equiv) and K_2CO_3 (3 equiv) in DMF at 23 °C for 3 h gave rise to amphimedine **1** in 96% yield as a dark yellow solid of mp >300 °C, identical in all aspects with an authentic sample by ^1H and ^{13}C NMR, IR, silica gel-TLC analysis in several solvent systems, and mass spectral comparison.

In summary, a concise synthesis of the alkaloid amphimedine has been achieved in eight steps (21–23% overall yield). This synthesis illustrates the utility of the palladium-catalyzed cross-coupling reaction of organostannanes with functionalized electrophiles in the elaboration of complex molecules. During the course of this study a dramatic solvent effect in a hetero-Diels–Alder reaction has been uncovered.

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Supplementary Material Available: Spectroscopic, physical, and analytical data for new compounds and experimental procedures for the preparation of **2**, **16**, and **1** (5 pages). Ordering information is given on any current masthead page.

Electronic Emission from Bis(bridging diphosphine) Derivatives of $Re_2(CO)_{10}$. Characterization of the Emissive State as $^3(d\sigma \rightarrow d\sigma^*)$

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We recently[1] reported electronic emission from d^7–d^7 singly metal–metal bonded compounds of the type $Pt^{III}_2(pop)_4L_2{}^{n-}$, where pop is $P_2O_5H_2{}^{2-}$ and L is, for example, a halide. The emission was unequivocally characterized as the first observation of emission from a d^7–d^7 metal–metal excited state by observation of a long progression in $\nu(Pt_2)$ for the low-temperature emission of the K^+ salt of the L = Br derivative. We have subsequently observed[2] similar emission for the previously reported[3] d^7–d^7 compounds $Ir^{II}_2(TMB)_4L_2{}^{n+}$, where TMB is 2,5-diisocyano-2,5-dimethylhexane.

Common factors in these compounds are bridging ligands (presumably preventing metal–metal dissociation) and third transition series metal ions (presumably enhancing spin-orbit coupling, hence radiative transitions from a low-energy metal–metal triplet-parentage state).

The compounds $M_2(CO)_{10}$ M = Mn, Tc, Re, have been the classic examples of highly dissociative metal–metal excited states, yielding in the case of $Mn_2(CO)_{10}$, $Mn(CO)_5$ radicals on the time scale of less than 20 ps in the gas phase.[4] The spectroscopy, photophysics, and photochemistry of these dimers has been exhaustively studied.[5] It is therefore of great interest to determine whether bridging ligands might enforce a long lived emissive state by preventing the homolysis pathway. Establishing a correlation with these compounds would make it completely clear that the same type of excited states are being considered in the case of the previously reported Pt(III) dimers. Guided by our previous work, we have investigated derivatives of $Re_2(CO)_{10}$. We now report that derivatives involving substitution of 2 equiv of either[6] bis(dimethylphosphino)methane (dmpm) or bis(diphenylphosphino)methane (dppm) are highly emissive at low temperature. In contrast, under the same conditions we find that both $Re_2(CO)_{10}$ and $Re_2(CO)_8(P(C_6H_5)_3)_2$ are nonemissive, consistent with the photophysical results.[4]

We have concentrated upon the dmpm derivative, $Re_2(dmpm)_2(CO)_6$ (I), because the absence of phenyl groups clarifies the electronic spectrum. In Figure 1 we show the emission

Table I. Emission Data for $Re_2(P\text{–}P)_2(CO)_6$ Compounds at 77 K

			2-methylpentane glass	
P–P	λ (nm)	solid τ (μs)	λ (μm)	τ (μs)
dmpm	705	23	690	31
dppm	620	64	610	76[a]

[a] In 2-methyltetrahydrofuran glass (49 μs). The absorption and emission spectra are insensitive to solvent.

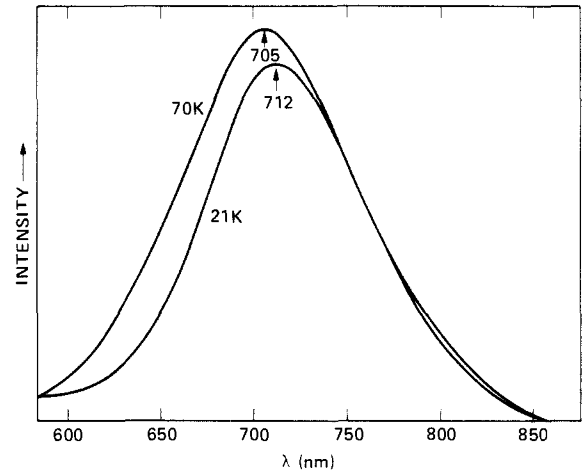

Figure 1. Emission spectrum of a solid sample of $Re_2(dmpm)_2(CO)_6$ at 20 and 70 K. The spectral slit width was 2 nm, and the exciting wavelength was 400 nm.

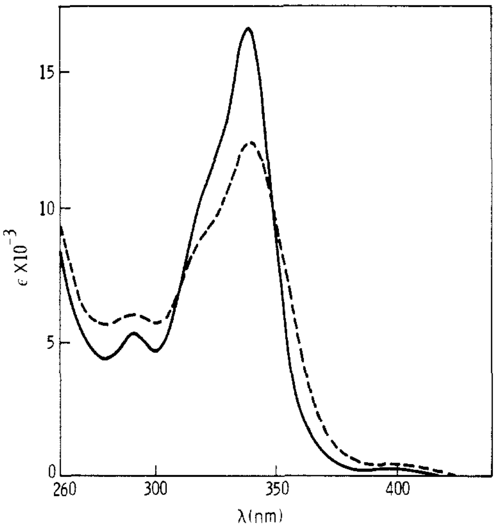

Figure 2. The absorption spectrum of $Re_2(dmpm)_2(CO)_6$ at room temperature (– –) and 77 K (—) in 2-methylpentane solution. The 77 K spectrum has been corrected for solvent contraction.

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spectrum of the pure solid at low temperature, while in Figure 2 we show the absorption spectrum. The emission excitation spectrum at 77 K in hydrocarbon glass was identical with the absorption spectrum in the wavelength range 250–450 nm.

The half-width of the emission is extraordinarily temperature sensitive, increasing by about 50% between 20 and 80 K, for the solid. It continues to increase at higher temperatures, up to the highest temperature, ≈250 K, at which emission can be detected with our instrumentation.[1] The thermal variation is probably due to hot-band (second-moment) effects[3] involving the anticipated very low excited state $\nu(Re_2)$, although thermal population of several spin-orbit components[7] might also be involved.

No emission has been detected from fluid solutions of the rhenium dimers. The most important factor appears to be the rigidity of the medium, as weak emission is detectable even at room temperature for poly(methyl methacrylate) films containing the dimers (emission lifetime 4.8 μs at 293 K for the dppm complex).

The emissive state is likely to be the $^3(d\sigma \rightarrow d\sigma^*)$ state. The lowest energy absorption reported for $Re_2(CO)_{10}$ is the $^1(d\sigma \rightarrow d\sigma^*)$ transition at 312 nm;[8] transitions of the type $^1(d\pi \rightarrow d\sigma^*)$ appear to lie at higher energy of $d\sigma \rightarrow d\sigma^*$ for the third-row compound. For the compound $Re_2(dmpm)_2(CO)_6$, we assign the band at 342 nm (ϵ 12 400) to the $^1(d\sigma \rightarrow d\sigma^*)$ transition. The pronounced narrowing of the band at lower temperature is characteristic[3] of this transition. The dppm derivative shows an analogous band at 325 nm (ϵ 8000). The lower energy of this band relative to $Re_2(CO)_{10}$ is consistent with other studies of phosphine derivatives.[8,9] Thus, it is unlikely that $^3(d\pi \rightarrow d\sigma^*)$ states are responsible for the emissions of the Re_2 compounds, and, by extension, the previously characterized emissions (vide supra) of d^7–d^7 compounds are likely also from $^3(d\sigma \rightarrow d\sigma^*)$ states because of their very similar characteristics.[10] The energy of the emission is quite consistent with previous estimates[4,5] of the energy of $^3(d\sigma \rightarrow d\sigma^*)$, the large singlet–triplet splitting being attributable to the ionic nature of the singlet state. Excitation into the $^1(d\sigma \rightarrow d\sigma^*)$ absorption with polarized light yields polarized emission,[11] $I/I \approx 0.7$. Since $^1(d\sigma \rightarrow d\sigma^*)$ is molecular z-polarized, the observed emission polarization ratio less than one implies the emission to be x,y-polarized which is also consistent with a $^3(d\sigma \rightarrow d\sigma^*)$ assignment (spin-orbit components $A_1 + E$ in D_4 symmetry).

In conclusion, we find that the $^3(d\sigma \rightarrow d\sigma^*)$ state of d^7–d^7 singly metal–metal bonded complexes may be a long-lived (emissive) excited state if metal–metal dissociation is prevented. Photochemical studies of these molecules are in progress in conjunction with Professor David Tyler at the University of Oregon. Initial results indicate that efficient reaction occurs with halocarbons which suggests that metal–metal dissociation may still occur in a fluid medium.

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Registry No. I, 90624-20-7; $Re_2(dppm)_2(CO)_6$, 95648-63-8.

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(10) The assignment of the very weak 400 nm (ϵ 400) absorption feature (Figure 2) exhibited by both Re dimers, which is also present in the excitation spectra, is uncertain. The weakness of the transition and the fact that it is not present in the spectra of analogous phosphine bridged manganese dimers suggests that it is a single–triplet absorption. The transition is too high in energy to be the emissive $^3(d\sigma \rightarrow d\alpha^*)$ state (this would give an unreasonably large Stokes shift) but may be the spin forbidden analogy of one of the higher energy $^1(d\pi – d\alpha^*)$ states (which are probably responsible for the bands to higher energy of $^1(d\sigma – d\sigma^*)$, see Figure 2). Unfortunately the weakness of the band prevented accurate determination of its polarization ratio.

(11) The polarization ratio is $(I_{vv} \cdot I_{hh})/(I_{vh} \cdot I_{hv})$.

Luminescence from a Novel Mixed-Valence Dirhodium Fluorophosphine Complex

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Fluorophosphine ligands coordinated to transition-metal complexes can engender unique oxidation–reduction chemistry. The dual function of fluorophosphines as good σ-donating and strong π-accepting ligands[1-4] is manifested in their ability to stabilize transition metals in several oxidation states.[5] Moreover, although the physical and chemical properties of electronically excited fluorophosphine complexes have yet to be defined, exhaustive spectroscopic studies of many other classes of transition-metal complexes during the past decade have demonstrated that ligands possessing low-lying π-accepting orbitals are effective in stabilizing metal complexes in long-lived lowest energy excited states.[6-13] Owing to our interest in developing new photoredox chemistry, we have begun investigations of fluorophosphine complexes in view of their demonstrated redox and anticipated excited-state properties. We now report the synthesis and spectroscopy of a long-lived, highly emissive binuclear complex in which a bidentate fluorophosphine ligand stabilizes rhodium in two different oxidation states, Rh(II) and Rh(0). Interestingly, our data suggest that the emissive excited state is primarily metal-localized with little metal-to-ligand charge-transfer character.

The previously reported $Rh_2(\mu\text{-}Cl)_2(PF_3)_4$ complex[14] reacts immediately with methylaminobis(difluorophosphine)[15] in benzene at room temperature. Addition of hexane to the resulting red-orange solution produces an orange solid. A dichloromethane solution of this compound layered with hexane yields red-orange prismatic crystals which have been identified by crystallographic analysis to be $Rh_2[(F_2P)\text{-}N(CH_3)\text{-}(PF_2)]_3Cl_2(PF_3)$ (**1**).[16] The molecular structure of **1**, represented by the ORTEP diagram shown

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(16) (a) Crystal data for $Rh_2[(F_2P)\text{-}N(CH_3)\text{-}(PF_2)]_3Cl_2(PF_3)$ (**1**): orthorhombic, $P2_12_12_1$; $a = 9.620\ (2)$ Å, $b = 12.755\ (2)$ Å, $c = 19.564\ (3)$ Å; $V = 2400.4\ (6)$ Å^3; $Z = 4$, $D_{calcd} = 2.40$ g/cm^3. A Nicolet P3F diffractometer was used to collect 9542 data ($2° \leq \theta \leq 32.5°$) at 27 ± 1 °C of which 4889 data were unique; 3880 data with $I > 3\sigma(I)$ were used in refinement. Structure refined to $R = 0.026$ and $R_w = 0.025$, GOF = 1.20; highest final difference peak, 0.6 e/Å^3 [0.9 Å from Rh(2)]. (b) The $P2_12_12_1$ space group requires the existence of two enantiomorphic structures; differences between the two enantiomorphs were slight (no thermal parameter differed by more than 1σ and no bond distance differed by more than 0.005 Å). The enantiomorph in this manuscript was favored because its refinement yielded better GOF (1.20 versus 1.26) and R_w (0.025 versus 0.027) values.

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