Inorganic Chemistry
Communication

Unusual, Bifurcated Photoreactivity of a Rhenium(I) Carbonyl Complex of Triethynylphosphine
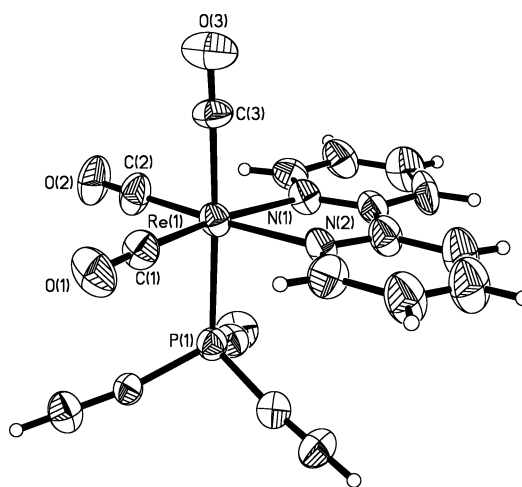
Sean E. Hightower, Robert C. Corcoran, and B. Patrick Sullivan*

Department of Chemistry, University of Wyoming, P.O. Box 3838, Laramie, Wyoming 82071

Preparations of the first metal complexes of triethynylphosphine (TEP) are described. They are of the type *fac*-Re(bpy)(CO)$_3$(TEP)$^+$ (**1**) and *cis,trans*-[Re(bpy)(CO)$_2$(TEP)L]$^{n+}$ (CH$_3$CN, $n = 1$, complex **2**; Cl, $n = 0$, complex **3**), where bpy is 2,2′-bipyridine. Complex **1** displays unusual photochemical behavior compared to analogous *fac*-[Re(bpy)(CO)$_3$(PR$_3$)]$^+$ complexes in that it emits from a state that has $\pi-\pi^*$ character but undergoes competitive photosubstitution of both TEP and CO. Density functional theory (DFT)/time-dependent DFT calculations predict that the lowest emitting state should, in fact, have $\pi-\pi^*$ character.

Tertiary phosphines are among the most common and versatile ligands in all of transition-metal chemistry. In our recent work directed toward the preparation of oligometallic metal-to-ligand charge-transfer (MLCT) excited states, we were surprised to find that triethynylphosphine (TEP)[1] has never been coordinated to a transition metal. Here we report the preparation of the first complexes of TEP and the discovery that the photochemistry and photophysics of *fac*-Re(bpy)(CO)$_3$(TEP)$^+$ (**1**), where bpy is 2,2′-bipyridine, is quite different from that of the other phosphine analogues, e.g., *fac*-Re(bpy)(CO)$_3$(PR$_3$)$^+$ (where R is, for example, Ph).[2] Complex **1** is prepared in the standard manner using *fac*-Re(bpy)(CO)$_3$OTf as the starting complex.[3] Isolation and purification is accomplished by crystallization. Characterization of the complex was achieved by ^{31}P and ^{1}H NMR and IR spectroscopies and elemental analysis.[4] A single-crystal X-ray diffraction study was performed on crystals grown by the slow evaporation of methanol. From examination of the X-ray structure of the complex shown in Figure 1, two features are apparent that are hallmarks of the coordinated TEP ligand. First, TEP is one of the smallest coordinated phosphines known, having a cone angle of 103.6°, and second, the Re–P bond length is 2.37 Å, considerably shorter than other cases in the literature (see, for example, the

* To whom correspondence should be addressed. E-mail: bpat@uwyo.edu.

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Figure 1. X-ray crystal structure of *fac*-[Re(bpy)(CO)$_3$(TEP)]$^+$ (**1**). Crystals as the triflate salt were grown from methanol/methylene chloride by vapor diffusion.

Re^I–PPh$_3$[5a] and Re^I–dppb bonds,[5b] which have values of 2.503 and 2.505 Å, respectively). It is probable that this short bond length is a direct consequence of the sterically unencumbered nature of the ligand relative to the larger phosphines. A modest structural trans effect[6] of 0.05 Å also is seen in the structure (i.e., the difference between the bond lengths of the *trans*- and *cis*-CO ligands).

(4) Preparation of *fac*-[Re(CO)$_3$(bpy)(P(C≡CH)$_3$)](OSO$_2$CF$_3$) (complex **1**): *fac*-Re(CO)$_3$(bpy)(OSO$_2$CF$_3$) (0.0504 g, 8.850 × 10^{-5} mol) was dissolved in 50 mL of CH$_3$CN and brought to reflux for 1 h. CH$_3$CN was removed under a reduced pressure. Without further purification, 50 mL of dry THF was added, followed by the addition of TEP (0.048 g, 4.497 × 10^{-4} mol). Under an argon atmosphere, the reaction mixture was brought to reflux for 6 h. The solvent was removed under reduced pressure, and the product was reprecipitated from CH$_2$Cl$_2$ by the addition of chilled hexanes, collected by suction filtration, and rinsed several times with chilled hexanes. No further purification was required. The yield was near-quantitative. Anal. Calcd: C, 35.25; H, 1.63; N, 4.11. Found: C, 35.05; H, 1.70; N, 3.98. ESI-MS (**1**): *m/z* 532.7 (calcd *m/z* 533.01 [**1** − OTf]$^+$). ^{1}H NMR (400 MHz, δ/ppm, CD$_3$COCD$_3$): 4.39 (d, 3H, $J_{P-C≡C-H}$ = 9.1 Hz), 7.98 (t, 2H, J = 13.1 Hz), 8.48 (t, 2H, J = 14.6 Hz), 8.92 (d, 2H, J = 8.2 Hz), 9.17 (d, 2H J = 5.5 Hz). ^{31}P{^{1}H} NMR (136 MHz, δ/ppm, CD$_3$COCD$_3$, referenced to H$_3$PO$_4$): −62.8. UV−visible [CH$_2$Cl$_2$; λ, nm (ϵ, M^{-1} cm^{-1})]: 350 (4430), 318 (17340), 308 (15 371), 256 (24 290). IR (CH$_2$-Cl$_2$, cm^{-1}): ν(CO) 1975, 1921; ν $_{C≡C}$ 2052.
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Complexes of the type *fac*-Re(bpy)(CO)₃(PR₃)⁺ are known to undergo a single photosubstitution of CO in competition with emission from a low-lying triplet state.[2,7] *fac*-Re(bpy)-(CO)₃(TEP)⁺ is no exception; however, it apparently has the highest known emission energy for complexes of this class, which is, in fact, close to that of Re(bpy)(CO)₄⁺, a known $\pi-\pi^*$ emitter.[7] This is aptly illustrated by an emission spectral comparison of complex **1**, *fac*-Re(bpy)(CO)₃(PPh₃)⁺, and *fac*-Re(bpy)(CO)₃(NCCH₃)⁺ recorded in a poly(methyl methacrylate) matrix at 20 °C. The emission maxima are observed at 484, 491, and 514 nm, respectively. Complex **1** exhibits vibronic structure characteristic of a $\pi-\pi^*$ emitter, whereas the other two do not. In CH₂Cl₂, the emission maximum is 484 nm, which compares with 476 nm for Re-(bpy)(CO)₄⁺. Apparently, TEP acts as a better acceptor ligand than PPh₃ and raises the emission energy substantially.

The photochemistry of **1** is distinctive compared to other *fac*-Re(bpy)(CO)₃(PR₃)⁺ complexes because *more than one photochemical channel is available* and it is of comparable importance. Solution measurements of the emission spectral manifold are distorted by the high photosensitivity of the complex, and although we have not yet measured the quantum yield of the reaction, we have identified the products from photolysis in CH₃CN. Thus, by following the photolysis with both IR and ³¹P NMR spectroscopy under conditions analogous to those described by Koike et al., it is observed that the reaction gives *fac*-Re(bpy)(CO)₃(NCCH₃)⁺, free TEP ligand, and a complex that we have characterized as *cis,trans*-Re(bpy)(CO)₂(TEP)(NCCH₃)⁺ (**2**).[8,9] The recent work of Ishitani, Turner, and co-workers on *fac*-Re(bpy)(CO)₃(PR₃)⁺ has established that an apparent excited-state trans effect, which labilizes the weak field ligand on the strong field axis, is responsible for photosubstitution of CO.[2] For complex **1**, a competition is set up between CO and TEP loss, which, after 2 h of photolysis, leads to a branching ratio of 1.5:1.

We further exploited this unique photoreactivity in a preparative manner for the formation of the complex *cis,trans*-Re(bpy)(CO)₂(TEP)Cl (**3**) by photolysis of **1** in the presence of a saturated NaCl or 0.32 M HCl solution. Complex **3** is obtained cleanly in 33.6% yield after column chromatography on silica gel using 2.5% MeOH/CH₂Cl₂ as the eluent.[10] *fac*-Re(bpy)(CO)₃Cl was isolated cleanly off the column as well. Comparison of the ν_{CO} values for **3** (1951 and 1879 cm⁻¹)[11] with, for example, *cis,trans*- Re(bpy)(CO)₂-(PPh₃)Cl (1938 and 1867 cm⁻¹) further demonstrates the better net acceptor ability of the TEP ligand. Again, evidence of the branched photochemistry is observed with the formation of *fac*-Re(bpy)(CO)₃Cl in competition with **3**.

To gain insight into the photochemical behavior of complex **1**, a series of density functional theory (DFT) and nonequilibrium time-dependent DFT (TDDFT)[12]/PCM[13] calculations were performed using the *Gaussian03*[14] suite of programs. Figure 2 (top) shows a gas-phase density-of-states diagram[14] where a selection of the calculated Kohn−Sham (K−S) orbitals in the highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) region is portrayed. These orbitals make up the majority of the one-electron excitations that mix to yield the three lowest-lying singlet and triplet states of complex **1**. Of note in Figure 2 is the large amount of d-orbital character for the three closely spaced K−S orbitals centered at ca. −9.6 eV and the dominant bpy character for the K−S orbitals from ca. −5.8 to −4.8 eV. From TDDFT, the lowest singlets are predicted to occur at 388 (0.006), 386 (0.005), and 365 (0.0756) nm and are all admixtures of one-electron transitions from the HOMO to HOMO-2 (MOs 96−94) to the LUMO (MO 97), with the last being assigned to the major MLCT because of its oscillator strength. The three lowest-lying triplets that are predicted to occur at 429, 403, and 389 nm are quite different in composition in that all are extensively mixed transitions, but the lowest energy one has substantial contribution from MO 93 to 97. As seen in Figure 2 (bottom), this one-electron excitation is almost pure $\pi-\pi^*$. Thus, both calculations and experiments suggest that the lowest energy-emitting triplet is not pure MLCT but has some $\pi-\pi^*$ character. We should also mention that calculations with the

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(9) Preparation of *cis,trans*-[Re(CO)₂(bpy)(P(C≡CH)₃)(NCCH₃)](PF₆) (complex **2**): complex **1-PF₆** (0.0936 g, 1.38 × 10⁻⁴ mol) was dissolved in 100 mL of anhydrous CH₃CN. The solution was purged with N₂(g) for 30 min and then photolyzed for 2 h (monitored by the disappearance of the green emission with a UV hand lamp). A water solution of ammonium hexafluorophosphate was added, and CH₃CN was then removed under reduced pressure. The crude complex (**2**) was filtered, dried, and then purified by column chromatography on silica gel (2.5% CH₃OH and CH₂Cl₂; 44% yield). Elem anal. Calcd: C, 34.79; H, 2.04; N, 6.09. Found: C, 34.58; H, 2.11; N, 5.93. ESI-MS (**2**): *m/z* 545.6 (calcd *m/z* 546.04 [**2** − PF₆]⁺). ¹H NMR (400 MHz, δ/ppm, CD₃COCD₃): 2.43 (s, 3H), 4.04 (d, 3H, $J_{P−C≡C−H}$ = 9.1 Hz), 7.26 (t, 2H, *J* = 5.3 Hz), 8.42 (t, 2H, *J* = 7.8 Hz), 8.79 (d, 2H, *J* = 8.2 Hz), 9.06 (d, 2H, *J* = 4.5 Hz). ³¹P{¹H} NMR (136 MHz, δ/ppm, CD₃COCD₃, referenced to H₃PO₄): −51.6. UV−visible [CH₂-Cl₂; λ, nm (ϵ, M⁻¹ cm⁻¹)]: 380 (6900), 296 (29570). IR (CH₂Cl₂, cm⁻¹): ν(CO) 1969, 1900.

(10) Preparation of *cis,trans*-Re(CO)₂(bpy)(P(C≡CH)₃)(Cl) (complex **3**): A vessel containing 150 mL of a saturated NaCl or 0.32 M HCl solution and 150 mg of complex **1** was irradiated under a N₂(g) atmosphere using a 450-W tungsten lamp for 48 h. Extraction with CH₂Cl₂, followed by evaporation under reduced pressure, resulted in a red/orange crude product. Column chromatography on silica gel using 2.5% MeOH/CH₂Cl₂ as the eluant afforded a yield of 34%. Anal. Calcd: C, 45.04; H, 2.05; N, 5.19. Found: C, 45.60; H, 2.78; N, 5.20. ¹H NMR (400 MHz, δ/ppm, CD₃COCD₃): 3.76 (d, 3H, J_{PCCH} = 8.6 Hz), 7.33 (t, 2H, *J* = 13.1 Hz), 8.20 (t, 2H, *J* = 14.6 Hz), 8.60 (d, 2H, *J* = 8.0 Hz), 8.91 (d, 2H, *J* = 5.0 Hz). ³¹P{¹H} NMR (136 MHz, δ/ppm, CD₃COCD₃, referenced to H₃PO₄): −57.2. UV−visible [CH₂-Cl₂; λ, nm (ϵ, M⁻¹ cm⁻¹)]: 428 (3520), 306 (33 160). IR (CH₂Cl₂, cm⁻¹): ν(CO) 1951, 1879.

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(12) The electronic ground state and geometry optimization were carried out using the B3LYP approximation, followed by a TDDFT calculation of the lowest excited states employing the same functional. The calculations utilized the 6-31G* basis set for the ligands and the LANL2 relativistic effective core potential for the transition metal. PCM calculations were employed to produce a number of singlet and triplet excited states of complex **1** in methylene chloride and acetonitrile based on the singlet/triplet ground-state geometry optimized in the gas phase. The self-consistent reaction field CPCM was implemented.

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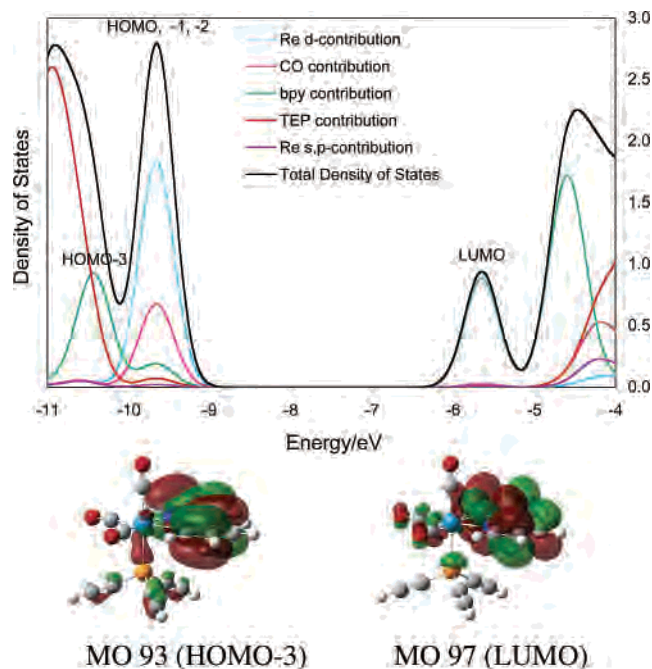
Figure 2. Density-of-states diagram derived from a DFT calculation on complex **1** showing the relevant orbitals in the HOMO−LUMO region (top). The bottom shows the orbital composition of MOs 93 and 97, which contribute to the lowest triplet.

inclusion of solvent (CH_2Cl_2 and CH_3CN) resulted in a greater contribution from the MO 93 to 97 excitation. Despite this success, no clear insight is provided into the unique bifurcated photoreactivity of the complex at this level of model chemistry. No excited state is seen to be thermally accessible from the lowest triplet at room temperature, as has been proposed for similar complexes,[2] and the nearest

transition exhibiting antibonding character with respect to both the Re−P and *trans*-Re−CO bonds is predicted to occur at 338 nm (involving MO 102). This issue is currently being examined, and it is possible that to explain the photoreactivity thoroughly from a computational point of view, nonadiabatic direct dynamics must be used.[15]

In summary, the physical and photophysical properties of the first Re[I] complexes of TEP demonstrate its high net acceptor strength relative to PPh_3, its small cone angle, and its ability to convey competitive photosubstitution from initial excitation into the MLCT excited-state manifold. Calculations show that the emitting state of **1** exhibits some $\pi-\pi^*$ character, which suggests that the behavior of the TEP ligand resembles a CO more than other PR_3 ligands. Last, complexes of the TEP ligand offer some unique opportunities for the synthesis of supermolecules containing multiple metal atoms both by coordination at an alkyne carbon and from addition reactions at the alkyne functional group to give cyclic and bridging ligands.

Supporting Information Available: The complete X-ray data (CIF) for compound **1** (bond lengths, angles, and coordinates) are included along with selected details of the DFT/TDDFT for the same (bond lengths, angles, eigenvalues for the MOs, orbital compositions, and the energies of the first eight singlets and triplets). This material is available free of charge via the Internet at http://pubs.acs.org.

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