to a solution of [Re(NH*p*-Tol)(CO)$_3$(bipy)] (**4a**) (0.034 g, 0.056 mmol) in THF (10 mL). The mixture was stirred for 3 h at room temperature. The color of the solution changed from green to orange. The solvent was removed under reduced pressure, and the orange solid was washed with $Et_2O$ (5 mL) to afford **8**. Yield: 0.022 g, 71%. IR (THF): 2003, 1899, 1884. $^1$H NMR ($CD_2Cl_2$): 8.97, 8.22, 8.05, and 7.51 [m, 2H each, bipy], 6.73, 6.69, 6.20, and 617 [AA′BB′, 4H, $C_6H_4$], 2.41 [q (7.5 Hz), 2H, $CH_2$], 1.09 [t (7.5 Hz), 3H, $CH_3$]. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): 199.59 [2CO], 196.71 [CO], 167.70 [$C_{ipso}$, $OC_6H_4Et$], 153.09 and 139.66 [bipy], 130.66 and 128.19 [$OC_6H_4Et$], 127.29 [bipy], 123.52 [$OC_6H_4Et$], 119.91 [bipy], 28.15 [$CH_2CH_3$], 16.38 [$CH_2CH_3$]. Anal. Calcd for $C_{21}H_{17}N_2O_4Re$: C, 46.06; H, 3.12; N, 5.11. Found: C, 46.29; H, 3.70; N, 5.29.

**Reaction of 4a with EtSH.** EtSH (4 μL, 0.056 mmol) was added to a solution of **4a** (0.034 g, 0.056 mmol) in THF (10 mL), and the mixture was stirred for 40 min at room temperature. The color of the solution changed from green to red. Volatiles were removed under vacuum, and the red solid was washed with $Et_2O$ (5 mL) to afford **9**. Yield: 0.017 g, 66%, red. IR (THF): 2005, 1904, 1888. $^1$H NMR ($CD_2Cl_2$): 9.03, 8.21, 8.07, and 7.51 [m, 2H each, bipy], 2.56 [q (7.5 Hz), 2H, S$CH_2$-$CH_3$], 2.03 [t (7.5 Hz), 3H, $SCH_2CH_3$]. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): 155.49, 153.33, 140.59, 127.11, and 123.59 [bipy], 25.46 [S$CH_2$-$CH_3$], 21.49 [$SCH_2CH_3$]. Anal. Calcd for $C_{15}H_{13}N_2O_3ReS$: C, 36.95; H, 2.68; N, 5.74. Found: C, 36.68; H, 2.79; N, 5.60. Insufficient solubility precluded the observation of CO signals.

**Reaction of 4a with Diphenylphosphine.** $HPPh_2$ (10 mL, 0.057 mmol) was added to a solution of **4a** (0.034 g, 0.056 mmol) in THF (10 mL), and the mixture was stirred for 30 min at room temperature. The color of the solution changed from green to dark blue. The solvent was removed under vacuum, and the solid was washed with hexane (5 mL) to afford **10a**, dark blue. Yield: 0.023 g, 67%. IR (THF): 2001, 1898. $^1$H NMR ($C_6D_6$): 8.35 [m, 2H, bipy] 7.48 [m, 4H, bipy], 7.15−6.05 [m, 12H, 2H bipy and 10H, 2 Ph,]. $^{31}$P NMR($C_6D_6$): −43.09. Anal. Calcd for $C_{25}H_{18}N_2O_3PRe$: C, 49.09; H, 2.96; N, 4.58. Found: C, 49.50; H, 2.41; N, 4.60.

**Reaction of 4b with Diphenylphosphine.** The procedure was as described for **10a**, using **4b** (0.030 g, 0.053 mmol) and $HPPh_2$ (10 μL, 0.057 mmol). Subsequent workup afforded **10b** as a dark blue powder. Slow diffusion of hexanes into a solution of **10b** in THF at room temperature afforded dark blue crystals, one of which was suitable for an X-ray analysis. Yield: 0.025 g, 72%. IR (THF): 2002, 1898. $^1$H NMR ($C_6D_6$): 8.60 [m, 2H, bipy] 7.39 [m, 4H, bipy], 7.33−6.73 [m, 12H, 2H bipy and 10H, 2 Ph]. $^{31}$P NMR ($C_6D_6$): −42.21. Anal. Calcd for $C_{27}H_{18}N_2O_3PRe$: C, 51.09; H, 2.85; N,4.40. Found: C, 51.21; H, 2.71; N, 4.15.

**Reaction of 10a with MeI.** MeI (3.0 μL, 0.049 mmol) was added to a solution of [Re($PPh_2$)(CO)$_3$(bipy)] (**10a**) (0.030 g, 0.049 mmol) in THF (10 mL) cooled at −70 °C. The mixture was allowed to warm to room temperature. The color of the solution changed from dark blue to orange. Volatiles were removed to afford [Re($PMePh_2$)(CO)$_3$(bipy)]I (**11**-I). Yield: 0.022 g, 60%. IR (THF): 2039, 1954, 1924. $^1$H NMR ($CD_2Cl_2$): 8.82, 8.66, and 8.22 [m, 2H each, bipy], 7.53−7.10 [m, 12H, 2H bipy and 10H, 2 Ph,], 1.60 [d(7.9 Hz), 3H, $PPh_2Me$]. $^{31}$P NMR ($C_6D_6$): 1.02. Anal. Calcd for $C_{26}H_{21}IN_2O_3PRe$: C, 41.44; H, 2.80; N, 3.71. Found: C, 41.26; H, 2.67; N, 3.85.

**Reaction of 10a with MeOTf.** MeOTf (5.5 μL, 0.049 mmol) was added to a solution of [Re($PPh_2$)(CO)$_3$(bipy)] (**10a**) (0.030 g, 0.049 mmol) in THF (10 mL) cooled at −70 °C. The color of the solution changed instantaneously from dark blue to orange. Volatiles were removed to afford [Re($PMePh_2$)(CO)$_3$(bipy)]OTf (**11**-OTf). Yield: 0.025 g, 77%. IR (THF): 2039, 1954, 1924. $^1$H NMR ($CD_2Cl_2$): 8.67, 8.48, and 8.16 [m, 2H each, bipy], 7.48−7.05 [m, 12H, 2H bipy and 10H, 2Ph,], 1.57 [d (7.9 Hz), 3H, $PPh_2Me$]. $^{31}$P NMR ($CD_2Cl_2$): 1.28. $^{19}$F NMR ($CD_2Cl_2$): −78.75. Anal. Calcd for $C_{27}H_{21}F_3N_2O_6PReS$: C, 41.08; H, 2.72; N, 3.61. Found: C, 41.25; H, 2.38; N, 3.68.

**Reaction of 6 with MeOTf.** A 5 mm NMR tube was charged with a solution of [Re($NPh_2$)(CO)$_3$(bipy)] (**6**) (20 g, 0.034 mmol) in $CD_2Cl_2$ (0.5 mL), capped with a rubber septum, and cooled to −70 °C. MeOTf (3.8 μL, 0.034 mmol) was injected, and the reaction was monitored by $^1$H NMR. After 2 h at room temperature the color of the solution changed from

green to yellow, and the $^1$H NMR showed the signals of [Re(OTf)(CO)$_3$(bipy)] (**1a**) and free NMePh$_2$.

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**Supporting Information Available:** $^1$H NMR spectra at variable temperature and tables giving positional and thermal parameters, bond distances, and bond angles for **2a**, **5**, **6**, and **10b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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