# The Nitrosyl Ligand and the Rhenium−Triflate Bond in Rhenium(I) Complexes

**Dario Veghini and Heinz Berke***

Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190,
CH-8057 Zürich, Switzerland

*Received August 18, 1995*[⊗]

The reaction of $ReCl_2L_2(CO)(NO)$ (L = $P(OMe)_3$ (**1a**), $PEt_3$ (**1b**)) with excess silver trifluoromethanesulfonate (AgOTf) in boiling acetonitrile led to an isomeric mixture of $[ReCl(CH_3CN)_2L(CO)(NO)][OTf]$ (L = $P(OMe)_3$ (**2a**) $PEt_3$ (**2b**)) (approximately 2:1 ratio) with the chloride ligands trans to CO or NO. The isomers of **2a** and **2b** could not be separated, except for a few yellow prisms of the trans Cl, NO compound of **2b**, the structure of which was established by an X-ray diffraction study. The cation of **2b** contains an octahedral Re atom bearing one phosphine ligand trans to one acetonitrile molecule (Re−N3 2.144(6) Å). A second acetonitrile ligand (Re−N2 2.143(6) Å) is located trans to the CO ligand (Re−C1 1.928(8) Å, C1−O2 1.142(10) Å) and the chlorine substituent is arranged trans to the NO group (Re−N1 1.810(3) Å, N1−O1 1.190(11) Å). The Cl−Re−NO moiety was found to be positionally disordered. For further characterization of these isomers by chemical means, **2a** and **2b** were reacted with bpy to yield stable [ReCl(bpy)(CO)L(NO)][OTf] derivatives (L = $P(OMe)_3$ (**3a**), $PEt_3$ (**3b**)). The solid state IR spectrum supports the assumption that the isomers of **3a** and **3b** co-crystallize in the same crystal framework. This apparently prevented separation by crystallization. The reaction of **1** with 1 or 2 equiv of AgOTf in boiling toluene allowed the preparation of the mono- and disubstituted complexes $ReCl(OTf)L_2(CO)(NO)$ (L = $P(OMe)_3$ (**4a**), $PEt_3$ (**4b**)) and $Re(OTf)_2L_2(CO)(NO)$ (L = $P(OMe)_3$ (**5a**), $PEt_3$ (**5b**)). The replacement of the triflate ligands in **5a** and **5b** by acetonitrile are slow reactions (approximately 5d for **5a** and 15h for **5b** at room temperature), which proceed with retention of the geometry. They result in the formation of the ionic $[Re(CH_3CN)_2L_2(CO)(NO)][OTf]_2$ products (L = $P(OMe)_3$ (**6a**), $PEt_3$ (**6b**)). The structure of **6a** was confirmed by an X-ray diffraction study. IR and $^{31}P$ NMR investigations of the acetonitrile monosubstituted intermediates of this reaction indicated a somewhat faster replacement of the triflate ligand disposed trans to the carbonyl group. In the presence of bpy, **5a** underwent in boiling toluene an Arbuzov-like phosphite dealkylation, producing a dinuclear $[Re(CO)(bpy)(NO)[P(O)(OMe)_2]]_2$ $[OTf]_2$ (**7**) complex in which the two Re fragments are linked by two phosphonite moieties, forming a planar six-membered ring. The reaction of **5b** with bpy gave only decomposition products. By analogy, $Re(OTf)(CO)_3(PEt_3)_2$ (**8**) was prepared and reacted with bpy under the same conditions as for **5b**. In this case $[Re(CO)_2(bpy)(PEt_3)_2][OTf]$ (**9**) was isolated demonstrating that the presence of the nitrosyl ligand significantly influences the reactivity of $Re^I$ complexes. The compounds **2b**, **5b**, **6a**, **7**, and **8** were characterized by X-ray analyses. Crystal data follow. $C_{12}H_{21}ClF_3N_3O_5PReS$ (**2b**): monoclinic, space group $P2_1/c$, $a = 13.581(6)$ Å, $b = 13.063(5)$ Å, $c = 12.608(5)$ Å, $\beta = 93.48(2)°$, $V = 2232.6(16)$ Å$^3$, $Z = 4$. The structure was solved by the Patterson method and refined by full-matrix least squares procedures to $R = 0.0441$, $R_w = 0.0699$ for 4239 observed reflections with $|F_o| \geq 4\sigma(|F_o|)$. $C_{14}H_{24}F_6N_3O_{14}P_2ReS_2$ (**6a**): monoclinic, space group $C2/c$, $a = 15.610(4)$ Å, $b = 11.159(3)$ Å, $c = 17.006(4)$ Å, $\beta = 91.50(2)°$, $V = 2961.3(12)$ Å$^3$, $Z = 4$. The structure was solved by the Patterson method and refined by full-matrix least squares procedures to $R = 0.0541$, $R_w = 0.0892$ for 3222 observed reflections with $|F_o| \geq 4\sigma(|F_o|)$. **5b**: triclinic, space group $P\bar{1}$, $a = 9.066(2)$ Å, $b = 12.161(3)$ Å, $c = 12.759(3)$ Å, $\alpha = 88.01(2)°$, $\beta = 82.83(2)°$, $\gamma = 86.53(2)°$, $V = 1392.6(6)$ Å$^3$, $Z = 2$. **7**: triclinic, space group $P\bar{1}$, $a = 9.158(3)$ Å, $b = 10.319(2)$ Å, $c = 14.641(4)$ Å, $\alpha = 103.54(2)°$, $\beta = 94.16(2)°$, $\gamma = 115.75(2)°$, $V = 1187.3(5)$ Å$^3$, $Z = 1$. **8**: triclinic, space group $\bar{P}1$, $a = 8.287(3)$ Å, $b = 9.672(3)$ Å, $c = 16.429(6)$ Å, $\alpha = 94.86(3)°$, $\beta = 90.23(3)°$, $\gamma = 112.20(2)°$, $V = 1214.0(7)$ Å$^3$, $Z = 2$.

## Introduction

Ligand sphere tuning in Lewis acidic transition metal complexes has become an important research field in coordination chemistry. Such Lewis acids require a vacant or loosely filled coordination site and desirably also a positive charge on the metal center. However, systems with complete vacancy of one ligand position are presumably for many practical cases not appropiate and it is of great interest to develop Lewis acidic complexes with some protection at this location using labile ligands, which allow opening up "upon request".[1] Low valent transition metal complexes containing weakly coordinating ligands like, for instance, $BF_4^-$, $PF_6^-$, $SbF_6^-$, and $CF_3SO_3^-$ generally show high reactivity and in many instances behave as Lewis acids.[2] The triflate anion, however, has to be considered a special case in this series of counterions.[3] Since its lability is strongly dependent on the electronic nature of the metal. Efficient Lewis acidic catalysts with an electron-donating ligand environment, like $Ti(Cp)_2(OTf)_2$ and $Zr(Cp)_2(OTf)_2(THF)$, do substitute both triflate ligands with carbonyl-containing organic compounds.[4] In contrast to this, the triflate ligand in $Re(CO)_5(OTf)$ can only be replaced by strong donors,

---

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

(1) (a) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (c) Beck, W.; Sunkel, K. *Chem. Rev.* **1988**, *88*, 1405.

(2) (a) Faller, J. W.; Ma, Y.; Smart, C. J.; DiVerdi, M. J. *J. Organomet. Chem.* **1991**, *420*, 237. (b) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. (c) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5296. (d) Bach, T.; Fox, D. N. A.; Reetz, M. T. *J. Chem. Soc., Chem. Commun.* **1992**, *1634*. (e) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579.

(3) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

S0020-1669(95)01082-2 CCC: $12.00

like acetonitrile or $P(nBu)_3$.[5] Compared to the $\{Re(CO)_5\}$ moiety the Re center in the nitrosyl-containing dicationic $\{Re(NO)(CO)L_2\}$ fragment should be of harder HSAB character. To our knowledge there are no precedent investigations of the nitrosyl influence on the rhenium−triflate interaction. Therefore we intended to trace the absolute lability of the triflate ligands coordinated to the *trans*-$\{ReL_2(CO)(NO)\}$ moiety (L = P donors) and the relative trans labilization effects of the NO and CO substituents.

## Experimental Section

**General Considerations.** All preparations were carried out under an atmosphere of dry nitrogen, by conventional Schlenk techniques. All of the described reaction products could be handled in air. THF, toluene, hexane, and pentane were dried and distilled before use. All other solvents were applied as purchased. The compounds *cis*,*trans*-$[ReCl_2(PR_3)_2(CO)(NO)]$ (R = OMe (**1a**), Et (**1b**)) were prepared as described previously.[6] The stationary chromatographic phase Lichroprep (Merck), $AgO_3SCF_3$, and 2,2′-bipyridine (Fluka) were used as received without further purification. Elemental analyses were carried out by the Analytical Department of the Organic Laboratory of Zürich University. IR spectra were recorded on a Biorad FTS-45 instrument. Mass spectra were run on a Finnigan MAT-8230 mass spectrometer with a 70 eV electron-impact ion source. $^1H$ and $^{13}C$ NMR spectra were obtained on a Varian Gemini 200 spectrometer operating at 200 and 50.3 MHz, respectively. $^{31}P$ and $^{19}F$ NMR were measured on a Gemini 300 at 121 MHz and 282 MHz, respectively.

**[Bis(acetonitrile)carbonylchloronitrosyl(trimethyl phosphito)rhenium] Trifluoromethanesulfonate (2a).** A solution of 1 g (1.85 mmol) of **1a** and 0.95 g (3.7 mmol) of $AgO_3SCF_3$ in 80 mL of acetonitrile was heated under reflux for 14 h. After evaporation of the solvent *in vacuo* and washing with two portions of 10 mL of hexane, the yellow product was extracted with dichloromethane (3 × 5 mL). **2a** could not be obtained in analytical pure form. IR ($CH_3CN$, $cm^{-1}$): 2044 s, 1774 s. $^1H$ NMR ($CD_3CN$): $\delta$ 2.59 (d, $^5J_{PH} = 0.7$ Hz, 3H, $CH_3CN$); 2.62 (d, $^5J_{PH} = 0.7$ Hz, 3H, $CH_3CN$); 3.6 (d, $^3J_{PH} = 14$ Hz, $POCH_3$)/3.85 (d, $^3J_{PH} = 12$ Hz, $POCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 98.3/98.8 (s). $^{19}F$ NMR ($CD_3CN$): $\delta$ −78.6 (s).

**[Bis(acetonitrile)carbonylchloronitrosyl(triethylphosphane)-rhenium(I)] Trifluoromethanesulfonate (2b).** A solution of 200 mg (0.36 mmol) of **1b** and 191 mg (0.74 mmol) of $AgO_3SCF_3$ in 20 mL of acetonitrile was heated under reflux for 9 h. After removal of the solvent *in vacuo* and washing with two portions of 10 mL of hexane, the yellow product was extracted with dichloromethane (3 × 5 mL). **2b** could not be obtained in analytically pure form. IR ($CH_3CN$): 2033 s, 1760 s. $^1H$ NMR ($CD_3CN$): $\delta$ 1.10−1.26 (m, $PCH_2CH_3$); 2.18−2.23 (m, $PCH_2CH_3$); 2.76 (sbr, 3H, $CH_3CN$); 2.83 (sbr, 3H, $CH_3CN$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −1.3/-2.3 (s). $^{19}F$ NMR ($CD_3CN$): $\delta$ −78.6 (s).

**[Bipyridine(carbonyl)chloronitrosyl(trimethyl phosphito)rhenium-(I)] Trifluoromethanesulfonate (3a).** A dichloromethane solution of **2a** was added to 312 mg (2 mmol) of 2,2′-bipyridine in 5 mL of dichloromethane, and the mixture was heated under reflux overnight. Evaporation of the solvent and repeated recrystallization from dichloromethane/pentane (1:1) at 5 °C gave air stable orange plates in low yield. IR (KBr pellets, $cm^{-1}$): 2040/2020, 1748/1781. $^1H$ NMR ($CDCl_3$): $\delta$ 3.99 (d, $^3J_{PH} = 13$ Hz, $POCH_3$)/ 4.05 (d, $^3J_{PH} = 11$ Hz, $POCH_3$); 7.54−9.65 (m, $H^{bpy}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 102.1/104.7 (s). Anal. Calcd for $C_{15}H_{19}ClN_3O_8$ $PSF_3Re$ (*M* 710.85): Re, 36.86. Found: Re, 36.63.

**[Bipyridine(carbonyl)chloronitrosyl(trimethylphosphane)rhenium-(I)] Trifluoromethanesulfonate (3b).** A dichloromethane solution of **2b** was added to 93 mg (0.6 mmol) of 2,2′-bipyridine in 5 mL of dichloromethane, and after bring heated at reflux overnight, the mixture was treated further as for the $P(OMe)_3$-substituted complex. IR (KBr pellets, $cm^{-1}$): 2020/1997, 1738/1760. $^1H$ NMR ($CDCl_3$): $\delta$ 1.24/1.26 (m, $PCH_2CH_3$), 2.36/2.36 (m, $PCH_2CH_3$), 7.25−9.55 (m, $H^{bpy}$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta$ 7.3/9.8 (s, $PCH_2CH_3$); 17.6/17.3 (d, $^1J_{PC} = 33/33$ Hz, $PCH_2CH_3$); 120.8 (q, $^1J_{CF} = 321$ Hz, $O_3SCF_3$); 122.8, 125.4, 125.6, 125.8, 126.2, 128.1, 128.6, 128.8, 140.1, 141.0, 142.3, 142.9, 148.6, 151.0, 153.4, 154.4, 154.7, 155.4, 155.6, 156.5 ($C^{bpy}$); 200.5 (d, $^2J_{PC} = 16$ Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −1.68/0.90 (s). Anal. Calcd for $C_{18}H_{23}O_5ClN_3PSF_3Re$ (*M* 702.88): C, 30.76; H, 3.27; N, 5.97; Re, 26.49. Found: C, 31.44; H, 3.30; N, 5.97; Re, 26.06.

**(*OC*-6-42)-Carbonylchloronitrosyl(trifluoromethanesulfonato)bis-(trimethyl phosphito)rhenium(I) (4a).** A solution of 110 mg (0.19 mmol) of **1a** in 10 mL of toluene and 50.2 mg (0.19 mmol) of $AgO_3SCF_3$ was heated under reflux for 3 h. The cooled suspension was filtered over Celite, and the filtrate was evaporated *in vacuo* to dryness. Recrystallization of the residue from boiling hexane gave yellow needles which were filtered off, washed with pentane (2 × 10 mL), and dried *in vacuo*. Yield: 103 mg (86%). IR (KBr pellets, $cm^{-1}$): 2041, 1770. $^1H$ NMR ($C_6D_6$): $\delta$ 3.4 (t, $^3J_{PH} = 8$ Hz, 18H, $POCH_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $C_6D_6$): $\delta$ 53.6 (s, $POCH_3$); 119.6 (q, $^1J_{CF} = 316$ Hz, $O_3SCF_3$); 196.0 (t, $^2J_{PC} = 12$ Hz, CO). $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ 104.9 (s). $^{19}F$ NMR ($C_6D_6$): $\delta$ −77.2 (s). MS (EI): $m/z = 677$ ($M^+$), 649 ($M^+ - CO$), 524 ($M^+ - O_3SCF_3$). Anal. Calcd for $C_8H_{18}O_{11}P_2F_3NReS$ (*M* 641.30): C, 14.19; H, 2.66; N, 2.07; Re, 27.51. Found: C, 14.44; H, 2.72; N, 1.94; Re, 26.53.

**(*OC*-6-42)-Carbonylchloronitrosyl(trifluoromethanesulfonato)bis-(triethylphosphane)rhenium (4b).** A solution of 120 mg (0.21 mmol) of **1b** in 8 mL of toluene and 86 mg (0.21 mmol) of $AgO_3SCF_3$ were heated under reflux for 50 min. A treatment similar to that for **1a** gave yellow needles, which were filtered off, washed with pentane (2 × 10 mL), and dried *in vacuo*. Yield: 120 mg (87%). IR (KBr pellets, $cm^{-1}$): 1998, 1744. $^1H$ NMR ($C_6D_6$): $\delta$ 0.83 (d × t, $^3J_{HH} = 7$ Hz, $^3J_{PH} = 16$ Hz, 18H, $PCH_2CH_3$); 1.87 (m, 12H, $PCH_2CH_3$). $^{13}C\{^1H\}$ NMR (50.3MHz, $C_6D_6$): $\delta$ 7.78 (s, $PCH_2CH_3$); 16.05 (d, $J_{PC} = 30$ Hz, $PCH_2CH_3$); 119.7 (q, $^1J_{CF} = 318$ Hz, $O_3SCF_3$); 205 (t, $^2J_{PC} = 8$ Hz, CO). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 4.4 (s). $^{19}F$ NMR ($C_6D_6$): $\delta$ −77.39 (s). MS (EI): $m/z = 665$ ($M^+$), 637 ($M^+ - CO$), 521 ($M^+ - O_3SCF_3$). Anal. Calcd for $C_{14}H_{30}O_5P_2F_3NReS$ (*M* 629.36): C, 25.29; H, 4.51; N, 2.10; Cl, 5.33; Re, 28.01. Found: C, 25.51; H, 4.82; N, 2.02; Cl, 5.48; Re, 27.83.

**(*OC*-6-13)-Carbonylnitrosylbis(trifluoromethanesulfonato)bis-(trimethyl phosphito)rhenium(I) (5a).** A solution of 1 g (1.77 mmol) of **1a** and 0.95 g (3.7 mmol) of $AgO_3SCF_3$ in 80 mL of toluene was heated under reflux for 10 h. After this time the mixture was allowed to cool to room temperature and filtered over Celite. After washing with 3 × 5 mL toluene, the collected solutions were reduced to 5 mL *in vacuo* and 7 mL hexane was added. On cooling to −20 °C, yellow needles were formed after 14 h. They were washed with 2 × 5 mL hexane and dried *in vacuo* overnight. Yield: 0.98 g (71%). IR (KBr pellets, $cm^{-1}$): 2047, 1802. $^1H$ NMR ($C_6D_6$): $\delta$ 3.4 (t, $^3J_{PH} = 11$ Hz, 18H, $POCH_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $C_6D_6$): $\delta$ 54.1 (s, $POCH_3$); 119.3 (q, $^1J_{CF} = 318$ Hz, $O_3SCF_3$); 119.6 (q, $^1J_{CF} = 318$ Hz, $O_3SCF_3$); 193.3 (t, $^2J_{CP} = 11$ Hz, CO). $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ 110.0 (s). $^{19}F$ NMR ($C_6D_6$): $\delta$ −77.0 (s); −76.9 (s). MS (EI): $m/z = 790$ ($M^+$), 614 ($M^+ - O_3SCF_3 - CO$). Anal. Calcd for $C_9H_{18}F_6NO_{14}SP_2Re$ (*M* 758.31): C, 13.67; H, 2.27; N, 1.77; Re, 23.56. Found: C, 13.60; H, 2.34; N, 1.98; Re, 23.16.

**(*OC*-6-13)-Carbonylnitrosylbis(trifluoromethanesulfonato)bis-(triethylphosphane)rhenium(I) (5b).** A solution of 2 g (3.63 mmol) of **1b** and 1.95 g (7.62 mmol) of $AgO_3SCF_3$ in 60 mL of toluene was heated under reflux for 10 h. The mixture was allowed to cool to room temperature and filtered over Celite. After removal of the solvent *in vacuo*, the product was extracted with dichloromethane (2 × 7 mL) and filtered through Lichroprep. Evaporation *in vacuo* gave a yellow powder which was sufficiently pure for further reactions. Yellow needles could be obtained by cooling a concentrated hot toluene solution to room temperature. Yield: 2.35 g (85%). IR (KBr pellets, $cm^{-1}$): 2012, 1770. $^1H$ NMR ($C_6D_6$): $\delta$ 0.80 (d × t, $J_{PH} = 16$ Hz, $J_{HH} = 8$ Hz, 18H, $PCH_2CH_3$); 1.96 (m, 12H, $PCH_2CH_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $C_6D_6$): $\delta$ 7.21 (s, $PCH_2CH_3$); 15.57 (d, $^1J_{PC} = 29$ Hz, $PCH_2CH_2$); 119.0 (q, $^1J_{CF} = 318$ Hz, $O_3SCF_3$); 119.3 (q, $^1J_{CF} = 318$ Hz, $O_3SCF_3$); 202.1 (t, $^2J_{PC} = 6$ Hz, CO). $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ 10.9 (s). $^{19}F$ NMR ($C_6D_6$): $\delta$ −76.62 (s); −76.92 (s). MS (EI): $m/z = 779$ ($M^+$); 630 ($M^+ - O_3SCF_3$). Anal. Calcd for $C_{15}H_{30}O_8P_2F_6$-

---

(4) (a) Hollis, T. K.; Robinson, N. P., Bosnich, B. *Organometallics* **1992**, *11*, 2745. (b) Hollis, T. K.; Odenkirk, W.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Tetrahedron* **1993**, *49*, 5415.

(5) Nitschke, J.; Schmidt, S. P.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 1972.

(6) Hund, H.-U.; Ruppli, U.; Berke, H. *Helv. Chim. Acta* **1993**, *76*, 963.

NReS$_2$ ($M$ 778.43): C, 23.14; H, 3.85; N, 1.79; Re, 23.92. Found: C, 24.70; H, 4.30; N, 1.62; Re, 23.52.

**(*OC*-6-13)-[Bis(acetonitrile)carbonylnitrosylbis(trimethyl phosphito)rhenium(I)] Bis(trifluoromethanesulfonate) (6a).** A solution of 50 mg (0.063 mmol) of **5a** in 5 mL of acetonitrile was stirred at room temperature for 5 days. The solution was reduced *in vacuo* to 1 mL of and 2 mL diethyl ether was added. Cooling to −20 °C resulted in the precipitation of yellow needles, which were dried in a stream of N$_2$. Yield: 50.6 mg (92%). IR (KBr pellets, cm$^{-1}$): 2072, 1826. $^1$H NMR ($CD_2Cl_2$): $\delta$ 2.76 (t, $^5J_{PH} = 2$ Hz, 3H, $CH_3CN$); 2.89 (sbr, 3H, $CH_3CN$); 4.0 (t, $^3J_{PH} = 6$ Hz, 18H, $POCH_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CD_3CN$): $\delta$ 4.82 (s, $\mathit{C}H_3CN$); 4.90 (s, $\mathit{C}H_3CN$); 55.95 (t, $^2J_{PC} = 3$ Hz, $POCH_3$); 122.02 (q, $^1J_{CF} = 320$ Hz, $CF_3SO_3$); 130.21 (s, $CH_3\mathit{C}N$); 133.46 (s, $CH_3\mathit{C}N$); 189.52 (t, $^2J_{PC} = 11$ Hz, CO). $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$ 101.4 (s). MS (EI): $m/z = 791$ ($M^+ - 2CH_3CN$). Anal. Calcd $C_{13}H_{24}O_{14}P_2F_6N_3ReS_2$ ($M$ 872.41): C, 17.90; H, 2.75; N, 4.81; Re, 21.32. Found: C, 18.27; H, 2.90; N, 4.65; Re, 21.25.

**(*OC*-6-13)-[Bis(acetonitrile)carbonylnitrosylbis(triethylphosphane)rhenium(I)] Bis(trifluoromethanesulfonate) (6b).** A solution of 1 g (1.28 mmol) of **5b** in 20 mL of $CH_3CN$ was stirred for 20 h at room temperature. After evaporation of the solvent, the addition of 2 mL of THF caused sudden crystallization of the product. Cooling to −20 °C for 14 h induced further precipitation of yellow microcrystals, which after washings with diethyl ether (2 × 5 mL) were dried in a stream of N$_2$. Yield: 0.85 mg (77%). IR (KBr pellets, cm$^{-1}$): 2040, 1793. $^1$H NMR (THF-$d_8$): $\delta$ 1.20 (d × t, $^3J_{PH} = 16$ Hz, $^3J_{HH} = 7$ Hz, 18H, $PCH_2CH_3$); 2.28 (m, 12H, $PCH_2CH_3$); 2.73 (s, 3H, $CH_3CN$); 2.89 (s, 3H, $CH_3CN$). $^{13}C\{^1H\}$ NMR (50.3 MHz, THF-$d_8$): $\delta$ 1.00 (s, $\mathit{C}H_3CN$); 4.97 (s, $\mathit{C}H_3CN$); 7.25 (s, $PCH_2\mathit{C}H_3$); 15.95 (t, $^2J_{PC} = 28$ Hz, $P\mathit{C}H_2CH_3$); 120.7 (q, $^1J_{CF} = 318$ Hz, $CF_3SO_3$); 130.70 (s, $CH_3\mathit{C}N$); 133.63 (s, $CH_3\mathit{C}N$); 194.8 (sbr, CO). $^{31}P\{^1H\}$ NMR (THF-$d_8$): $\delta$ 4.68 (s). MS (EI): $m/z = 630$ ($M^+ - 2CH_3CN - O_3SCF_3$), 602 ($M^+ - 2CH_3CN - O_3SCF_3 - CO$). Anal. Calcd for $C_{19}H_{36}P_2N_3O_8SF_3Re$ ($M$ 771.42): C, 26.52; H, 4.18; N, 4.88; Re, 21.64. Found: C, 27.36; H, 4.30; N, 4.75; Re, 21.43.

**{Re(bpy)[P(O)(OMe)$_2$(CO)(NO)}$_2$[O$_3$SCF$_3$]$_2$ (7).** Heating of a solution of 34 mg (0.22 mmol) of 2,2′-bipyridine and 130 mg (0.16 mmol) of **5a** in 15 mL toluene for 14 h under reflux resulted in the precipitation of an orange solid. After cooling to room temperature the solution was decanted and the product was extracted with 3 mL of acetonitrile. Addition of 1 mL of diethyl ether caused the precipitation of [bpyCH$_3$][O$_3$SCF$_3$] at −20 °C. After filtration and addition of 1 mL pentane at room temperature, the solution was cooled to −20 °C. Orange prisms were isolated, washed with diethyl ether (3 x 5 mL), and dried *in vacuo*. Yield: 94 mg (90%). IR (KBr pellets, cm$^{-1}$): 2037, 1764. $^1$H NMR ($CDCl_3$): $\delta$ 3.02 (d, $^3J_{PH} = 12$ Hz, 6H, $POCH_3$), 3.36 (d, $^3J_{PH} = 12$ Hz, 6H, $POCH_3$), 7.8−9.4 (m, $H^{bpy}$, 8H). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta$ 51.9 (d, $^3J_{PH} = 9$ Hz, $POCH_3$); 52.8 (d, $^3J_{PH} = 6$ Hz, $POCH_3$); 120.7 (q, $^1J_{CF} = 318$ Hz, $CF_3SO_3$); 155.5, 156.8, 157.3, 158.5 (s, $C^{bpy}$); 199.3 (d, $^2J_{PC} = 12$ Hz, CO). $^{31}P\{^1H\}$ NMR ($CD_3CN$): $\delta$ 96.4 (s). Anal. Calcd for $C_{28}H_{28}N_6O_{16}P_2S_2F_6Re_2$ ($M$ 1316.78): C, 25.54; H, 2.12; N, 6.38; Re, 28.28. Found: C, 25.72; H, 2.28; N, 6.19; Re, 27.68.

**(*OC*-6-13)-Tricarbonylbis(triethylphosphane)(trifluoromethanesulfonato)rhenium (I) (8).** A solution of 200 mg (0.34 mmol) of *mer*-Re(CO)$_3$(PEt$_3$)$_2$Br and 88 mg (0.35 mmol) of AgO$_3$SCF$_3$ in 15 mL of dichloromethane was heated at reflux. After 18 h the solution was allowed to cool to room temperature and then the volume was reduced to 3 mL. Addition of 15 mL of pentane and allowing the mixture to stand at −20 °C gave colorless needles. Yield: 153 mg (62%). IR (KBr pellets, cm$^{-1}$): 2025, 1937. $^1$H NMR ($C_6D_6$): $\delta$ 0.66−0.96 (m, $PCH_2CH_3$); 1.72−1.79 (m, $PCH_2CH_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, $C_6D_6$): $\delta$ 7.67 (s, $PCH_2\mathit{C}H_3$); 19.10 (t, $^3J_{PC} = 15$ Hz, $P\mathit{C}H_2CH_3$); 118.58 (q, $^1J_{CF} = 318$ Hz, $CF_3SO_3$); 193.44 (sbr, CO cis OTf); 195.47 (t, $^2J_{CP} = 9$ Hz, CO trans OTf). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 6.75 (s). MS (EI): $m/z = 656$ ($M^+$); 628 ($M^+ - CO$); 600 ($M^+ - 2CO$); 571 ($M^+ - 3CO$); 507 ($M^+ - O_3SCF_3$). Anal. Calcd for $C_{22}H_{30}O_6F_3SP_2Re$ ($M$ 727.39): C, 36.32; H, 4.12; Re, 28.41. Found: C, 30.82; H, 5.11; Re, 25.53.

**(*OC*-6-13)-[Bipyridinedicarbonylbis(triethylphosphane)rhenium(I)] Trifluoromethanesulfonate (9).** A solution of 450 mg (0.68 mmol) of **8** and 110 mg (0.7 mmol) of 2,2′-bipyridine in 30 mL of toluene was heated under reflux for 4 days. Then the solvent was removed *in vacuo*, the product extracted with 100 mL of dichloromethane, and the extract concentrated to a volume of a few milliliters and transfered to a chromatography column with silica as the stationary phase. Elution with dichloromethane/acetonitrile (2/1) gave an orange solution, which was reduced to 5 mL *in vacuo*. Addition of diethyl ether at −30 °C afforded fine orange needles. Yield: 214 mg (44%). IR (KBr pellets, cm$^{-1}$): 1923 s, 1835 s, 1603 brm. $^1$H NMR ($CD_2Cl_2$): $\delta$ 0.83 (m, 18H, $PCH_2CH_3$); 1.42 (m, 12H, $PCH_2CH_3$); 7.77 (m, 2H, $H5^{bpy}$); 8.22 (m, 2H, $H4^{bpy}$); 8.68 (m, 2H, $H3^{bpy}$); 9.04 (m, 2H, $H6^{bpy}$). $^{13}C\{^1H\}$ NMR (50.3MHz, $CD_2Cl_2$): $\delta$ 7.50 (s, $PCH_2\mathit{C}H_3$); 17.37 (t, $^1J_{PC} = 29$ Hz, $P\mathit{C}H_2CH_2$); 122.20 (q, $^1J_{CF} = 318$Hz, $CF_3SO_3$); 125.42 (s), 127.71 (s), 139.76 (s), 152.66 (s), 155.77 (s): all $C^{bpy}$; 203.20 (sbr, CO). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ −2.37 (s). Anal. Calcd for $C_{25}H_{35}N_2O_5F_3SP_2Re$ ($M$ 783.45): C, 38.32; H, 4.85; N, 3.50; Re, 23.76. Found: C, 38.06; H, 4.78; N, 3.78; Re, 23.52.

**Table 1.** IR Data for Complexes **1**−**9** (KBr Pellets, cm$^{-1}$)

| compd | $\nu$(CO) | $\nu$(NO) | $\nu$(CN), $\nu$(PO) |
|---|---|---|---|
| **1a** | 2025$^a$ | 1748$^a$ | |
| **1b** | 1990$^a$ | 1728$^a$ | |
| **2a** | 2053$^b$ | 1778$^b$ | |
| **2b** | 2034$^b$ | 1760$^b$ | |
| **3a** | 2040/2020$^c$ | 1748/1781$^c$ | |
| **3b** | 2020/1997$^d$ | 1737/1760$^d$ | |
| **4a** | 2041 | 1770 | |
| **4b** | 1998 | 1744 | |
| **5a** | 2047 | 1802 | |
| **5b** | 2012 | 1767 | |
| **6a** | 2072 | 1826 | 2331w, 2299w (CN) |
| **6b** | 2040 | 1793 | 2328w, 2296w (CN) |
| **7** | 2037 | 1764 | 1079 (P═O) |
| **8** | 2025, 1937, 1904 | | |
| **9** | 1918, 1835 | | |

$^a$ In $CH_2Cl_2$. $^b$ In $CH_3CN$. $^c$ Major component. $^d$ Minor component.

**Qualitative NMR Investigation of the Transformation of 5b to 6b.** An NMR tube was loaded with *cis,trans*-[Re(O$_3$SCF$_3$)$_2$(PEt$_3$)$_2$(CO)(NO)] (**5b**) (41.4 mg, 0.05 mmol) and $CD_3CN$ (0.7 mL) under an N$_2$ atmosphere. A $^{31}$P NMR spectrum of this sample was measured every 30 min at 25 °C until the conversion of **5b** to **6b** was complete and the signals for **A** (at 8.10 ppm) and **B** (at 7.05 ppm) had disappeared (15 h). The relative concentration of all species intervening in the reaction were determined by direct integration and referenced to the signal of **5b**.

**Crystal Structure Determinations.** All crystals measured were glued onto a glass fiber using epoxy resin and mounted to the diffractometer (Mo K$\alpha$, $\lambda = 0.710\,73$ Å). The unit cell parameters were determined and refined from a set of 24 equivalent reflections ($20° < 2\theta < 28°$). Data were collected through $\omega - 2\theta$ scans with variable scan speeds and a 0.9° scan width in all measurements. After every 97 collected reflections, three standard reflections were measured and only in **6a** was a decay of 15% in intensity observed. All the structures were solved using the SHELXTL PLUS program package,[7] the heavy atoms were located by the Patterson method and standard Fourier technique was used for the location of the remaining non-hydrogen atom positions in the molecules. All hydrogen atoms were included as fixed contributors in the calculation of the atomic positions. An empirical absorption correction (DIFABS[8] ) was employed for **5b**, **6a**, and **7**. The minimum/maximum residues found for all compounds were located in every case in the vicinity of the rhenium atoms. In **2b** the NO and Cl ligands showed some degree of disorder and were refined with a sof of 0.80. The disordered positions were extracted from the difference Fourier map and refinement with a sof of 0.20 provoked a decrease of the *R*-factor. In **5b** and **6a** the CO and NO positions are disordered as indicated by the equal Re−N, Re−C, and N−O, C−O distances, respectively, and by the temperature factors of the N- and C-atoms. The structure of **6a** could only be solved in the *C*2/*c* space group with the Re center in the special position 0, *y*, 0.25. A plane of

---

(7) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Clarendon Press: New York, 1985; p 175.

(8) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(9) Hund, U.-H. Ph.D. Thesis, University of Zürich, 1991.

**Table 2.** Crystallographic Data and Processing Parameters for the X-ray Diffraction Studies of Complexes **5b**, **7**, and **8**

| | **5b** | **7** | **8** |
|---|---|---|---|
| composition | $C_{15}H_{30}F_6NO_8P_2ReS_2$ | $C_{32}H_{34}F_6N_8O_{16}P_2Re_2S_2$ | $C_{16}H_{30}F_3O_6P_2ReS$ |
| cryst dim (mm) | 0.42 × 0.30 × 0.21 | 0.62 × 0.44 × 0.41 | 0.43 × 0.32 × 0.15 |
| fw | 778.7 | 1399.1 | 655.6 |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 9.066(2) | 9.158(3) | 8.287(3) |
| $b$ (Å) | 12.161(3) | 10.319(2) | 9.672(3) |
| $c$ (Å) | 12.759(3) | 14.641(4) | 16.429(6) |
| $\alpha$ (deg) | 88.01(2) | 103.54(2) | 94.86(3) |
| $\beta$ (deg) | 82.83(2) | 94.16(2) | 90.23(3) |
| $\gamma$ (deg) | 86.53(2) | 115.75(2) | 112.20(2) |
| $V$ (Å$^3$) | 1392.6(6) | 1187.3(5) | 1214.0(7) |
| $Z$ | 2 | 1 | 2 |
| $\rho_{calc}$ (g·cm$^{-3}$) | 1.857 | 1.957 | 1.794 |
| diffractometer used | Siemens R3m/V | Siemens R3m/V | Nicolet R3 |
| $T$ (K) | 298 | 233 | 298 |
| $\mu$ (mm$^{-1)}$ | 4.755 | 5.406 | 5.334 |
| $2\theta$ range (deg) | 3−50 | 4−56 | 4−50 |
| scan type | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ |
| scan speed (deg/min) | variable: 2.00/14.65 | variable: 2.39/14.7 | variable: 2.39/14.7 |
| no. of unique data | 4941 | 5718 | 4284 |
| no. of obsd data | 4503[b] | 5164[a] | 4010[a] |
| no. of parms. refin | 316 | 307 | 262 |
| $R^c$ | 2.82 | 2.92 | 2.81 |
| $R_w{}^d$ | 2.96 | 4.73 | 3.23 |
| goodness of fit | 2.24 | 3.61 | 2.98 |
| weight sch (1/$w$) | $\sigma^2(F) + 0.0000F^2$ | $\sigma^2(F) + 0.0000F^2$ | $\sigma^2(F) + 0.0000F^2$ |
| max/min resid dens (e·Å$^{-3}$) | 0.96/−0.74 | 1.09/−1.12 | 0.74/−1.06 |

[a] With $|F_o| \geq 6\sigma(|F_o|)$. [b] With $|F_o| \geq 4\sigma(|F_o|)$. [c] $\sum|F_o - F_c|/\sum F_o$. [d] $[\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **5b**

| | | | |
|---|---|---|---|
| Re−P1 | 2.493(1) | Re−P2 | 2.495(1) |
| Re−N1/C3 | 1.801(4) av. | Re−O4/O1 | 2.150(3) av. |
| S1−O1 | 1.474(3) | S1−O2 | 1.430(5) |
| S1−O3 | 1.419(5) | S2−O4 | 1.480(3) |
| S2−O5 | 1.419(4) | S2−O6 | 1.424(4) |
| P1−Re−P2 | 175.0(1) | O1−Re−O4 | 82.1(1) |
| Re−O1−S1 | 129.7(2) | Re−O4−S2 | 130.6(2) |

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for **7**

| | | | |
|---|---|---|---|
| Re1−P1 | 2.382(2) | Re1−N1 | 1.762(5) |
| Re1−N2 | 2.155(4) | Re1−N3 | 2.157(4) |
| Re1−O6 | 2.051(5) | Re1−C1 | 1.940(5) |
| P1−O3 | 1.578(6) | P1−O4 | 1.582(5) |
| P1−O6A | 1.514(4) | N1−O1 | 1.190(7) |
| C1−O2 | 1.133(7) | | |
| P1−Re1−N1 | 90.0(2) | P1−Re1−N2 | 100.3(1) |
| P1−Re1−O6 | 90.5(1) | P1−Re1−N3 | 170.7(1) |
| Re1−P1−O4 | 111.1(1) | Re1−P1−O6A | 118.2(2) |
| Re1−O6−P1A | 151.3(3) | Re1−N1−O1 | 177.2(5) |
| Re1−C1−O2 | 178.5(5) | | |

pseudosymmetry is thus passing between the CO, NO groups and the two acetonitrile ligands causing mutual reflection of these substituents. Table 2 lists details of crystal parameters, data collection and structure refinement. Selected bond lengths and bond angles are given in Tables 3, 4, and 6.

## Results and Discussion

**Reaction of *cis*,*trans*-[ReCl$_2$(PR$_3$)$_2$(CO)(NO)] (R = OMe (1a), R = Et (1b)) with Silver Triflate in Boiling Acetonitrile and Ligand Substitution with 2,2′-Bipyridine.** The starting compounds *cis*,*trans*-[ReCl$_2$(PR$_3$)$_2$(CO)(NO)] (R = OMe (**1a**), R = Et (**1b**)) are available via the reaction of [Re($\mu$-Cl)Cl(CO)$_2$(NO)]$_2$ with 4 equiv of PR$_3$ in high yield.[6] We attempted the reaction of these derivatives with 2 equiv of AgO$_3$SCF$_3$ in boiling acetonitrile which leads to the replacement of one chloride and one phosphorus donor generating isomers of [ReCl(NCCH$_3$)$_2$(PR$_3$)(CO)(NO)] [O$_3$SCF$_3$] complexes (R = OMe (**2a**), Et (**2b**), see Scheme 1).

**Table 5.** Selected Structural Data for Metal Complexes Bearing the Phosphonate Ligand

| | P=O (Å) | Re−P (Å) | M−P−O (deg) |
|---|---|---|---|
| [Re(bpy)(CO)(NO)[P($\mu$-O)(OMe)$_2$]]$_2$ (**7**) | 1.514(4) | 2.382(2) | 118.2(2) |
| [(CO)$_4$Mn[P($\mu$-O)Ph$_2$]]$_2$[25b] | 1.553(9) | | 114.7(3) |
| [(CO)$_4$Re[P($\mu$-O)Me$_2$]]$_2$[25a] | 1.53(2) | 2.470(7) | 114.2(7) |
| ReOCl(OMe)[P(O)(OMe)$_2$](PPh$_3$))$_2$[30a] | 1.488(7) | 2.420(2) | 120.5(3) |
| Re(Cp*)I(CO)$_2$[P(O)(OMe)$_2$][30b] | 1.471(14) | 2.417(5) | not reported |
| Os(C$_6$H$_6$)I[P(O)(OMe)$_2$]$_2$[30c] | 1.53(3)<br>1.50(3) | | 123(1)<br>122(1) |

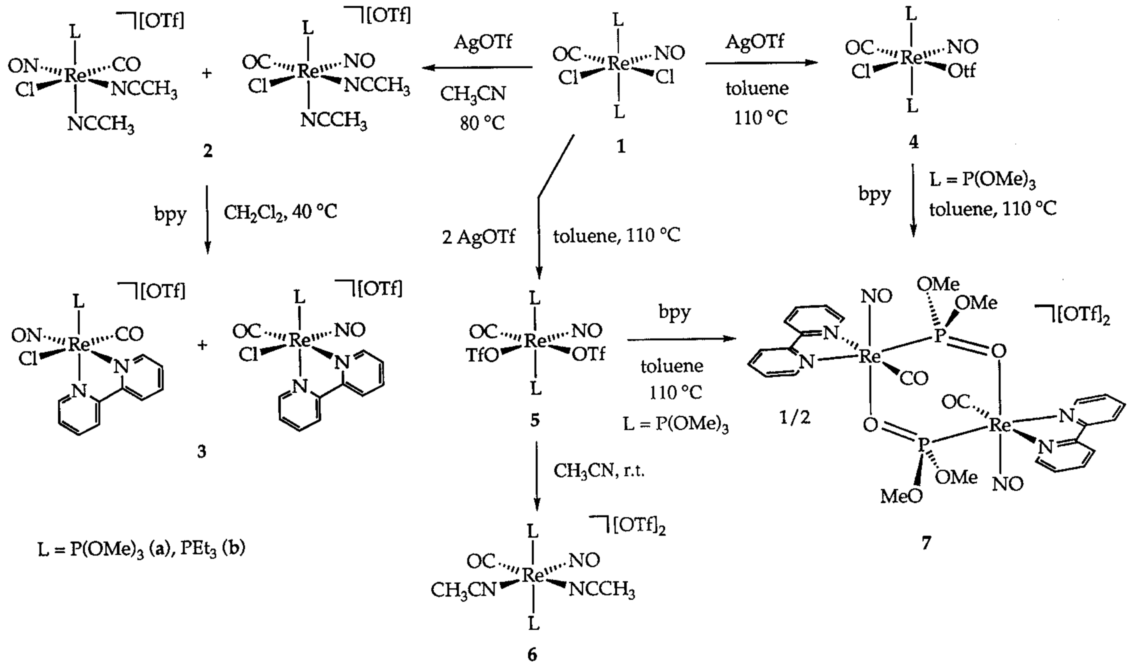
**Table 6.** Selected Bond Distances (Å) and Angles (deg) for **8**

| | | | |
|---|---|---|---|
| Re−P1 | 2.497(1) | Re−P2 | 2.507(2) |
| Re−O11 | 2.223(4) | Re−C1 | 1.922(4) |
| Re−C2 | 1.934(6) | Re−C3 | 1.856(5) |
| C1−O1 | 1.176(5) | C2−O2 | 1.166(7) |
| C3−O3 | 1.188(7) | S−O11 | 1.490(4) |
| S−O12 | 1.416(3) | S−O13 | 1.433(5) |
| P1−Re−P2 | 92.4(1) | | |
| Re−O11−S | 121.3(2) | Re−C1−O1 | 178.2(5) |
| Re−C2−O2 | 175.1(4) | Re−C3−O3 | 176.5(5) |

The change of the reagent ratio (2:1) has no influence on the course of the reaction. Compounds **2a** and **2b** are rather stable in acetonitrile; however, their isolation as pure solids proved to be difficult. This is probably due to facile loss of the coordinated acetonitrile molecules, which can be confirmed by $^1$H NMR spectroscopy. In fact, when crude **2a** or **2b** is dissolved in THF or acetone the intensity of the resonances assigned to coordinated acetonitrile groups decreases, while the signal of free acetonitrile increases. For this reason the spectroscopic analyses of **2a** and **2b** were carried out with crude material in CD$_3$CN or CH$_3$CN.

The IR spectra of **2a** and **2b** show single $\nu$(CO) and $\nu$(NO) bands which are typical of the *cis*-{Re(CO)(NO)} fragment (see Table 1). However in the $^{31}$P NMR spectrum two distinguished

**Scheme 1**



singlet signals are detected for each type of complex (**2a**, major 98.8 ppm, minor 98.3 ppm; **2b**, major −1.3 ppm, minor −2.3 ppm), which confirm the presence of two isomers in an approximate 2:1 ratio. In the $^{13}$C NMR spectrum coordinated acetonitrile ligands display two distinct doublets shifted by about 0.5 ppm with respect to free acetonitrile. Apparently this coupling arises from the interaction with only one phosphorus ligand of **2a** or **2b**.

Attempts to prepare crystals of **2b** were finally successful and it was possible to isolate a few yellow prisms from an acetonitrile/diethyl ether solution at room temperature. One of these proved to be suitable for a single-crystal X-ray diffraction study. The asymmetric unit of **2b** consists of a disordered enantiomeric pair of one diastereomer and contains noncoordinating triflate counterions. The isolation of crystals of the other diastereomer was not possible.

The structure of the cation of **2b** is shown in Figure 1. Further characterization of this isomeric mixture was attempted chemically by the preparation of more stable derivatives of **2a** and **2b**, assuming that the acetonitrile substitution in **2a** and **2b** would proceed with retention of configuration at the Re center. Thus, **2a** and **2b** were reacted with excess 2,2′-bipyridine in boiling dichloromethane. After 14 h the reaction was completed (IR monitoring) and orange prisms of [ReCl(PR$_3$)(CO)(bpy)(NO)][O$_3$SCF$_3$] (R = OMe (**3a**), Et (**3b**)) were isolated by repeated crystallization of the crude products (Scheme 1). Independent of the kind of the phosphorus donor substituent, the solid state IR spectra of these compounds showed doubling of the $\nu$(CO) and $\nu$(NO) bands (see Table 1) stressing the presence of two isomers in an approximate 2:1 ratio. The same ratio of isomers was also detected in the $^{31}$P (for **3a**, major 104.7 ppm, minor 102.1 ppm; for **3b**, major −1.68 ppm, minor 0.90 ppm) and in the $^{1}$H NMR spectra. All attempts to separate the isomers of **3a** and **3b** by chromatography or to enrich one of them by fractional crystallization were unsuccessful.[10]

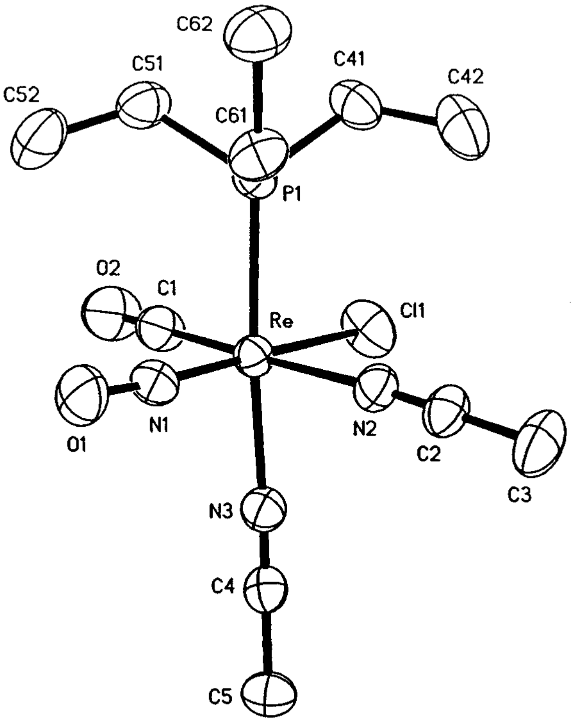


**Figure 1.** Molecular structure of the cation of [ReCl(CH$_3$CN)$_2$(PEt$_3$)(CO)(NO)][O$_3$SCF$_3$] (**2b**). Ellipsoids are drawn with 20% probability.

**Reaction of *cis,trans*-[ReCl$_2$(PR$_3$)$_2$(CO)(NO)] with Silver Triflate in Toluene.** The reaction of **1a** and **1b** with 1 equiv of AgO$_3$SCF$_3$ in boiling toluene afforded the monosubstituted *trans*-[ReCl(O$_3$SCF$_3$)(PR$_3$)$_2$(CO)(NO)] complexes (R = OMe (**4a**), Et (**4b**)) in high yield (Scheme 1). With respect to **1a** and **1b**, the $\nu$(CO) and the $\nu$(NO) bands of **4a** and **4b** are shifted to higher wavenumbers, presumably as a result of a decreased electron density on the metal. In the $^{13}$C NMR spectra the $C_{CO}$ nuclei display triplets, which demonstrates the presence of two magnetically equivalent phosphorus atoms (for **4a**, 196.0 ppm; for **4b**, 205.1 ppm). This is confirmed in the $^{31}$P NMR spectrum by the presence of a singlet signal at 104.9 ppm for **4a** and 4.4 ppm for **4b**. In acetonitrile the triflate ligand in **4b** can apparently be replaced by solvent molecules. This causes a shift of the $\nu$(CO) absorption of about 20 cm$^{-1}$ (2022 cm$^{-1}$).

---

(10) A low quality crystal structure of 3a confirmed the proposed geometry. In the crystal framework the Cl, NO, and CO are disordered. The cell parameters are as follows: space group $P\bar{1}$, $a$ = 7.211(3) Å, $b$ = 13.273(6) Å, $c$ = 13.311(6) Å, $\alpha$ = 73.70(2)°, $\beta$ = 82.70(2)°, $\gamma$ = 75.02(2)°, $V$ = 1179.299) Å$^3$, $Z$ = 1.

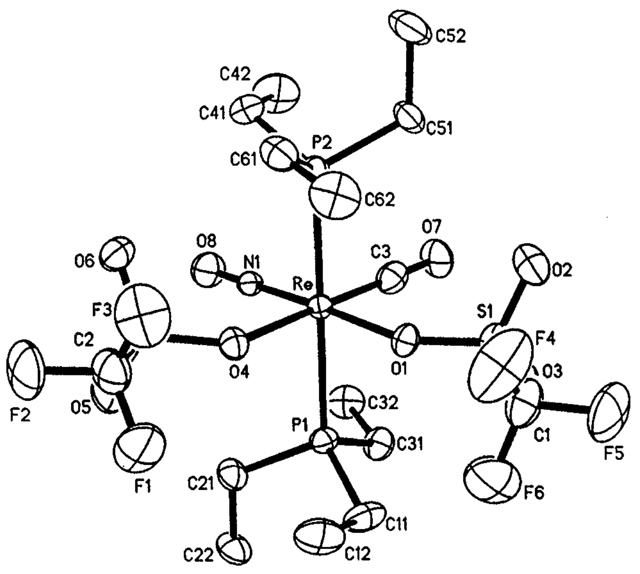


**Figure 2.** Molecular structure of Re($O_3SCF_3$)$_2$($PEt_3$)$_2$(CO)(NO) (**5b**). Ellipsoids are drawn with 30% probability.

However, the $\nu$(NO) band (1748 $cm^{-1}$) keeps its position with respect to **4b**. This indicates that the triflate groups in **4b** and also in **4a** are located trans to CO. Another support for this regioselectivity argument is provided by the X-ray diffraction study of *trans*-[ReCl($FBF_3$)($PEt_3$)$_2$(CO)(NO)],[11] which was obtained on a route comparable to **4b** by the reaction of **1b** with $AgBF_4$ and in which the CO and $BF_4$ groups are located trans.

The reaction of **1a** and **1b** with 2 equiv of $AgO_3SCF_3$ proceeded in boiling toluene to yield disubstituted *cis,trans*-[Re($O_3SCF_3$)$_2$($PR_3$)$_2$(CO)(NO)] complexes (R = OMe (**5a**), Et (**5b**)) (Scheme 1). The IR absorptions for the CO and NO ligands in **5a** and **5b** (Table 1) are observed at higher wavenumbers with respect to **1a** and **1b**, but display a smaller shift in comparison with **4a** and **4b**. This demonstrates a very weak M−CO, NO back-donation in these compounds. The chemical equivalence of the phosphorus donors in **5a** and **5b** is indicated by the occurrence of a singlet in the corresponding $^{31}P$ NMR (for **5a**, 110.6 ppm; for **5b** 10.9 ppm) and triplet signals for the CO substituents in the $^{13}C$ NMR spectra (**5a**, 193.3 ppm; **5b**, 202.1 ppm). Likewise in the $^{13}C$ NMR spectra the two coordinated triflate ligands are chemically inequivalent and appear as two quartets (119.3 ppm and 119.6 ppm for **5a**; 119.0 ppm and 119.3 ppm for **5b**). This also suggests that both triflate substituents do not exchange on the NMR time scale.

The crystal structure of **5b** was determined by an X-ray diffraction study (Figure 2). The Re center in **5b** has a pseudooctahedral environment with trans phosphorus donors. The CO and the NO ligand trans to the two triflate substituents are disordered. The Re atom, the CO and NO groups, and the oxygen atoms of the two terminally bound triflate ligands lie approximately in one plane (deviation average 0.04 Å). Significant bond lengths and angles are given in Table 3. The Re−P distances in **5b** (2.494(1) Å average) are about 0.05 Å longer than in an isoelectronic *cis,trans*-[$ReCl_2$($PEt_3$)$_2$(CO)(NO)][9] complex (2.440(2) Å average). The average value of the Re−O4,O1 distances (2.150 (3) Å) is found between those of *cis,fac*-[Re($O_3SCF_3$)($PEt_3$)$_2$(CO)$_3$] (**8**) (2.223(4) Å) and *cis,trans*-[Re[$O_3S(C_6H_4)CH_3$]$_2$ [P(OiPr)$_3$]$_2$(CO)(NO)][12] (2.107(5) Å average) and is similar to the value found in the aryloxy compound *cis,fac*-[Re[$O(C_6H_4)CH_3$]($PPh_3$)$_2$(CO)$_3$][13] (2.143(9) Å). The relative shortness of the Re−O distance in **5b** is explained by the presence of strong $\pi$-acceptors CO and NO in trans position to the triflate ligands. The $O_3SCF_3$ groups display the expected geometry observed for instance in the structures of Fe(Cp*)(CO)$_2$($O_3SCF_3$),[14] Zr(Cp)$_2$($O_3SCF_3$)$_2$(THF),[15] and Ti(Cp)$_2$($O_3SCF_3$)$_2$.[16] The distance of the sulfur atoms to the linking oxygens (O1 and O4) is about 0.05 Å longer than that to the terminal ones.

**Triflate Displacement in *cis,trans*-[Re($O_3SCF_3$)$_2$($PR_3$)$_2$(CO)(NO)] by Acetonitrile.** The formation of isomeric mixtures of **2a** and **2b** and of **3a** and **3b** in the chloride substitution processes described above indicated that the chloride abstraction in **1a** and **1b** does not proceed with regiospecificity trans to CO or NO. The complexes **1a** and **1b** and **5a** and **5b** are isostructural, and therefore by analogy, we intuitively expect that a triflate ligand replacement in **5a** and **5b** could occur competitively for both positions. The exchange of coordinated triflate ligands with acetonitrile is normally a facile process,[3] since the acetonitrile ligand is capable of forming quite stable complexes.[17] When **5a** and **5b** were reacted with acetonitrile at room temperature, a two-stage process was observed by IR and $^{31}P$ NMR spectroscopy. These reactions were completed after 5 d (**5a**) and 15 h (**5b**) (IR monitoring). The products of the 2-fold triflate replacements **6a** and **6b** were isolated by repeated recrystallizations from dichloromethane/pentane solutions (Scheme 1). **6b** is quite unstable at room temperature under $N_2$ even in the solid state and decomposes within 2−3 months. Under similar conditions **6a** is stable at room temperature. The solid state IR spectra of these complexes indicate the presence of coordinated nitriles, since they display two $\nu$(CN) bands in the region of 2350−2200 $cm^{-1}$ (see Table 1). Quite unexpectedly**,** the $\nu$(CN) bands of **6a** and **6b** were found at higher wavelengths in comparison with free acetonitrile (2249 $cm^{-1}$).[18] A shift to very high energies is also manifested for the $\nu$(CO), $\nu$(NO) IR absorptions, indicating extremely weak back-bonding to these ligands. So, for instance, the stretching frequency of the NO group in **6a** (1826 $cm^{-1}$) is rather close to that of the free $NO^+$ cation (1845 $cm^{-1}$).[18] The NMR data of **6a** and **6b** confirm the presence of {$ReL_2$(CO)(NO)} units. In the $^1H$ NMR spectrum at room temperature the two coordinated acetonitrile ligands are inequivalent and display broad singlets (**6a**, 2.76 ppm, 2.89 ppm; **6b**, 2.73 ppm, 2.89 ppm). In the corresponding $^{31}P$ NMR spectra both phosphorus atoms are chemically equivalent and exhibit singlets at 101.4 ppm for **6a** and 4.7 ppm for **6b**. The crystal structure analysis of **6a** (Figure 3) is in agreement with the spectroscopic data.

**Competitive Labilization Exerted by the CO and NO Ligands.** The substitution of the triflate ions in **5a** and **5b** are slow processes permitting the investigation of intermediate products. For this reason, the reaction from **5b** to **6b** was pursued in $CD_3CN$ by $^{31}P$ NMR spectroscopy. The evolution of the concentrations of the intervening species is plotted in Figure 4 as a function of time.

The two reaction intermediates **A** and **B** are considered to be isomeric monosubstituted *trans*-[Re($NCCH_3$)($O_3SCF_3$)$L_2$(CO)(NO)]$^+$ cations. The different slopes of the curves of **A** and **B** within the first 50 min suggests that there is no

---

(11) Nefedov, S. E.; Veghini, D.; Berke, H. Unpublished results.

(12) Eremenko, I. L.; Bakhmutov, V. I.; Ott, F.; Berke, H. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1993**, *38*, 1541.

(13) Simpson, R. D.; Bergman, R. G. *Angew. Chem.* **1992**, *104*, 209.

(14) Humprey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.

(15) Thewalt, U.; Lasser, W. Z. *Naturforsch.* **1983**, *38B*, 1501.

(16) Thewalt, U.; Klein, H.-P. *Z. Kristallogr.* **1980**, *153*, 307.

(17) (a) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, 1. (b) Chan, L. Y. Y.; Isaacs, E. E.; Graham, W. A. G. *Can. J. Chem.* **1977**, *55*, 111.

(18) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience Publication: New York, 1986.

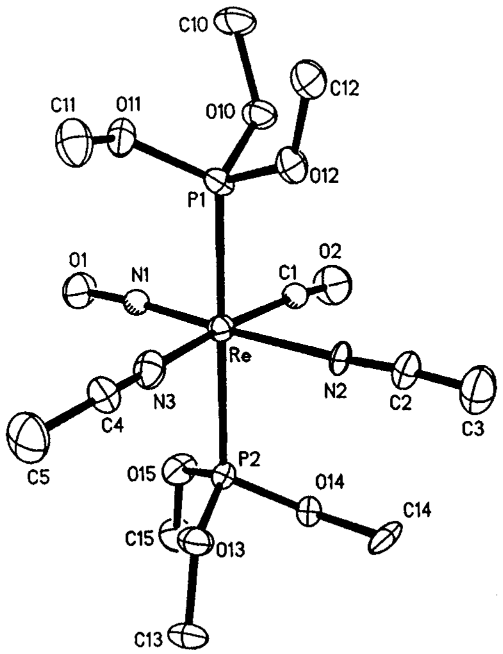


**Figure 3.** Molecular structure of $[Re(CH_3CN)_2[P(OMe)_3]_2(CO)(NO)][O_3SCF_3]_2$ (**6a**). Ellipsoids are drawn with 20% probability.

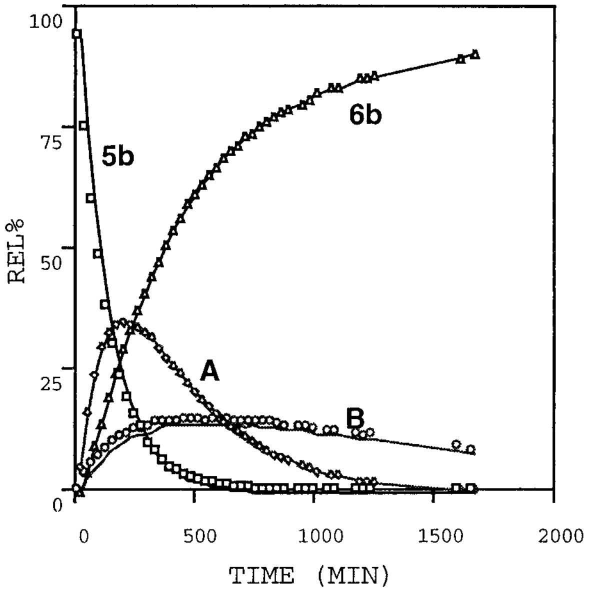


**Figure 4.** Reaction of $Re(O_3SCF_3)_2(PEt_3)_2(CO)(NO)$ (**5b**) with $CD_3CN$ in $CD_3CN$ at room temperature ($^{31}P$ NMR monitoring) The relative percent (*y* axis) gives the ratio of concentration of the observed species $C_i(t)$ with respect to the initial total concentration $C_0$.

equilibrium between them. This is expected for substitutionally inert complexes with $d^6$ configuration at the metal center. Intermediate **A** reacts significantly faster than **B**: after about 20 h (under NMR conditions), the concentration of **A** is close to zero, while 15% of the initial Re complex has been transformed into **B**. When the concentration of **A** is about zero after approximately 1300 min, **B** still is present in the reaction mixture in about 20% of the original amount. From this one may also conclude that there are independent reaction pathways for **A** and **B**. Trogler et al. reported[6] the kinetics of the triflate exchange by acetonitrile in $Re(CO)_5(OTf)$ under pseudo-first-order conditions which were, on a qualitative scale, significantly faster than the formation of the intermediate **A**. The retardation of the triflate exchange in **5a** and **5b** is apparently due to the phosphorus donor substitution and to the influence of the nitrosyl group.

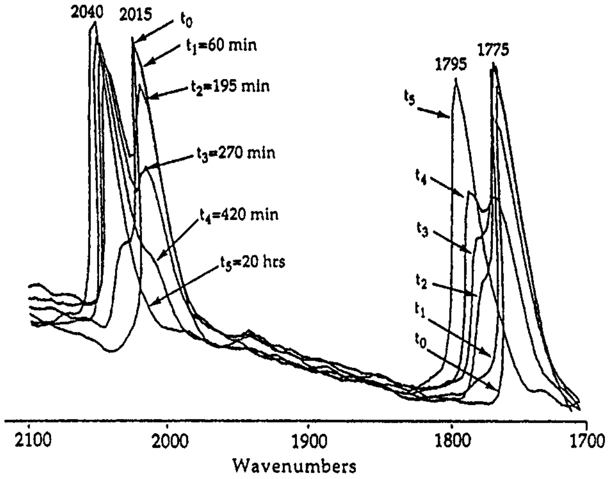
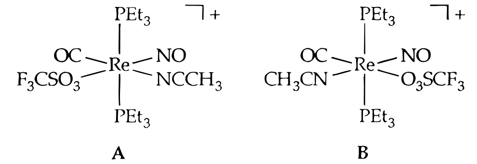


**Figure 5.** Evolution of the IR spectra of **5b** ($\nu$(CO) and $\nu$(NO) absorption region) during triflate ligand replacement with $CH_3CN$ in $CH_3CN$.

**Chart 1**



For the characterization of **A** and **B** we also took into account the shifts of the $\nu$(CO) and $\nu$(NO) bands to higher wavelengths, which are observable during the course of the reaction. Figure 5 shows a selection of IR spectra recorded at different stages of the reaction. Although all bands overlap, it is evident that the absorption bands of the carbonyl groups move faster to higher frequencies than those in the nitrosyl region. In fact at $t_4$, the $\nu$(CO) band corresponds almost completely to the absorption of **6b**, while the $\nu$(NO) band is still to the major part due to the starting material or the intermediates. This would again support the assumption of a faster triflate substitution trans to the CO ligand. Thus, we propose the following structural assignment shown in Chart 1 for **A** and **B**.

This conclusion parallels the insertion preference of CO into the Re−$CH_3$ bonds in *cis,trans*-$[Re(CH_3)_2(PEt_3)_2(CO)(NO)]$,[9] which occurs trans to the carbonyl ligand.

**Triflate Replacement in *cis,trans*-$[Re(O_3SCF_3)_2(PR_3)_2(CO)(NO)]$ by 2,2′-Bipyridine.** The $Re^I$ coordination chemistry of bipyridine derivatives has attracted great attention in the last 15−20 years, because of their potential photochemically and electrochemical applications.[19−21] This prompted quite a number of synthetic investigations of $Re^I$ bipyridine derivatives.[22] For a synthetic access to bpy compounds with the {Re(CO)(NO)} fragment, we have tried to utilize **5a** and **5b** as a starting material. There are quite a few reports where coordinated triflate ligands are replaced by 2,2′-bipyridine. For instance, incorporation of a third bipyridine ligand into cis-$[Ir(bpy)_2(OTf)_2]^+$ proceeds readily in ethylene glycol.[23] In the $d^6$

---

(19) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Sacksteder, L.; Lee, M.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1993**, *115*, 8230.

(20) (a) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790. (b) Mabrouk, P. A.; Wrighton, M. S. *Chem. Phys. Lett.* **1984**, *103*, 332.

(21) Ishitami, O.; George, M. W.; Ibusuki, T.; Johnson, F. P. A.; Koike, K.; Nozaki, K.; Pac, C.; Turner, J.; Westwell, J. R. *Inorg. Chem.* **1994**, *33*, 4712.

(22) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5238.

(23) Sullivan, B. P.; Meyer, T. J. J. *Chem. Soc., Chem. Commun.* **1984**, 403.

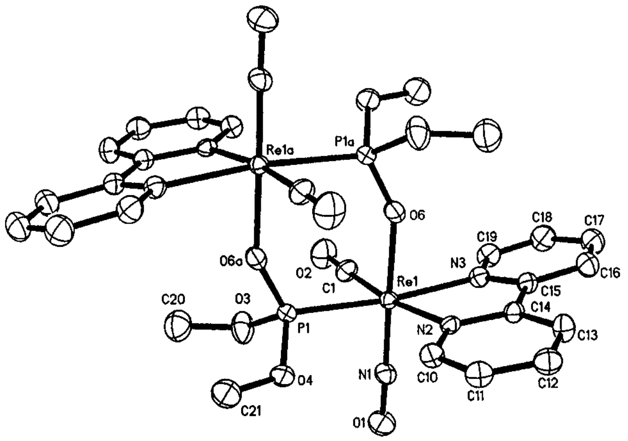


**Figure 6.** Molecular structure of $[Re(bpy)(CO)(NO)[PO(OMe]_2)]_2$-$[O_3SCF_3]_2$ (**7**). Ellipsoids are drawn with 30% probability.

ruthenium(II) dicarbonyl diimines, *cis*-$[Ru(CO)_2(L_2)(OTf)_2]$ ($L_2$ = phen, bpy), substitution by phen or bpy has been observed[24] to form $[Ru(CO)_2(L_2)_2][OTf]_2$. These dicationic products are obtained in high yield in boiling ethanol. By analogy, we attempted the reaction of **5a** and **5b** with 2,2′-bipyridine (Scheme 1).

The reaction of **5b** with 2,2′-bipyridine (approximate ratio 1:1) proceeds in boiling toluene with decomposition and leads to a variety of products. The use of more polar solvents like THF, nitromethane, or dibutyl ether had no influence on this reaction behavior. In contrast to this, the analogous reaction with **5a** revealed a new product, **7**, which was not air sensitive in either solid state or in solution and could readily be recrystallized from acetonitrile/ether solutions. In the solid state the IR absorption bands of the CO, NO groups in **7** are shifted to lower frequencies with respect to **5a** (Table 1) indicating enhanced back-bonding from the metal to these $\pi$ acids. An intense absorption band at 1079 $cm^{-1}$ was attributed to a P═O vibration.[18,25] In addition to this, the $^{31}P$ NMR spectrum of **7** displayed a singlet signal at 96 ppm, which remained unchanged from 10 to 80 °C. Both of these spectroscopic data are consistent with the presence of a phosphonite unit. The methyl groups of this moiety are chemically inequivalent and therefore appear as two doublet signals in the $^1H$ (3.02 and 3.36 ppm) and in the $^{13}C$ NMR spectra (51.9 and 52.8 ppm). The coordination of only one P donor per Re atom is indicated in the $^{13}C$ NMR spectrum by a doublet signal at 199.3 ppm, which was assigned to the CO ligands.

A concentrated acetonitrile/ether solution of **7** gave orange prisms at −20 °C, which were suitable for an X-ray diffraction study (Figure 6). The unit cell contains a dinuclear rhenium dication, two noncoordinating triflate anions, and two solvent molecules of acetonitrile. There is no apparent interaction between all these parts. The rhenium cation is built from two identical mononuclear fragments related by a crystallographic center of inversion. The core of it forms a planar heteronuclear six membered ring (deviation from planarity 0.005 Å), which consists of two rhenium atoms spaced by two $\{(MeO)_2P(O)\}$ fragments: Re1 is coordinated to P1 (Re−P1 2.381(2) Å) and to O6A (Re−O6A 2.051(5) Å). The coordinated bipyridine ligand is trans to P1 (through N3) and to CO (through N2, Re−C1 1.940(5) Å, C1−O2 1.133(7) Å) at equal distances from the metal center (2.156(4) Å). The nitrosyl ligand (Re−N1 1.762(5) Å and N1−O1 1.190(7) Å) is located cis to the CO group and trans to the oxygen atom O6 of the $\{(MeO)_2P(O)\}$ unit.

A selection of the bond distances and angles of **7** is given in Table 4. The pseudooctahedral environment of the Re center shows slight distortions, probably induced by the narrow bite angle (75.5(2)°) of the chelating bipyridine.[26] Significant deviations from linearity are observed in the OC−Re−N3 (172.1(2)°) and P1−Re−N2 (170.7(1)°) arrangements, while the $\{ON-Re-OP(OMe)_2R'\}$ fragment is practically linear (178.4(2)°). The driving force for the planarity of the heteronuclear ring may originate from the possibility of enhanced $\pi$ conjugation in conjunction with the presence of the $\pi$ acidic nitrosyl ligand trans to O6. Comparable $\{Re-O-P\}_2$ units were observed in the dinuclear complexes $\{(CO)_4Re[P(O)Me_2]\}_2$[25a] and $\{(CO)_4Mn[P(O)Ph_2]\}_2$.[25b] In these molecules no nitrosyl is present, and the six-membered heteronuclear rings are puckered. Moreover, the Re−OP distance in $\{(CO)_4Re[P(O)Me_2]\}_2$[25a] is significantly longer than that in **7** (2.164(18) Å vs 2.054(5) Å in **7**). The double bond nature of the P═O fragment in **7** is also indicated by the P−O6 distance (1.514(4) Å), which is about 0.05 Å shorter than the average bond lengths for P−O3,O4 (1.580(6) Å). This shortening is consistent with the position of the corresponding IR band at relatively high wavenumbers.

Table 5 compares some structural data for metal complexes bearing the phosphonate ligand. In dinuclear compounds with coordinated phosphoryl units, the P═O bond is generally elongated with respect to the free molecules of this type. In addition to this the dinuclear species reported in Table 5 show M−P−O angles less than 120°. In mononuclear complexes they always have 120° or greater values.

The assembly of **7** from mononuclear units apparently took place with a high degree of stereoselectivity. In fact, in **7** the NO substituent is selectively trans to the P═O group. As we described previously, the replacement of a triflate ligand in **5** occurs faster trans to CO. Under the relative drastic reaction conditions applied (boiling toluene), it is assumed that other reaction channels become available and that one phosphorus donor and one triflate are now preferably replaced by bpy forming the intermediate cationic enantiomers of $[Re(O_3SCF_3)(bpy)[P(OMe)_3](CO)(NO)]^+$ (**I**). They display a structure closely related to **3a**. The formation of the phosphonite ligand is supposed to occur by an Arbuzov dealkylation process of the coordinated phosphite[27] in **I**, which leads to enantiomers of $Re(O_3SCF_3)(bpy)[P(\mu-O)(OMe)_2](CO)(NO)$ (**II**) and $CH_3O_3SCF_3$. Normally an Arbuzov reaction is induced by soft Lewis bases like $I^-$, $Br^-$, or amines; the possibility that the softer bpy molecule functions as a base is in contradiction with the observation that the reaction of **5a** with an 1:1 stoichiometric amount of bpy affords **7** in around 90% yield. It cannot be excluded that bpy catalyzes the Arbuzov reaction of **5a**, but certainly it is not participating in stoichiometric quantity. However, when a large excess of bpy is applied, $[bpyCH_3][O_3SCF_3]$ can be separated from **7** by fractional crystallization; it could in this case arise from the subsequent reaction of bpy with $CH_3O_3SCF_3$. Another interesting point is the self-recognition process of the two phosphonite containing enantiomers **II**, which leads to a meso-form of **7**. This selectivity is probably dictated by steric reasons. In fact, if two molecules

---

(24) (a) Black, D. S. C.; Deacon, G. B.; Thomas, N. C. *Aust. J. Chem.* **1982**, *35*, 2445; (b) *Trans. Met. Chem.* **1980**, *5*, 317; (c) *Polyhedron* **1983**, *2*, 409.

(25) (a) Mundig, G.; Schilling, B.; Weishaupt, M.; Lindner, E.; Strähle, J. *Z. Anorg. Allg. Chem.* **1977**, *437*, 169. (b) Hoehne, S.; Lindner, E.; Schilling, B. *J. Organomet. Chem.* **1977**, *139*, 315. (c) Mronga, N.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1983**, *502*, 35. (d) Boone, B. J.; Jablonski, C. R.; Jones, P. G.; Newlands, M. J.; Yu, Y. *Organometallics* **1993**, *12*, 3042.

(26) (a) Arbuzov, B. A. *Pure Appl. Chem.* **1964**, *9*, 307. (b) Brill, T. B.; Landon, S. J. Chem. Rev. **1984**, *84*, 577.

(27) Civitello, E. R.; Dragovitch, P. S.; Karpishin, T. B.; Novick, S. G.; Bierach, G.; O'Connell, J. F.; Westmoreland, T. D. *Inorg. Chem.* **1993**, *32*, 237.

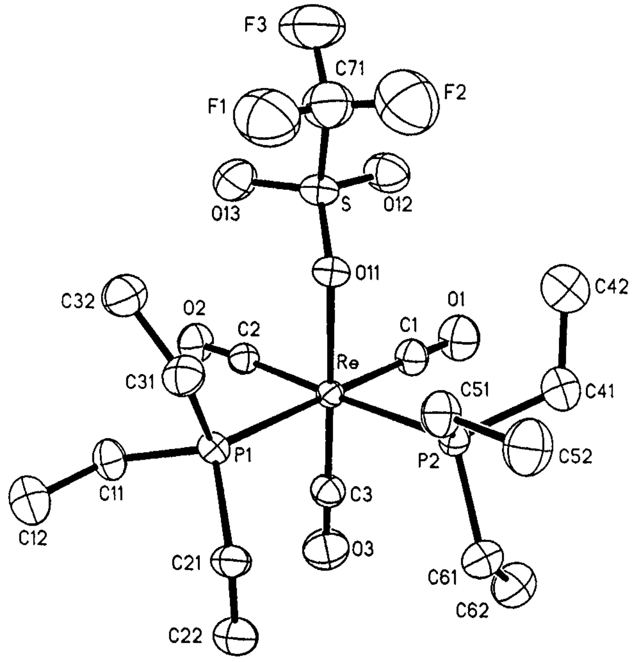


**Figure 7.** Molecular structure of $Re(O_3SCF_3)(PEt_3)_2(CO)_3$ (**8**). Ellipsoids are drawn with 40% probability.

of **II** with the same configuration combine, the resulting isomer is expected to suffer from steric repulsions between the aromatic bpy ligand, the heteronuclear six-membered ring and the P substituents. Additional evidence for this idea is provided by the reaction of **4a** with 2,2′-bipyridine, which, under the same reaction conditions as for **5a**, leads to formation of a cation structurally related to **7**.

The stability of **5b** may be related to the presence of the nitrosyl ligand. Therefore it was sought to prepare a $Re(O_3SCF_3)(PEt_3)_2(CO)_3$ complex where the nitrosyl and one triflate ligands of **5b** are replaced by two carbonyl groups and to comparatively investigate its reactivity toward 2,2′-bipyridine.

**Reaction of *cis,fac*-[Re(O₃SCF₃)(PEt₃)₂(CO)₃] (8) with 2,2′-Bipyridine.** The halide replacement in *trans,mer*-$[ReCl(PEt_3)_2(CO)_3]$ with $AgO_3SCF_3$ proceeds readily in boiling dichloromethane. *cis,mer*-$[Re(O_3SCF_3)(PEt_3)_2(CO)_3]$ (**8**) is isolated in 65% yield (eq 1).

$$ReCl(CO)_3(PEt_3)_2 \xrightarrow[CH_2Cl_2,\ 40\ °C]{AgO_3SCF_3,\ -AgCl} Re(O_3SCF_3)(CO)_3(PEt_3)_2 \quad (1)$$

The spectroscopic data of **8** are very similar to those of the analogous *cis,fac*-$[Re(O_3SCF_3)(PMe_3)_2(CO)_3]$ complex reported by Bergman and Simpson,[13] which suggests that the phosphorus donors are cis to each other.

Various crystal structures of complexes of the type *cis,fac*-$[Re(OR)L_2(CO)_3]$ (L = P, As donors, R = alkyl, aryl) are reported in the literature.[13,28] However, to our knowledge, studies on triflate derivatives are still lacking. Therefore an X-ray diffraction study of **8** was carried out. In **8**, the Re center is octahedrally coordinated with minor deviations from the ideal geometry (Figure 7). Three CO groups occupy a face of the octahedron, while one triflate and two $PEt_3$ substituents complete the coordination sphere around the metal. Important bond distances and angles of **8** are reported in Table 6. The Re−C3 bond (1.856(5) Å, trans to the OTf group) is about 0.07 Å shorter than the average value for the other two Re−C bonds in **8** (1.934(6) Å and 1.922(4) Å) indicating an enhanced $\pi$ back bonding character in the Re−C3 interaction. The Re−OTf bond in **8** is significantly weaker than in the nitrosyl containing **5b** (2.223(4) Å in **8** vs 2.150(3) Å in **5b**). The S−O bond lengths in the triflate substituent are only sligthly affected by coordination, presumably because of the mostly ionic nature of the M−OTf interaction. The bond parameters of a majority of triflate containing complexes are indeed very similar.

The reaction of **8** with 2,2′-bipyridine proceeded with evolution of CO. After 4 days IR monitoring showed that the $\nu$(CO) bands of **8** had disappeared completely in the reaction mixture. Column chromatography and recrystallization afforded the orange product **9** in 44% yield (eq 2).

$$Re(O_3SCF_3)(CO)_3(PEt_3)_2 \xrightarrow[toluene,\ 110\ °C]{bpy,\ -CO} [Re(bpy)(CO)_2(PEt_3)_2][O_3SCF_3] \quad (2)$$

The IR spectrum of **9** shows two intense $\nu$(CO) absorption bands at 1918 and 1835 $cm^{-1}$, and its $^{13}C$ NMR spectrum exhibits a broad signal at 203.2 ppm, which indicates the presence of two symmetry related CO groups. The $^{31}P$ NMR spectrum displays a singlet at −2.4 ppm for the equivalent phosphorus donors. In the solid state IR spectrum of **9** the triflate group causes absorption bands at 1263 $cm^{-1}$, 1154 $cm^{-1}$ ($\nu_s$ ($SO_2$)) and 638 $cm^{-1}$ ($\delta_s$ ($SO_3$)) and which can be assigned to the free counterion.[29] It is noteworthy that a new synthetic approach was reported for the preparation of type **9** compounds[22] which differs from that in eq 2. The yield for these complexes were higher than in our case (about 80%), but the reaction must be carried out under photolytic conditions.

From all our observations on the specific influence of the NO ligand one may finally conclude that the nitrosyl ligand in **5a** and **5b** stabilizes the rhenium-triflate interaction. This is indicated by the X-ray data: the Re−OTf bond in **5b** is 0.070(4) Å shorter than in **8**. Consequently the reactivity of **5a** and **5b** and **8** are rather different: **8** reacts with bpy producing **9**, while, under analogous reaction conditions, decomposition for **5b**, or Arbuzov-like dealkylation for **5a**, is observed. Apparently there is a stabilization effect exerted by the NO group, which is also recognizable within the ligand sphere of the type **5** complexes: the triflate ligand replacement by acetonitrile in **5b** is on a qualitative scale slower than the same process trans to the nitrosyl substituent.

**Acknowledgment.** We thank the Swiss National Science Foundation for financial support.

**Supporting Information Available:** Full tables of data collection parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and *U* values for **2b**, **5b**, **6a**, **7** and **8** (41 pages). Ordering information is given on any current masthead page.

IC9510829

---

(28) Mandal, S. K.; Ho, D. M.; Orchin, M. *Inorg. Chem.* **1991**, *30,* 224.

(29) Johnston, D. H.; Shriver, D. F. *Inorg. Chem.* **1993**, *32,* 1045.

(30) (a) Carvalho, M. F. N. N.; Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1987**, *335,* C23. (b) Einstein, F. W. B.; Rickard, C. E. F.; Klahn, A.; Leiva, C. *Acta Crystallogr.* **1991**, *C47,* 862. (c) Schubert, U.; Werner, R.; Zinner, L.; Werner, H. *J. Organomet. Chem.* **1983**, *253,* 363.