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Luminescent Rhenium(I) Carbon Wires: Synthesis, Photophysics, and Electrochemistry. X-ray Crystal Structure of $[Re(^tBu_2bpy)(CO)_3(C\equiv CC\equiv C)Re(^tBu_2bpy)(CO)_3]$

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$[Re(^tBu_2bpy)(CO)_3(C\equiv CC\equiv C)Re(^tBu_2bpy)(CO)_3]$, which consists of an extended linear $O\equiv C-Re-C\equiv C-C\equiv C-Re-C\equiv O$ unit, has been synthesized by the coupling of two $[Re(^tBu_2bpy)(CO)_3(C\equiv CH)]$ units; both of these complexes and the related $[Re(^tBu_2bpy)(CO)_3(C\equiv CC_6H_{13})]$ complex are shown to exhibit rich photophysical behavior. The electrochemical properties of these complexes have also been studied. The X-ray crystal structure of $[Re(^tBu_2bpy)(CO)_3(C\equiv CC\equiv C)Re(^tBu_2bpy)(CO)_3]$ has been determined.

Introduction

There has been a growing interest in the design of metal-containing rigid-rod materials, in view of their potential applications in many areas of material science. The acetylides, with their unsaturation, are especially attractive candidates for the synthesis of one-dimensional molecular wires and nonlinear optical and liquid crystalline materials.[1,2] In recent reports on the successful isolation of acetylide-bridged rhenium(I) organometallics,[3,4] no attempts had been made to incorporate luminophores into these units, despite the well-documented photophysical properties of rhenium(I) diimines.[5] We believe that the introduction of acetylide moieties into the d^6 metal diimine system has the added advantage of rendering the metal center more electron rich, thus raising the energy of the d−d states, which would improve the population of the MLCT state.[6] This, together with our recent efforts on the design and synthesis of luminescent mononuclear and polynuclear alkynylmetal complexes,[6,7] has prompted us to initiate a program to investigate the possibility of incorporating the rhenium(I) diimine luminophores into the acetylide backbone.[6c] In this report, the synthesis, photophysics, and electrochemistry of $[Re(^tBu_2bpy)(CO)_3(C\equiv CH)]$ (**1**) and its coupling product $[Re(^tBu_2bpy)(CO)_3(C\equiv CC\equiv C)Re(^tBu_2bpy)(CO)_3]$ (**2**) will be described ($^tBu_2bpy$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine). The related complex $[Re(^tBu_2bpy)(CO)_3(C\equiv CC_6H_{13})]$ (**3**) has also been synthesized. The X-ray crystal structure of **2** has been determined.

Experimental Section

Materials and Reagents. $[Re(CO)_5Cl]$ was obtained from Strem Chemicals, Inc. (Trimethylsilyl)acetylene was purchased from Lancaster Synthesis Ltd. 1-Octyne and copper(II) acetate were obtained from Aldrich Chemical Co. All solvents were purified and distilled using standard procedures before use.[8] All other reagents were of analytical grade and were used as received.

Syntheses of Rhenium Complexes. All reactions were carried out in the dark under anaerobic and anhydrous conditions using standard Schlenk techniques.

$[Re(^tBu_2bpy)(CO)_3(C\equiv CH)]$ (1). A methanolic solution (15 mL) of $[Re(^tBu_2bpy)(CO)_3(C\equiv CSiMe_3)]$[6c] (100 mg, 0.157 mmol) and an excess of KOH (0.5 g) was stirred at room temperature for 48 h. The product was filtered, and the filtrate was evaporated to dryness *in vacuo* and purified by column chromatography on silica gel using a petroleum ether−diethyl ether mixture as eluent. Subsequent recrystallization from acetone gave air-stable red-orange crystals of **1** (yield 86 mg, 97%). ^1H NMR (270 MHz, acetone-d_6, 298 K, relative to TMS): δ 1.4 (s, 18H, ^tBu), 1.5 (s, 1H, $\equiv CH$), 7.4 (dd, 2H, 5- and 5′-pyridyl H), 8.0 (d, 2H, 3- and 3′-pyridyl H), 8.9 (d, 2H, 6- and 6′-pyridyl H). $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$, 298 K, relative to TMS): δ 30 (Me C), 35 (4° C of the ^tBu group), 89 ($Re-C\equiv \mathit{C}-H$), 118 ($Re-\mathit{C}\equiv C-H$), 119, 124, 152, 155, 162 (pyridyl C), 191, 197 (CO). Positive FAB-MS: ion clusters at

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m/*z* 564 {M}$^+$. IR (Nujol mull, cm^{-1}): ν(C≡C) 1948; ν(CO) 2015, 1893. Anal. Found: C, 51.30; H, 4.79; N, 4.73. Calcd for [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡CH)]·1.5(CH$_3$)$_2$CO: C, 50.75; H, 5.23; N, 4.31.

[Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡CC≡C)Re(^{t}Bu$_2$bpy)(CO)$_3$] (2). A solution of **1** (100 mg, 0.178 mmol) in the presence of Cu(OAc)$_2$ (48.4 mg, 0.266 mmol, 1.5 equiv) in pyridine (5 mL) was stirred at *ca*. 60 °C for 24 h. The solution was then evaporated to dryness *in vacuo* and the residue purified by column chromatography on silica gel using diethyl ether as eluent. Subsequent recrystallization from acetone gave **2** as air-stable red rod-shaped crystals (yield 45 mg, 45%). ^{1}H NMR (270 MHz, acetone-d_6, 298 K, relative to TMS): δ 1.4 (s, 18H, ^{t}Bu), 7.6 (dd, 2H, 5- and 5′-pyridyl H), 8.5 (d, 2H, 3- and 3′-pyridyl H), 8.8 (d, 2H, 6- and 6′-pyridyl H). ^{13}C{^{1}H} NMR (67.8 MHz, CDCl$_3$, 298 K, relative to TMS): δ 30 (Me C), 35 (4° C of the ^{t}Bu group), 124 (Re—C≡*C*—), 117 (Re—*C*≡C—H), 119, 123, 152, 155, 162 (pyridyl C), 198, 207 (CO). Positive FAB-MS: ion clusters at *m*/*z* 1126 {M}$^+$, 1098 {M − CO}$^+$, 1070 {M − 2CO}$^+$. IR (Nujol mull, cm^{-1}): ν(C≡C) 1981; ν(CO) 2003, 1903, 1883. Anal. Found: C, 50.35; H, 4.70; N, 4.46. Calcd for [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡CC≡C)Re(CO)$_3$(^{t}Bu$_2$bpy)]·2(CH$_3$)$_2$CO: C, 50.31; H, 4.84, N, 4.51.

[Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡CC$_6$H$_{13}$)] (3). This was synthesized by modification of a literature procedure previously published by us,[6c] except 1-octyne was used in place of 3,3-dimethylbut-1-yne to give orange crystals of **3** (51 mg, 45%). ^{1}H NMR (270 MHz, acetone-d_6, 298 K, relative to TMS): δ 0.8 (t, 3H, Me H), 0.9−1.75 (m, 8H, H of C(4) to C(7) of the octynyl unit), 1.4 (s, 18H, ^{t}Bu), 1.8 (t, 2H, −CH$_2$− attached to the C≡C unit), 7.7 (dd, 2H, 5- and 5′-pyridyl H), 8.6 (d, 2H, 3- and 3′-pyridyl H), 8.9 (d, 2H, 6- and 6′-pyridyl H). Positive FAB-MS: ion clusters at *m*/*z* 648 {M}$^+$, 620 {M − CO}$^+$, 539 {M − octynyl}$^+$. IR (Nujol mull, cm^{-1}): ν(C≡C) 2102; ν(CO) 2001, 1901, 1876. Anal. Found: C, 54.28; H, 5.69; N, 4.39. Calcd for [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡CC$_6$H$_{13}$)]·0.5(CH$_3$)$_2$CO: C, 54.13; H, 5.92; N, 4.14.

Physical Measurements and Instrumentation. UV−visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, IR spectra as Nujol mulls on a Bio-Rad FTS-7 Fourier-transform infrared spectrophotometer (4000−400 cm^{-1}), and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^{1}H NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform NMR spectrometer with chemical shifts reported relative to TMS. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed by Butterworth Laboratories Ltd.

Emission−lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay signals were recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope, and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a 10-cm^3 round-bottom flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze−pump−thaw cycles.

Cyclic voltammetric measurements were performed by using a Princeton Applied Research (PAR) universal programmer (Model 175), potentiostat (Model 173), and digital coulometer (Model 179). The ferrocenium−ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 mol dm^{-3} NBu$_4$PF$_6$). The working electrode was a glassy-carbon (Atomergic Chemetals V25) electrode with platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported previously.[7c]

Table 1. Crystal and Structure Determination Data for 2

formula	Re$_2$O$_6$N$_4$C$_{46}$H$_{48}$·2CH$_3$COCH$_3$
fw	1241.48
T, K	298
a, Å	11.490(9)
b, Å	20.914(3)
c, Å	12.375(5)
β, deg	113.58(3)
V, Å^3	2725(1)
cryst syst	monoclinic
space group	$P2_1/a$ (No. 14)
Z	2
F(000)	1228
D_c, g cm^{-3}	1.513
cryst dimens, mm	0.20 × 0.15 × 0.35
λ, Å (graphite monochromated, Mo Kα)	0.710 73
μ, cm^{-1}	44.91
transmissn factors	0.596−1.000
collecn range, deg	$2\theta_{max} = 50$ (h, 0−12; k, 0−22; l, −12 to +12)
scan mode; scan speed, deg min^{-1}	$\omega-2\theta$; 16
scan width, deg	$1.47 + 0.35 \tan \theta$
no. of data collected	4592
no. of unique data	4359
no. of data used in refinement, m	2790
no. of params refined, p	278
R^a	0.074
$R_w{}^a$	0.091
goodness of fit, S	2.98
max shift, $(\Delta/\sigma)_{max}$	0.05
residual extrema in final diff map, e Å^{-3}	+1.97, −1.26

[a] $w = 4F_o{}^2/\sigma^2(F_o{}^2)$, where $\sigma^2(F_o{}^2) = [\sigma^2(I) = (0.018F_o{}^2)^2]$ with $I > 3\sigma(I)$.

Crystal Structure Determination. Crystals of **2** were obtained by slow evaporation of their acetone solution. Diffraction data for **2** were measured at 298 K on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) to $2\theta_{max} = 50°$. Three standard reflections measured after every 300 reflections showed a decay of 9.73%. The intensity data were corrected for decay and Lorentz and polarization effects. The empirical absorption corrections were based on the ψ-scan of four strong reflections. Crystal and structure determination data for **2** are summarized in Table 1. The space group was determined from systematic absences and the structure solved by heavy-atom Patterson methods and expanded using Fourier techniques[9] and refinement by full-matrix least squares with the MSC-Crystal Structure Package TEXSAN on a Silicon Graphics Indy computer. The complex molecule consists of two halves related by a center of symmetry at (0.5, 0, 0) with the acetylenic unit at the center. The 33 non-hydrogen atoms were refined ansiotropically; the atoms of the acetone solvent molecule have high thermal factors and were refined isotropically. H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. The final agreement factors are given in Table 1. The final atomic coordinates and thermal parameters of the non-hydrogen atoms of **2** are collected in Table 2. Selected bond distances and angles are summarized in Table 3. The atomic coordinates of the hydrogen atoms are given as Supporting Information.

Results and Discussion

Removal of the trimethylsilyl group in [Re(^{t}Bu$_2$bpy)(CO)$_3$(C≡CSiMe$_3$)] was accomplished by its reaction

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Table 2. Fractional Coordinates and Thermal Parameters[a] for Non-Hydrogen Atoms and Their Esd's for 2

atom	x	y	z	B_{eq}
Re(1)	0.15640(6)	0.01836(3)	0.26256(5)	3.69(1)
O(1)	0.389(1)	−0.0616(7)	0.410(1)	8.5(4)
O(2)	0.021(1)	−0.1021(6)	0.128(1)	6.7(3)
O(3)	0.285(1)	0.0448(7)	0.090(1)	6.9(3)
O(4)	0.470(3)	0.089(1)	0.796(2)	19.4(10)
N(1)	0.0030(10)	0.0860(6)	0.1778(10)	3.5(3)
N(2)	0.223(1)	0.1105(6)	0.345(1)	4.0(3)
C(1)	0.303(2)	−0.0330(9)	0.357(2)	5.7(5)
C(2)	0.073(2)	−0.0571(8)	0.177(1)	4.7(4)
C(3)	0.233(2)	0.0355(7)	0.158(2)	5.8(4)
C(4)	0.074(1)	0.0058(8)	0.387(1)	4.5(4)
C(5)	0.027(2)	0.0026(7)	0.457(1)	4.6(4)
C(6)	−0.108(1)	0.0710(7)	0.095(1)	4.5(4)
C(7)	−0.205(2)	0.1146(9)	0.038(1)	5.1(4)
C(8)	−0.186(1)	0.1787(8)	0.070(1)	4.1(4)
C(9)	−0.073(1)	0.1929(7)	0.161(1)	4.2(4)
C(10)	0.022(1)	0.1473(7)	0.214(1)	3.3(3)
C(11)	0.144(1)	0.1615(7)	0.307(1)	3.2(3)
C(12)	0.181(1)	0.2220(8)	0.355(1)	4.1(3)
C(13)	0.303(1)	0.2325(8)	0.446(1)	4.1(4)
C(14)	0.377(2)	0.1798(9)	0.485(1)	5.5(4)
C(15)	0.338(2)	0.1206(8)	0.436(1)	5.4(4)
C(16)	−0.287(1)	0.2287(9)	0.008(1)	5.4(4)
C(17)	−0.310(2)	0.229(1)	−0.127(2)	8.3(6)
C(18)	−0.408(2)	0.210(1)	0.019(2)	7.2(5)
C(19)	−0.249(2)	0.2946(9)	0.060(2)	6.9(5)
C(20)	0.341(2)	0.2980(9)	0.501(1)	5.2(4)
C(21)	0.477(2)	0.311(1)	0.530(2)	9.8(7)
C(22)	0.325(2)	0.300(1)	0.614(2)	10.2(7)
C(23)	0.267(2)	0.351(1)	0.426(2)	10.5(7)
C(24)	0.375(4)	0.054(2)	0.762(3)	16(1)
C(25)	0.273(4)	0.093(2)	0.757(3)	17(1)
C(26)	0.369(8)	0.007(4)	0.743(6)	56(5)

[a] $^{8}/_{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 2

Re(1)−C(1)	1.94(2)	Re(1)−C(2)	1.93(2)
Re(1)−C(3)	1.87(2)	Re(1)−C(4)	2.13(2)
C(4)−C(5)	1.19(2)	C(5)−C(5*)	1.43(4)
Re(1)−N(1)	2.18(1)	Re(1)−N(2)	2.17(1)
C(1)−O(1)	1.12(2)	C(2)−O(2)	1.15(2)
C(3)−O(3)	1.23(2)		
N(1)−Re(1)−N(2)	73.4(4)	Re(1)−C(1)−O(1)	178(1)
Re(1)−C(2)−O(2)	178(1)	Re(1)−C(3)−O(3)	178(1)
C(3)−Re(1)−C(4)	175.6(6)	Re(1)−C(4)−C(5)	176(1)
C(4)−C(5)−C(5*)	178(2)		

with excess base (KOH) under an inert atmosphere of nitrogen at room temperature to give [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡CH)] (**1**). Subsequent purification by column chromatography on silica gel followed by recrystallization from diethyl ether gave **1** in high yield (*ca.* 97%). Reaction of **1** with 1.5 equiv of Cu(OAc)$_2$ in pyridine at *ca.* 60 °C gave the coupling product [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡CC≡C)Re(CO)$_3$(^{t}Bu$_2$bpy)] (**2**), which was purified by column chromatography on silica gel, followed by subsequent recrystallization from acetone. [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡CC$_6$H$_{13}$)] (**3**) was prepared according to modification of a procedure recently reported by us.[6c] All the newly synthesized compounds gave satisfactory elemental analyses and have been characterized by IR, positive FAB-MS, and ^{1}H and ^{13}C NMR spectroscopy. Complex **2** has also been characterized by X-ray crystallography.

Figure 1 depicts the perspective drawing of complex **2** along with atomic numbering. The structure of **2** shows a slightly distorted octahedral geometry about each Re atom with the three carbonyl ligands on each Re arranged in a facial fashion. The O≡C−Re−C≡C−C≡C−Re−C≡O unit is essentially linear with bond angles of 175.6(6)−178(2)°. The C≡C and C−C bond lengths of 1.19(2) and 1.43(4) Å, respectively, are similar to those in butadiyne. The slightly longer Re(1)−C(4) bond (2.13(2) Å) compared to other Re−CO bonds (1.87(2)−1.94(2) Å) is indicative of little or no significant metal to ligand π back-bonding to the acetylide unit. Similar Re−C bond distances are reported in related rhenium(I) acetylide systems.[3,4,6c] A separation of 8.1 Å is observed between the two Re centers. The N−Re−N bond angles of 73.4(4)° are less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridine ligand. All other bond distances and angles are normal.

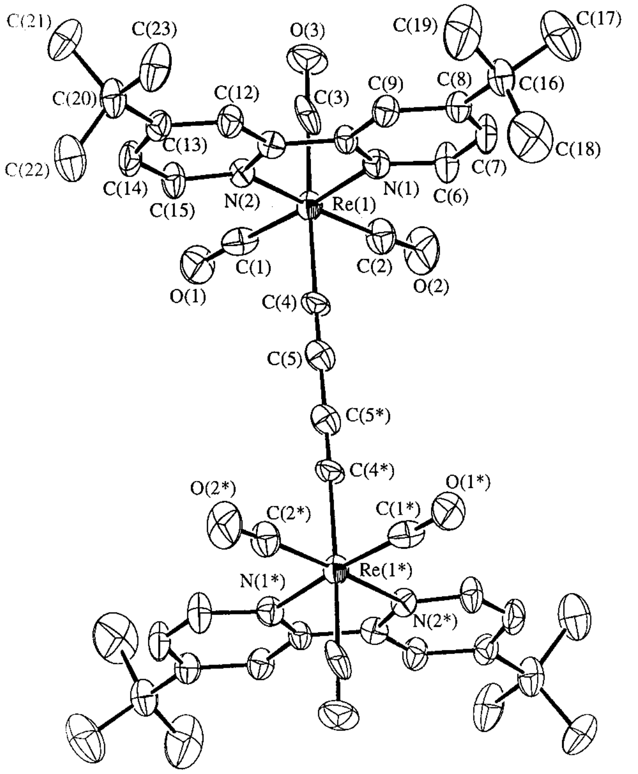

Figure 1. Perspective drawing of complex **2** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The electronic absorption spectra of **1** and **3** show intense absorption bands at *ca.* 404 and 424 nm, respectively, in tetrahydrofuran, tentatively assigned as the d$_\pi$(Re) → π^*(^{t}Bu$_2$bpy) MLCT transition[5] (Table 4). The red shift in MLCT absorption energies of these complexes relative to [Re(^{t}Bu$_2$bpy)(CO)$_3$Cl][6c] and the higher absorption energies for **1** than for **3** are consistent with the stronger σ-donating ability of the acetylide compared to the chloro moiety (R = C≡CC$_6$H$_{13}$ > C≡CH > Cl), rendering the Re center more electron rich, which raises the energy of the Re d orbitals. This is in line with the σ-donor ability sequence observed from photoelectron spectroscopic studies of the CpFe(CO)$_2$X system.[10] Similar findings have been reported in the related Re(I)−acetylide and Re(I)−alkyl systems.[5f,6c,11]

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Table 4. Photophysical and Electrochemical Data for Complexes 1−3

complex	medium (T/K)	abs, λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})	emissn, λ_{em}/nm (τ_0/μs)	redn, $E_{1/2}$, V^a vs SCE	oxidn, E_{pa}, V^a vs SCE
1	acetone (298)	388 (3140)	680 (<0.1)	−1.61	+1.07, +1.84
	CH_2Cl_2 (298)	273 (13 030), 292 (15 520), 398 (2880)	660 (<0.1)		
	THF (298)	404 (2900)	670 (<0.1)		
	Et_2O (298)	274 sh (13 110), 294 (17 710), 330 sh (3130), 418 (3050)	670 (0.25)		
	EtOH/MeOH (4:1 v/v) (298)	272 sh (12 880), 292 (15 150), 386 (2730)	660 (<0.1)		
	EtOH/MeOH (4:1 v/v) (77)		545 (3.00)		
	solid (298)		610 (0.25)		
	solid (77)		590		
2	acetone (298)	450 (2550)	690, 750 (<0.1)	−1.62	+0.72, +1.33, +1.84
	CH_2Cl_2 (298)	330 (15 140), 362 (8510), 458 (3010)	620, 750 (<0.1)		
	THF (298)	480 (2580)	630, 730 (<0.1)		
	Et_2O (298)	275 (30 180), 300 (26 640), 346 (9420), 492 (2400)	660 (0.15)		
	EtOH/MeOH (4:1 v/v), (298)	342 (10 260), 432 (3155)	690, 750 (<0.1)		
	EtOH/MeOH (4:1 v/v) (77)		590 (3.00, 0.45)^b		
	solid (298)		690 (0.26)		
	solid (77)		650		
3	acetone	406 (2260)	690 (<0.1)	−1.62	+0.97, +1.85
	THF	424 (3570)	690 (<0.1)		
	Et_2O	258 sh (23 235), 298 (22 080), 346 sh (2780), 440 (3010)	680 (0.14)		
	EtOH/MeOH (4:1 v/v) (298)	250 sh (21 640), 278 sh (16 310), 296 (19 520), 400 (3310)	690 (<0.1)		
	EtOH/MeOH (4:1 v/v) (77)		560 (1.60)		
	solid (298)		600 (0.17)		
	solid (77)		580		

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} = anodic peak potential; working electrode, glassy carbon; scan rate, 100 mV s^{-1}; MeCN (0.1 mol dm^{-3} $^nBu_4NPF_6$). [b] Biexponential decay.

Solvatochromism has been observed for the low-energy absorption, with the transition energies following the order of increasing polarity of the solvent: Et_2O < THF < CH_2Cl_2 < Me_2CO < EtOH/MeOH (Table 4). This is typical of MLCT (dπ(Re) → π*(L)) transitions. Complex **2** shows an intense low-energy absorption band in the region of 430−495 nm, the transition energy of which is also dependent on the solvent polarity. However, an assignment of this low-energy absorption band as a pure dπ(Re) → π*(^{t}Bu$_2$bpy) MLCT transition is not favored on the basis of the following grounds. In view of the close σ-donor abilities of the butadiynyl (C≡CC≡CH) ligand and the acetylide (C≡CH) ligand,[10] it is not unreasonable to assume that the σ-donor ability of C≡CC≡C−Re(^{t}Bu$_2$bpy)(CO)$_3$, with a Re(CO)$_3$L unit containing π-acceptor CO ligands at the Re metal center, is weaker or at least similar to that of C≡CC≡CH, leading to a dπ(Re) → π*(^{t}Bu$_2$bpy) MLCT transition of higher or similar energy for **2**. Thus, it is unlikely that the exceptionally low-energy band in **2** arises from such a transition. Moreover, if a dπ(Re) → π*(^{t}Bu$_2$bpy) MLCT is responsible for this low-energy transition band (480 nm in THF), an extinction coefficient equal to twice that of the 404-nm band in **1** (THF) would be expected.

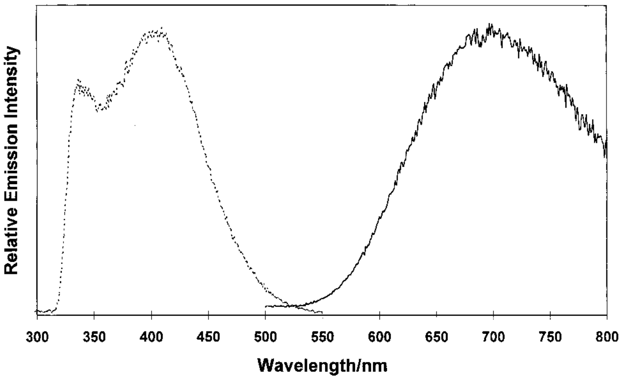

Figure 2. Excitation (- - -) and emission (—) spectra of complex **3** in degassed acetone at 298 K. The sudden drop of intensity below 340 nm is an artifact due to the cutoff wavelength of acetone.

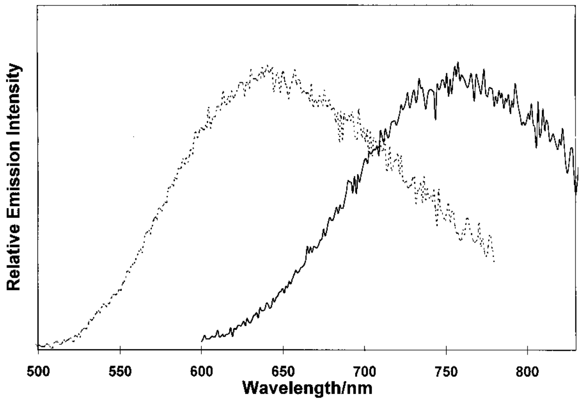

Figure 3. Emission spectra of complex **2** in degassed THF at 298 K with excitation wavelength at 380 nm (- - -) and 480 nm (—).

Excitation of **1** and **3** at λ >350 nm resulted in long-lived orange-red emissions at *ca.* 660−690 nm in solution, tentatively assigned as originating from a ^{3}MLCT (dπ(Re) → π*(^{t}Bu$_2$bpy)) transition, the lifetime range of which is typical of such transitions (submicroseconds at 298 K, microseconds at 77 K). The photophysical data are summarized in Table 4. The excitation and emission spectra of **3** in degassed acetone are depicted in Figure 2. Similar findings have been observed in related Re(I) acetylide systems.[6c] The fact that the emission energies are not particularly solvent sensitive, despite a large shift in the MLCT absorption band, is typical of dπ(Re) → π*(L) MLCT transitions and appears to be general for metal carbonyl complexes.[12] It is found that the red-orange emissions of **1** and **3** observed in an ethanol−methanol mixture (4:1 v/v) at 298 K are blue-shifted to give more intense yellow-green emissions in the glass at 77 K. Such luminescence rigidochromism has also been reported in other Re(I) diimine systems.[12] Excitation of **2** at λ 350−400 nm also resulted in long-lived luminescence at *ca.* 660−690 nm, probably ^{3}MLCT

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(12) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711. Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I.; Snyder, R. *Inorg. Chem.* **1991**, *30*, 4871.

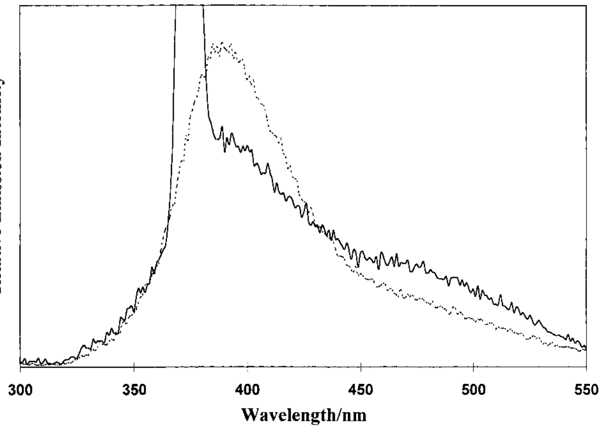

Figure 4. Excitation spectra of complex **2** in degassed acetone at 298 K with emission wavelength monitored at 630 nm (- - -) and 750 nm (—). The sharp band at 375 nm is an artifact due to monitoring at 750 nm.

(dπ(Re) → π*(^{t}Bu$_2$bpy)) in origin. However, upon excitation at $\lambda \geq 450$ nm, a lower lying emission at *ca.* 750 nm appears (Figure 3). The excitation spectra of **2** monitored at the two different bands are shown in Figure 4.[13] Given the greater ease of reduction and oxidation of the −C≡CC≡C− unit than of −C≡C− as predicted by Hückel MO theory,[14] it is not unlikely that the 750 nm band in **2**, which is absent in the mononuclear counterpart, is of either ^{3}MLCT (dπ(Re) → π*(C≡CC≡C−Re)) or ^{3}LLCT (π(C≡CC≡C−Re) → π*(^{t}Bu$_2$bpy)) parentage. An assignment of the 750 nm band as ^{3}IL (π → π*(−C≡CC≡C−)) has been excluded in view of its exceptionally low energy. With reference to previous spectroscopic work on oligoacetylenic chromophores, a red shift of the π → π*(−C≡C−) transition eneriges of *ca.* 0.24 eV has been estimated on going from a di- to a triacetylenic system.[15] Assuming a similar shift would occur for a metal to π*(−C≡C−) transition, an emission energy of 0.24 eV to the blue of the 750 nm band should occur at *ca.* 655 nm in **1** which, if present, is likely to be obscured by the 670 nm band of dπ(Re) → π*(^{t}Bu$_2$bpy) MLCT origin.

The cyclic voltammograms of complexes **1**−**3** all show a reversible to quasi-reversible reduction couple at *ca.* −2.0 V *vs.* the ferrocenium−ferrocene couple, assignable to the reduction of the ^{t}Bu$_2$bpy ligand (Table 4). Complexes **1** and **3** show two irreversible oxidation waves at +1.07, +1.84 and +0.97, +1.85 V, respectively. On the other hand, complex **2** displays three irreversible oxidation waves at +0.72, +1.33, and +1.84 V. It is likely that the oxidation waves at *ca.* +1.84 V in complexes **1**−**3** are Re in origin. Similar assignments have been made for related Re(I) diimines.[5] The first oxidation, which becomes thermodynamically more favorable with longer carbon chains (*i.e.*, the ease of oxidation increases from **1** to **2**), is in agreement with the predictions from Hückel MO theory, where the HOMO energies increase with increasing C≡C units.[14] This, together with the greater ease of the first oxidation of **3** than of **1**, substantiates that the first oxidation is predominantly ligand-centered (−C≡C−) in nature. The additional oxidation wave observed in **2** at *ca.* +1.33 V may represent the oxidation at the second −C≡C− unit. Unlike the related Re(I) nitrosyl system studied by Gladysz and co-workers,[4b,c] no reversible reduction couple attributed to −C≡C− reductions are observed. The reason might be kinetic rather than thermodynamic in nature, since Hückel MO theory predicts that the LUMO energies usually decrease with an increasing number of −C≡C− units.[14]

Further work on the preparation of related unsymmetrical coupling products are in progress.

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Supporting Information Available: Text giving details of the X-ray crystal structure determination and tables of hydrogen coordinates and thermal parameters, general displacement parameter expressions, *U*, all bond distances involving non-hydrogen atoms, and all bond angles involving non-hydrogen atoms for **2** (9 pages). Ordering information is given on any current masthead page.

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[13] A reviewer raised the point about the possibility of the presence of a luminescent impurity in **2**. We have also been aware of this possibility. However, although we cannot completely exclude this possibility, we do not favor this assignment on the basis of the following grounds. First, an assignment of the 750 nm band to an impurity emission is unlikely, since it is difficult to envisage a possible impurity, whether organic or inorganic in nature, to emit at such low energies. Excitation of other rhenium(I) acetylides such as **1** and **3** at $\lambda = 450-480$ nm do not give emission at similar energies. Second, the possibility of the 630-nm emission as due to an impurity has also been disfavored. The most probable impurity that would emit at this energy would be a trace amount of **1** in **2**. However, we found that there is a small discrepancy between the emission wavelengths of **1** and **2** in the same solvent system. For example, **1** emits at 670 nm, while **2** emits at 630 nm in THF. Third, the excitation spectra of **2** monitored at the two different emission bands are also very similar in the high-energy regime. Fourth, the room-temperature solid-state emission spectra of **1** and **2** occur at 610 and 690 nm, respectively. If **1** is really present as an impurity in **2**, it should also show up in the solid-state spectra, since **1** also has a much larger luminescence quantum efficiency than does **2** in the solid state.

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