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Unexpected Alkyne Transfer between Gold and Rhenium Atoms and Its Application to the Synthesis of Alkynyl Rhenium(I) Compounds

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*Summary: The reaction between the rhenium complexes [Re(OTf)(L)(CO)$_3$] (L = bipy, t-Bu$_2$bipy) and the alkynyl gold compounds (PPh$_4$)[Au(C≡Cpy)$_2$] and (PPh$_4$)[Au(C≡C−C$_6$H$_4$−C≡Cpy)$_2$] in a 2:1 molar ratio affords binuclear cationic rhenium(I) derivatives through a previously unreported alkyne transmetalation process involving the two metals. This reaction can be used for the synthesis of mononuclear rhenium alkynyls by changing the molar ratio between the reagents to 1:1. These new luminescent complexes were characterized spectroscopically. The X-ray structure of the binuclear compound [{Re(bipy)(CO)$_3$}$_2$(μ-C≡Cpy)](OTf) (**2**) was also determined.*

Introduction

The development of molecular rods and wires is attracting considerable attention owing to their potential applications in many areas of materials science. The synthesis of such compounds is generally based on a "complexes as ligands" approach in which a polytopic bridging ligand has metal units added to its binding domains in a stepwise fashion. A significant number of this class of species containing transition metal fragments are known, but rhenium(I) tricarbonyl diimine complexes have been particularly widely used as building blocks[1] because of their well-known photophysical, photochemical, and redox properties.[2]

Given that we had recently described the synthesis and photophysical analysis of a series of linear ditopic σ-pyridylacetylide gold complexes[3] and that the chemistry of gold acetylides has received enormous attention,[4] we assessed the possibility of using them as metalloligands to generate luminescent heterometal rods by reaction with appropriate rhenium(I) diimine complexes. Surprisingly, however, rather than the generation of heterometal rods, we observed a previously undescribed transmetalation process involving the gold and the rhenium compounds.

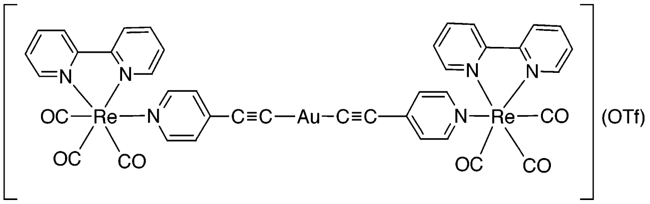

Figure 1. Drawing of the attempted compound **1**.

Results and Discussion

In an attempt to obtain **1**, we reacted (PPh$_4$)[Au(C≡Cpy)$_2$] with the rhenium(I) complex [Re(OTf)(bipy)(CO)$_3$] in a 1:2 molar ratio in refluxing THF for 3 h.

Workup of the resulting solution afforded, after recrystallization from CH$_2$Cl$_2$/ether, a yellow air-stable solid that was spectroscopically analyzed. The IR spectrum displayed, together with four carbonyl vibrations, a band at 2092 cm^{-1} for the asymmetric C≡C stretch that was shifted 15 cm^{-1} down in comparison with the corresponding C≡C vibration of the gold precursor. The wavenumber of the pyridine CN vibration was increased from 1584 to 1601 cm^{-1}. Although these IR changes are indicative of the coordination of Re(I) at the pyridyl N

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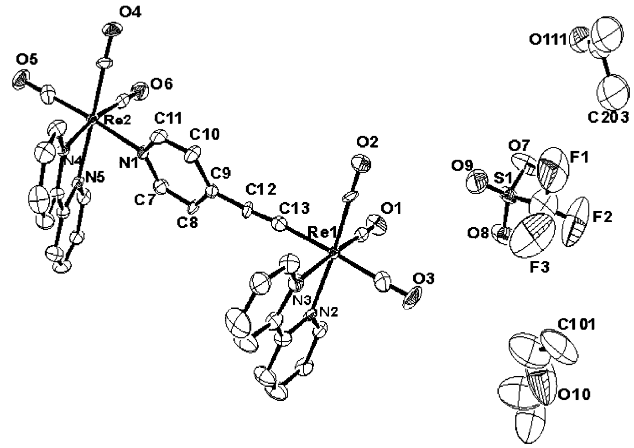


Figure 2. ORTEP drawing of the molecular structure and numbering scheme of compound **2**.

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) of Compound 2

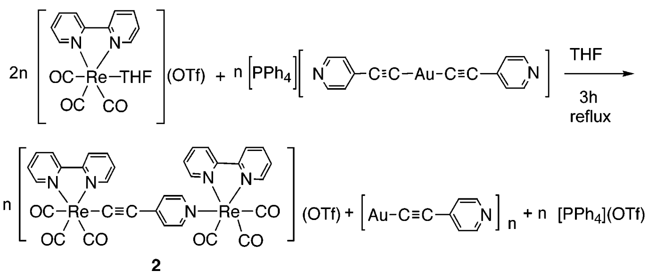
Re(2)−N(1)	2.214(7)
Re(1)−C(13)	2.131(9)
C(12)−C(13)	1.209(12)
Re(1)−N(2)	2.175(8)
Re(1)−N(3)	2.170(8)
Re(2)−N(4)	2.177(7)
Re(2)−N(5)	2.146(7)
Re(1)−C(12)−C(13)	175.7(8)
C(5)−Re(2)−N(1)	176.3(3)
C(13)−C(12)−C(9)	176.6(10)
C(3)−Re(1)−C(13)	175.7(3)
N(3)−Re(1)−N(2)	74.1(3)
N(5)−Re(2)−N(4)	75.1(3)

donor atoms and the ^{1}H NMR spectrum showed the presence of both bipyridine and 4-ethynylpyridine ligands, the proton integration indicated a 2:1 molar ratio between these ligands instead of the expected 1:1 for **1**. Furthermore, the FAB(+) MS spectrum showed its most intense peak at *m*/*z* 954.3, which could not be assigned to any reasonable fragment derived from **1**. Thus, to ascertain the nature of the obtained compound, its molecular structure was determined by X-ray analysis of a single crystal formed by vapor diffusion of diethyl ether into an acetone solution. Figure 2 shows the perspective drawing of **2** with the atomic numbering; selected bond distances and angles are given in Table 1.

The structure establishes the presence of the binuclear rhenium(I) cation, $[\{Re(bipy)(CO)_3\}_2(\mu\text{-}C{\equiv}Cpy)]^+$, and triflate anion. The cation consists of two distorted octahedral $Re(bipy)(CO)_3$ moieties bridged by a 4-ethynylpyridine ligand. The carbonyl ligands appear in a facial arrangement, forcing the organic ligand to be trans to a carbonyl group in both rhenium octahedra. As observed in other Re(I) tricarbonyl diimine systems,[5,6] the N−Re−N (74.1(3)° and 75.1(3)°) bond angles were found to be less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridine ligand. The C(5)Re(2)N(1) and C(3)Re(1)C(13) angles were close to 180°, and the Re−C and Re−N distances were not significantly different from those reported elsewhere. On the other hand, the C≡C length (1.209(12) Å) is typical of Re(I) σ-acetylide derivatives.[6]

Remarkably, the nature of **2** reveals that the ethynylpyridine group was transferred from the gold compound to the Re(I) complex; the overall reaction can be represented as shown in Scheme 1.

Scheme 1. Transmetalation Process



Note that in the transmetalation reaction the gold atom forms a very insoluble polymer[7] with the remaining 4-ethynylpyridine ligand, and this polymer precipitates along with the salt $(PPh_4)OTf$ from the reaction solution. This seems to favor the formation of compound **2** over that of the trimetallic **1**. The IR spectrum of this solid displays a C≡C stretch band at 2126 cm^{-1} that confirms the identity of the polymer. Interestingly, this is a clean process, since no traces of metallic gold were deposited during the reaction.

To examine the scope of this process and to determine whether the length of the organic ligand attached to the gold favors the formation of rhenium/gold rods over the transmetalation process, we reacted the rhenium(I) diimine complex with the linear gold derivative $(PPh_4)[Au(C{\equiv}C{-}C_6H_4{-}C{\equiv}Cpy)_2]$ under the same conditions as described above. The process was monitored by IR spectroscopy, and the products identified were $[\{Re(bipy)(CO)_3\}_2(\mu\text{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C\text{-}py)](OTf)$ (**3**) and the corresponding gold polymer, $(AuC{\equiv}C{-}C_6H_4{-}C{\equiv}Cpy)_n$, as was shown by NMR and IR spectroscopies, mass spectrometry, and elemental analyses. Again, the transfer of the organic group from gold to the rhenium center was the preferred route. On the other hand, the reaction performed using the rhenium complex stabilized with the functionalized *t*-Bu$_2$bipy ligand and $(PPh_4)[Au(C{\equiv}Cpy)_2]$ did not substantially modify either the nature of the products or the yields and reaction times, and allowed us to isolate the related $[\{Re(t\text{-}Bu_2bipy)(CO)_3\}_2(\mu\text{-}C{\equiv}Cpy)](OTf)$ (**4**), which was fully spectroscopically characterized, confirming the wide applicability of the transmetalation reaction.

To confirm the transmetalating properties of the acetylenic gold compounds, we reacted $(PPh_4)[Au$-

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(7) This compound has been prepared and characterized in our laboratory by mixing [AuCl(tht)] and 4-ethynylpyridine in the presence of sodium acetate, in THF/MeOH. Analogous compounds have been reported by Espinet et al. (Alejos, P.; Coco, S.; Espinet, P. *New J. Chem.* **1995**, *19*, 799).

Table 2. Electronic Absorption and Emission Data at 298 K in CH_2Cl_2 Solution for Compounds [Re(OTf)(bipy)(CO)$_3$], 2, [Re(OTf)(*t*-Bu$_2$bipy)(CO)$_3$], 4, and 5

	absorption spectra		emission			
compound	λ_{max}, nm ($10^{-3}\,\epsilon$, $M^{-1}\,cm^{-1}$)	λ_{exc}, nm	λ_{max}, nm	ϕ ($\times10^{-3}$)	k_f ($\times10^6$, s^{-1})	k_{nr} ($\times10^6$, s^{-1})
[Re(OTf)(bipy)(CO)$_3$]	285(12.2), 308(11.7), 320(11.0), 357(3.7)	358	579	22	0.107	4.748
[{Re(bipy)(CO)$_3$}$_2$(μ-C≡Cpy)](OTf) (**2**)	297(35.9), 311(30.6), 322(28.3), 355(31.2)	358	642	4.1	0.077	18.685
[Re(OTf)(*t*-Bu$_2$bipy) (CO)$_3$]	284(16.0), 304(13.1), 316(11.3), 354(4.6)	358	566	29	0.152	5.084
[{Re(*t*-Bu$_2$bipy)(CO)$_3$}$_2$(μ-C≡Cpy)$_2$](OTf) (**4**)	292(33.0), 307(28.5), 318(25.0), 358(24.0)	358	622	7.7	0.051	6.528
[Re(bipy)(CO)$_3$(C≡Cpy)$_2$] (**5**)	291(28.6), 330(9.6),408(2.83)	358	627	4.3	0.036	8.367

(C≡Cpy)$_2$] with the rhenium(I) complex [Re(OTf)(bipy)(CO)$_3$] in a 1:1 molar ratio, and after a simple workup procedure, we isolated the alkynyl Re(I) compound [Re(C≡Cpy)(bipy)(CO)$_3$] (**5**), which has not been described previously.

The process reported here has no precedent in the literature, since to our knowledge the only examples in which organogold compounds transfer their organic group (aryl group) to other transition metals include d^0, d^5, d^8, and d^{10} metallic centers.[8,9] Consequently, this reaction represents a new, effective strategy toward the synthesis of alkynyl rhenium bipyridine compounds, the obtention of which has necessitated the development of alternative routes[1j,5j] to the classical reaction between [ReCl(bipy)(CO)$_3$] and lithium acetylides, which has been reported not to yield the corresponding alkynyls.[10] Moreover, it represents a valuable nontoxic method, which can be carried out under air without reduction of the transmetalated metal center.

Photoluminescence Studies. Absorption spectra for the complexes **2**, **4**, **5**, and their triflate precursors were obtained in CH_2Cl_2, and the results are shown in Table 2. Compound **3** was obtained together with minor impurities that precluded its photoluminescence analysis.

Spectra were very similar to those of analogous Re(I) tricarbonyl diimine complexes, and the assignments were made accordingly.[1a−c,g−j,2g,11−16] A typical spectrum consists of several strong UV bands, assigned as ligand-centered transitions. One broad shoulder was observed at lower energy in every case, and it was assigned to an MLCT transition, dπ(Re(I)) → π*(bipy). The extinction coefficient of the lower energy band increases ca. 8 times on going from the triflate rhenium precursor to the binuclear complex **2** and ca. 5 times in the case of compound **4**. Given that the extinction coefficient of the mononuclear **5** compares well with that of the triflate mononuclear rhenium compounds, we conclude that the increase of ϵ for **2** and **4** should be assigned to a new MLCT band that arises from coordination of the pyridine nitrogen to the second metal.

The results of room-temperature luminescence measurements in CH_2Cl_2 aerated solutions are also summarized in Table 2. The complexes display broad emission spectra, which have also been assigned as MLCT-based luminescence, typical of this type of compound.[1j,2g,6,10−16] The emission maximum is shifted to the red with the presence of the ethynyl pyridine ligand, and the quantum yield is reduced accordingly.

Emission decay times ranged from 50 to 200 ns and followed first-order decay kinetics.

There is a tendency toward a decrease in the decay time with the increase in the emission wavelength, which follows the same trend as the luminescence quantum yields, and is also associated with the increase in the nonradiative rate constant (Table 2).

For the mononuclear complexes, a correlation was found between the radiative rate constant, k_f, values (Table 2) and the extinction coefficient at the maximum of the highest wavelength shoulder (attributed to a dπ(Re(I)) → π*(bipy) MLCT transition) in the absorption spectrum. However, this was not observed in the case of the binuclear complexes. This could be due to the presence of a new MLCT band (arising from the bonding of pyridine nitrogen to the metal in the binuclear complexes) that does not contribute to the emission, at least at the wavelength at which the MLCT dπ(Re(I)) → π*(bipy) band emits.

Experimental Section

General Procedures. All manipulations were performed under prepurified nitrogen using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. Infrared spectra were recorded on a FT-IR 520 Nicolet spectrophotometer. ^{1}H NMR (δ(TMS) = 0.0 ppm) spectra were obtained on Bruker DXR 250, Varian Gemini 200, and Varian Mercury 400 spectrometers. Elemental analyses of C, H, and N were carried out at the Institut de Bio-Orgànica in Barcelona. FAB(+) and electrospray (+) mass spectra were recorded on a Fisons VG Quattro spectrometer.

Spectrophotometric and Spectrofluorimetric Titrations. Absorption spectra were recorded on a Shimadzu UV-2510 PC, UV−vis recording spectrophotometer and fluorescence emission on an SPEX Jobin-Yvon Fluorolog 3 spectrofluorimeter. The absorbance of the excitation wavelength was maintained lower than ca. 0.15.

Fluorescence Decay Measurements. The samples were excited at 358 nm using a coaxial flash lamp (IBH, 5000 system) filled with nitrogen. The lamp pulses were monitored using a synchronization photomultiplier, and the PM signal was shaped in a constant fraction discriminator (Canberra 2126) and directed to a time to amplitude converter (TAC, Canberra 2145) as start pulses. Emission wavelength was selected with a monochromator (Oriel 77250) imaged in a fast photomultiplier (9814B Electron Tubes Inc.), and the PM signal was shaped as before and delayed before entering the TAC as stop pulses. The analogue TAC signals were digitized (ADC, ND582) and stored on a PC. The analysis of the decays was carried out using the method of modulating functions extended by global analysis, as implemented by Striker.[17]

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[ReCl(CO)$_5$] (Strem Chemicals, 98%), 2,2′-bipyridine (Aldrich, 99%), 4,4′-*tert*-butyl-2,2′-bipyridine (Aldrich, 98%), and silver triflate (Aldrich, >99%) were used as received. [ReCl(bipy)(CO)$_3$],[12] [ReCl(*t*-Bu$_2$bipy)(CO)$_3$],[18] [Re(OTf)(bipy)(CO)$_3$],[19] [Re(OTf)(*t*-Bu$_2$bipy)(CO)$_3$],[19] [PPh$_4$][Au(C≡Cpy)$_2$],[3] and [PPh$_4$][Au(C≡CC$_6$H$_4$C≡Cpy)$_2$][3] were prepared as described previously.

Synthesis of [{Re(bipy)(CO)$_3$}$_2$(*μ*-C≡Cpy)](OTf) (2). Solid [PPh$_4$][Au(C≡Cpy)$_2$] (32 mg, 0.04 mmol) was added to a THF (25 mL) solution of [Re(OTf)(bipy)(CO)$_3$] (50 mg, 0.08 mmol). The resulting mixture was heated for 3 h at 65 °C, filtered through Celite, and concentrated to dryness. The solid residue was dissolved in CH$_2$Cl$_2$ (3 mL), and the addition of diethyl ether caused the precipitation of compound **1** as a yellow solid, which was washed with CHCl$_3$ and vacuum-dried. Yield: 21 mg (43%). IR (KBr, cm^{-1}): 2092 w, *ν*(C≡C); 2023 s, 2007 vs, 1897 vs, 1883 vs, *ν*(C≡O). ^{1}H NMR (298 K, acetone-*d*$_6$): 9.31 (d, *J*(H−H) = 5.5 Hz, 2H, H_6, $H_{6'}$ (bipy)Re−N), 9.03 (d, *J*(H−H) = 5.5 Hz, 2H, H_6, $H_{6'}$ (bipy)Re−C), 8.64 (d, *J*(H−H) = 8.3 Hz, 4H, H_3, $H_{3'}$ (bipy)Re−N and (bipy)Re−C), 8.37 (t, *J*(H−H) = 8.0 Hz, 2H, H_4, $H_{4'}$ (bipy)Re−N), 8.25 *J*(H−H) = 7.9 Hz, 2H, H_4, $H_{4'}$ (bipy)Re−C), 7.95 (d, *J*(H−H) = 5.1 Hz, 2H, $\mathrm{H}_{\alpha\mathrm{pyr}}$), 7.89 (t, *J*(H−H) = 7.6 Hz, 2H, H_5, $H_{5'}$ (bipy)Re−N), 7.70 (t, *J*(H−H) = 7.6 Hz, 2H, H_5, $H_{5'}$ (bipy)Re−C), 6.60 (d, *J*(H−H) = 5.1 Hz, 2H, $\mathrm{H}_{\beta\mathrm{pyr}}$). FAB (+) *m*/*z*: 954.3 (M$^+$, calc 954.4); 926.3 (M$^+$ − CO, calc 926.4); 898.3 (M$^+$ − 2 CO, calc 898.4). Anal. Calc: C, 36.98; H, 1.81; N, 6.34. Found: C, 37.02; H, 1.85; N, 6.37.

Syntheses of [{Re(bipy)(CO)$_3$}$_2$(*μ*-C≡C−C$_6$H$_4$-C≡C-py)](OTf) (3) and [{Re(*t*-Bu$_2$bipy)(CO)$_3$}$_2$(*μ*-C≡Cpy)$_2$](OTf) (4). Details of the synthesis of **2** also applied to **3** and **4**.

3: Yield: 27 mg (42%). IR (KBr, cm^{-1}): 2201 w, *ν*(py*C*≡*C*), 2090 w, *ν*(*C*≡*C*Re); 2022 s, 2005 vs, 1898 vs, 1882 vs, *ν*(C≡O). ^{1}H NMR (298 K, acetone-*d*$_6$): 9.45 (d, *J*(H−H) = 5.5 Hz, 2H, H_6, $H_{6'}$ (bipy)Re−N), 9.12 (d, *J*(H−H) = 4.8 Hz, 2H, H_6, $H_{6'}$ (bipy)Re−C), 8.70 (m, 4H, H_3, $H_{3'}$ (bipy)Re−N and (bipy)Re−C), 8.48 (d, *J*(H−H) = 6.7 Hz, 2H, $\mathrm{H}_{\alpha\mathrm{pyr}}$), 8.43 (t, *J*(H−H) = 8.0 Hz, 2H, H_4, $H_{4'}$ (bipy)Re−N), 8.30 (*J*(H−H) = 7.8 Hz, 2H, H_4, $H_{4'}$ (bipy)Re−C), 7.99 (t, *J*(H−H) = 7.8 Hz, 2H, H_5, $H_{5'}$ (bipy)Re−N), 7.75 (t, *J*(H−H) = 7.6 Hz, 2H, H_5, $H_{5'}$ (bipy)Re−C), 7.54 (d, *J*(H−H) = 6.7 Hz, 2H, $\mathrm{H}_{\beta\mathrm{pyr}}$), 7.18 (d, *J*(H−H) = 8.6 Hz, 2H, $\mathrm{H_o}$), 6.81 (d, *J*(H−H) = 8.6 Hz, 2H, $\mathrm{H_m}$). FAB (+) *m*/*z*: 1054.7 (M$^+$, calc 1054.8); 1026.7 (M$^+$ − CO, calc 1026.8).

4: Yield: 22 mg (45%). IR (KBr, cm^{-1}): 2090 w, *ν*(C≡C); 2024 s, 2008 vs, 1899 vs, 1887 vs, *ν*(C≡O). ^{1}H NMR (298 K, acetone-*d*$_6$): 9.22 (d, *J*(H−H) = 5.9 Hz, 2H, H_6, $H_{6'}$ (*t*-Bu$_2$bipy)-Re−N), 8.95 (d, *J*(H−H) = 5.9 Hz, 2H, H_6, $H_{6'}$ (*t*-Bu$_2$bipy)Re−C), 8.67 (m, 4H, H_3, $H_{3'}$ (*t*-Bu$_2$bipy)Re−N and (*t*-Bu$_2$bipy)Re−C), 7.98 (d, *J*(H−H) = 6.6 Hz, 2H, $\mathrm{H}_{\alpha\mathrm{pyr}}$), 7.72 (m, 4H, H_5, $H_{5'}$ (*t*-Bu$_2$bipy)Re−N and (*t*-Bu$_2$bipy)Re−C), 6.66 (d, *J*(H−H) = 6.6 Hz, 2H, $\mathrm{H}_{\beta\mathrm{pyr}}$), 1.43 (s, 9H, C(CH$_3$)$_3$ (*t*-Bu$_2$bipy)Re−N), 1.41 (s, 9H, C(CH$_3$)$_3$ (*t*-Bu$_2$bipy)Re−C). ES (+) *m*/*z*: 1180.3 (M$^+$, calc 1179.2); 1152.3 (M$^+$ − CO, calc 1151.2), 641.2 (M$^+$ − Re(*t*-Bu$_2$bipy)(CO)$_3$, calc 640.6). Anal. Calc: C, 45.17; H, 3.91; N, 5.27. Found: C, 45.20; H, 3.94; N, 5.29.

Synthesis of [Re(bipy)(CO)$_3$(C≡Cpy)$_2$] (5). Solid [PPh$_4$][Au(C≡Cpy)$_2$] (64 mg, 0.08 mmol) was added to a THF (30 mL) solution of [Re(OTf)(bipy)(CO)$_3$] (50 mg, 0.08 mmol). The resulting mixture was heated for 3 h at 65 °C, filtered, and concentrated to dryness. The crude was extracted with toluene and precipitated with hexane, to give **5** as an orange product. Yield: 21 mg (50%). IR (KBr, cm^{-1}): 2085 w, *ν*(C≡C); 2003 s, 1900 vs, 1894 vs, *ν*(C≡O). ^{1}H NMR (298 K, acetone-*d*$_6$): 9.10 (d, *J*(H−H) = 6.0 Hz, 2H, H_6, $H_{6'}$ bipy), 8.67 (d, *J*(H−H) = 8.4 Hz, 2H, H_3, $H_{3'}$ bipy), 8.27 (t, *J*(H−H) = 8.4 Hz, 2H, H_4, $H_{4'}$ bipy), 8.09, (d, *J*(H−H) = 8.1 Hz, 2H, $\mathrm{H}_{\alpha\mathrm{pyr}}$), 7.72 (t, *J*(H−H) = 7.6 Hz, 2H, H_5, $H_{5'}$ bipy), 6.62 (d, *J*(H−H) = 8.1 Hz, 2H, $\mathrm{H}_{\beta\mathrm{pyr}}$). MALDI-TOF *m*/*z*: 530.0 (M + H$^+$, calc 529.4); 502.0 (M + H$^+$ − CO, calc 501.4). Anal. Calc: C, 45.42; H, 2.27; N, 7.95. Found: C, 45.49; H, 2.32; N, 8.07.

Table 3. Crystal Data and Details of the Structure of [{Re(bipy)(CO)$_3$}$_2$(*μ*-C≡Cpy)](OTf) (2)

empirical formula	$C_{33}H_{20}N_5O_6Re_2{\cdot}SO_3CF_3{\cdot}C_4H_{10}O{\cdot}1/2C_3H_6O$
fw	1207.17
temperature (K)	200(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space group	P-1
unit cell dimens	
a (Å)	10.3373(8)
b (Å)	14.2816(17)
c (Å)	16.949(3)
α (deg)	114.060(13)
β (deg)	92.889(11)
γ (deg)	99.020(10)
V (Å^3)	2238.4(5)
Z	2
D_{calc} (mg/m^3)	1.791
absorp coeff (mm^{-1})	5.522
F(0 0 0)	1164
cryst size (mm^3)	0.489 × 0.319 × 0.292
θ range for data collection (deg)	2.01−27.50
index ranges	$-13 \le h \le 13$ $-18 \le k \le 18$ $-22 \le l \le 21$
no. of reflns collected	39 495
no. of indep reflns	9901 [*R*(int) = 0.15333]
completeness to *θ* = 27.50°	96.3%
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	9901/0/549
goodness-of-fit on F^2	1.074
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0534$, $wR_2 = 0.1325$
R indices (all data)	$R_1 = 0.0807$, $wR_2 = 0.1598$
extinction coeff	0.0013(2)
largest diff peak and hole	2.427 and −4.184 e Å^{-3}

X-ray Crystal Structure Determination of Complex 2. Crystals were grown by vapor diffusion of diethyl ether into an acetone solution of **2**, removed from the Schlenk, and covered with a layer of a viscous perfluoropolyether (Fomblin Y). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for complex **2** are presented in Table 3.

The structures were solved, using the WINGX package,[20] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[21]

Complex **2** crystallized with one molecule of acetone and one of ethyl ether. All non-hydrogen atoms of **2** were anisotropically refined except those of the acetone molecule, which could only be refined isotropically and 50% of occupancy. All the hydrogen atoms of **2** were positioned geometrically and refined by using a riding model. Refinement converged at R1 = 0.053 and wR2 = 0.132 for 7436 unique reflections with $I > 2\sigma(I)$. R1 and wR2 are defined as $\mathrm{R1} = \sum||F_\mathrm{o}| - |F_\mathrm{c}||/[\sum|F_\mathrm{o}|]$ and $\mathrm{wR2} = \{[\sum w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2]/[\sum w(F_\mathrm{o}^2)^2]\}^{1/2}$. Largest difference peak and hole were respectively 0.96 and 0.77 Å close to Re-(2).

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Supporting Information Available: X-ray structural information for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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