measured for hydride complexes in acetonitrile are ca. 7.5 pK_a units higher than those measured in H_2O.

The acidity of $CpCr(CO)_3H$ in MeOH ($pK_a = 6.4$, by extrapolation from measurements in 70:30 $MeOH/H_2O$) has been found to be greater than that of $H_2Fe(CO)_4$ ($pK_a = 6.8$),[5c,d] a reversal of the acidity order obtained in acetonitrile. In general, the pK_a values measured for hydride complexes in acetonitrile are ca. 6.7 pK_a units greater than those measured in MeOH.

Lastly, these acetonitrile acidity measurements agree with the small amount of reported gas-phase data. Stevens and Beauchamp, using ion cyclotron resonance spectroscopy,[48] have reported that $HCo(CO)_4$ is far more acidic than either $H_2Fe(CO)_4$ or $HMn(CO)_5$ (it is not clear which of the latter two compounds is the more acidic). Recent theoretical work calculates a larger total protonation energy,[49] and a smaller LUMO/HOMO energy difference,[50] for $Mn(CO)_5^-$ than for $Co(CO)_4^-$. Modified extended-Hückel theory calculates that ΔH for gas-phase proton transfer onto H_2O increases in the order $HCo(CO)_4 < H_2Fe(CO)_4 < HMn(CO)_5$,[51] in agreement with the order of acidities in CH_3CN in Table II. It seems likely that *differential* solvation effects have little effect on the acidity of transition-metal hydride in solution.

Acknowledgment. This research was supported by NSF Grant CHE82-07597. The authors are grateful to Dr. Michael Wright for a gift of $[Cp^*Fe(CO)_2]_2$ and to Robert Hembre for a gift of $Na_2Ru(CO)_4$, to Dr. R. Wegman for advice on the preparation of $HCo(CO)_4$, to Prof. R. G. Pearson for a preprint of ref 5d, and to Prof. J. F. Coetzee and Prof. J. I. Brauman for helpful discussions on CH_3CN purification and acidity in nonaqueous solvents.

Registry No. $HCo(CO)_4$, 16842-03-8; $HCo(CO)_3P(OPh)_3$, 57574-46-6; $H_2Fe(CO)_4$, 12002-28-7; $CpCr(CO)_3H$, 36495-37-1; $CpMo(CO)_3H$, 12176-06-6; $HMn(CO)_5$, 16972-33-1; $HCo(CO)_3PPh_3$, 19537-79-2; $CpW(CO)_3H$, 12128-26-6; $Cp^*Mo(CO)_3H$, 78003-92-6; $H_2Ru(CO)_4$, 42781-58-8; $CpFe(CO)_2H$, 35913-82-7; $CpRu(CO)_2H$, 57349-59-4; $H_2Os(CO)_4$, 22372-70-9; $HRe(CO)_5$, 16457-30-0; $Cp^*Fe(CO)_2H$, 80409-91-2; $CpW(CO)_2(PMe_3)H$, 31811-36-6.

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Picosecond Spectroscopic Studies of (d^8–d^8) Binuclear Rhodium and Iridium Complexes: A Comparison of $^1B_2$ and $^3B_2$ Reactivity in Bis(1,5-cyclooctadiene)bis(μ-pyrazolyl)diiridium(I)

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Abstract: Picosecond transient kinetics and difference spectra have been recorded for the singlet and triplet ($d\sigma^*p\sigma$) excited states in the d^8–d^8 dimers $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) and $[Ir(\mu\text{-pz})(COD)]_2$ (pz = pyrazolyl, COD = 1,5-cyclooctadiene). The singlet excited state in the rhodium dimer ($\tau = 820$ ps) displays a strong transient absorption feature maximizing at 440 nm that is not present in the spectrum of the triplet excited state. This intense absorption feature, characteristic of a $^1(d\sigma^*p\sigma)$ electronic configuration, is assigned to a $^1(d\sigma^*p\sigma) \rightarrow {}^1(p\sigma^2)$ excitation. The singlet excited state lifetime of the iridium dimer in cyclohexane is less than 20 ps. Though the solvent 1,2-dichloroethane (DCE) quenches luminescence from both singlet and triplet excited states in $[Ir(\mu\text{-pz})(COD)]_2$ and oxidatively adds to the dimer upon steady-state illumination, picosecond spectroscopy finds *no* evidence for any chemical reactivity of the very short-lived singlet excited state. The quenching of $[Ir(\mu\text{-pz})(COD)]_2$ singlet luminescence in DCE appears to result from enhanced singlet → triplet intersystem crossing in DCE relative to that in cyclohexane. Also, the invariance of triplet yield in these two solvents indicates that the efficiency of intersystem crossing is near unity.

Considerable spectroscopic work on d^8–d^8 binuclear complexes of rhodium, iridium, and platinum has shown that the lowest energy singlet and triplet excited states can be described by a $d\sigma^*p\sigma$ electronic configuration.[1] This configuration leads to $^{1,3}A_{2u}$ excited states in tetragonal (local D_{4h} symmetry) complexes such as $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) and to $^{1,3}B_2$ states in the lower symmetry (local C_{2v}) "A-frame" complexes exemplified by $[Ir(\mu\text{-pz})(COD)]_2$ (Ir_2) (pz = pyrazolyl, COD = 1,5-cyclooctadiene). Luminescence from both singlet and triplet excited states has been reported for these complexes, as well as for a number of related molecules. The Ir_2 complex has adjacent vacant coordination sites at the metal centers that afford the opportunity for multielectron redox reactions. Recently, Caspar and Gray have reported net photochemical, two-electron reduction of substrates whose initial, one-electron-transfer products are unstable.[2] Prior studies have shown that d^8–d^8 species with both D_{4h} and C_{2v} symmetries are powerful one-electron photoreductants.[1d,3] In all the above studies, the long-lived (hundreds

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of nanoseconds) triplet states were well-characterized by time-resolved spectroscopic techniques. In contrast, the subnanosecond-lived, singlet states have only been observed *during* excitation with a 10-ns laser pulse.[4]

If the dσ*pσ description is valid for the $^1A_{2u}$ and $^3A_{2u}$ excited states of $Rh_2(TMB)_4{}^{2+}$, there should be a marked difference in the absorption cross sections of these two states. Formation of a spin-paired excited state with a $(p\sigma)^2$ electronic configuration is much more allowed from the $^1A_{2u}$ than from the $^3A_{2u}$ state. A second point of interest regarding the properties of the singlet and triplet states of these d^8–d^8 binuclear complexes is the possibility of differences in their redox reactivities. In particular, the rate constant for quenching by DCE (DCE = 1,2-dichloroethane) is 7×10^5 $M^{-1}s^{-1}$ for the $^3B_2$ state of Ir_2 and $>3 \times 10^9$ M^{-1} s^{-1} for the $^1B_2$ state of Ir_2.[2] The spectra and redox reactivities of these singlet and triplet (dσ*pσ) states have been investigated by picosecond transient absorption sepctroscopy and are described below.

Experimental Section

Kinetics and Spectral Measurements. ΔA spectra and kinetics were recorded after photoexcitation by a single pulse from a Nd/YAG laser system, which was actively and passively mode-locked. The laser's output was spatially filtered both within the oscillator cavity and between the first and second amplifiers to ensure a smoothly varying, spatial energy distribution within each pulse. A detailed description of the picosecond laser system has been presented elsewhere.[5] Only highlights are reported here.

The photoexcitation wavelength was 532 nm, and monitoring light was generated by focusing 532-nm pulses into a 10-cm cell of D_2O and H_2O (80:20 by volume). The instrumental response time under these conditions was 20–25 ps. All data points are plotted with their corresponding statistical error, which is the standard deviation of the mean of 50 independent ΔA measurements. All ΔA measurements were made within a specified range of photoexcitation energies, and data from excitations outside this range were not used. The reported ΔA spectra and kinetics were measured at empirically determined photoexcitation energies below the onset of multiphoton absorption processes.

The samples were held at room temperature in argon-filled chambers during experimentation. The main reservoir was magnetically stirred to create regions of high and low velocity. Glass tubes transferred sample solution continuously from the high- to the low-pressure regions of the reservoir through a 2 mm path length sample cell, which was inserted into this transfer line. In this way, each ΔA measurement was made on a fresh sample.

Sample Preparation. $[Ir(\mu\text{-}pz)COD]_2$ (pz = pyrazolyl, COD = 1,5-cyclooctadiene)[6] and $[Rh_2(TMB)_4](BPh_4)_2$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane, Ph = C_6H_5)[7] were prepared by published procedures, the latter supplied by Dr. V. M. Miskowski. $[Ir(\mu\text{-}pz)(COD)]_2$ was purified by a slight modification of the published procedure. After evaporation of the tetrahydrofuran reaction solution, the crude product was extracted with benzene and eluted on a column of Florisil (MCB) under an inert atmosphere. Evaporation of the benzene solution yielded deep-red crystals of $[Ir(\mu\text{-}pz)(COD)]_2$. Spectrophotometric-grade cyclohexane (Aldrich, Gold Label), acetonitrile (Burdick & Jackson), and 1,2-dichloroethane (Burdick & Jackson) were each degassed with seven freeze–pump–thaw cycles ($<10^{-5}$ torr) and stored under vacuum over activated molecular sieves (4 Å for C_6H_{12} and 1,2-DCE; 3 Å for CH_3CN). Solvents were transferred by flask-to-flask distillation on a high-vacuum ($<10^{-5}$ torr) line directly into the flow cell containing the solid compound to be studied. The solution was further degassed with three-to-five freeze–pump–thaw cycles and then blanketed with 1 atm of purified Ar. Absorption spectra of the samples were recorded in the flow cell before and after laser excitation in order to determine the extent of photodecomposition.

Results

$Rh_2(TMB)_4{}^{2+}$. In prior work on the $Rh_2(TMB)_4{}^{2+}$ complex, a $^3A_{2u}$ lifetime of about 30 ns was determined. Fluorescence was detectable with a quantum yield (Φ_{fl}) of 4.6×10^{-2}.[7] However, the lifetime of the $^1A_{2u}$ state remained unknown. Figure 1 presents ΔA spectra of the $^1A_{2u}$ and $^3A_{2u}$ states as well as the kinetics of the intersystem crossing process. The ΔA kinetics data at 440 nm (bottom panel) are fit by a single exponential decay function with a lifetime for the $^1A_{2u}$ state of 820 ± 20 ps.[8] The relaxation of the $^1A_{2u}$ state yields the longer-lived $^3A_{2u}$ state. The ΔA spectrum of the $^3A_{2u}$ state is reported from 350 to 750 nm. However, that of the $^1A_{2u}$ state is reported only from 350 to 500 nm. The probe light stimulated emission from the $^1A_{2u}$ state, preventing reliable ΔA measurements beyond 500 nm during its lifetime. This was not the case for the $^3A_{2u}$ state.

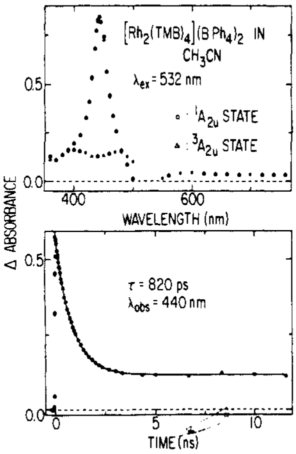

Figure 1. Transient kinetics (lower) and difference spectra (upper) for $[Rh_2(TMB)_4]^{2+}$ in CH_3CN (1.4×10^{-4} and 2.3×10^{-4} M, respectively) generated with 532-nm laser excitation. The kinetics were recorded at 440 nm, and the solid line is a single exponential function that decays with a lifetime of 820 ps. The difference spectra were recorded 100 ps after excitation, during the lifetime of the $^1A_{2u}$ excited state (○), and 11.5 ns after excitation, during the lifetime of the $^3A_{2u}$ excited state (△).

The dramatically different ΔA spectra of the $^1A_{2u}$ and $^3A_{2u}$ states support prior assignments of these states to a dσ*pσ electronic configuration. The strong ΔA increase at 440 nm is very similar to intense dσ* → pσ absorptions in related complexes such as $Pt_2(pop)_4{}^{4-}$, $Pt_2(pop)_4{}^{5-}$, $Rh_2(TMB)_4{}^{2+}$, and $Rh_2(TMB)_4{}^{+}$ (pop = $P_2O_5H_2{}^{2-}$).[1] If the 440-nm absorption band of the $^1A_{2u}$(dσ*pσ) state arises from a dσ* → pσ excitation, producing a $^1(p\sigma^2)$-type excited state, then the corresponding spin-forbidden dσ* → pσ transition of the $^3A_{2u}$ state should be much less intense and maximize near 390 nm. Note, the pσ^2 electronic configuration has only filled orbitals so it cannot give rise to a triplet state. Thus, a strong triplet–triplet absorption to a pσ^2-type state from the $^3A_{2u}$ state is not possible. The contrasting difference spectra for these two states bear out these expectations. Indeed, the observed ΔA increases for the $^3A_{2u}$ state in the 400–500-nm region are not likely to be (dσ* → pσ)-type transitions,[4] in which case the actual difference in the absorption cross section for (dσ* → pσ)-type transitions between these two states would be even larger than indicated in Figure 1.

A corollary of the above reasoning is that if the strong ΔA increase at 440 nm ($S_1 \rightarrow S_n$) for the initial state (S_1) does not arise from a dσ* → pσ transition, there should be a terminal triplet (T_n) corresponding to the terminal singlet state (S_n). In this case, the final triplet (T_1) produced after relaxation of the initial state (S_1) should have an intense, allowed absorption ($T_1 \rightarrow T_n$) to the corresponding terminal triplet in the ca. 440-nm region. The fact that an intense triplet–triplet band does not appear again supports our assignment of the 440-nm band of the $^1A_{2u}$ state to a dσ* → pσ transition.[9]

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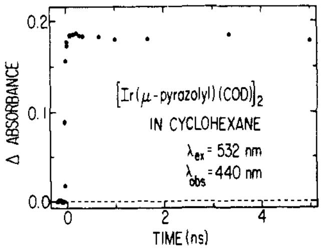

Figure 2. Transient kinetics for $[Ir(\mu\text{-}pz)(COD)]_2$ in cyclohexane solution (4.5×10^{-4} M) recorded at 440 nm, following 532-nm laser excitation.

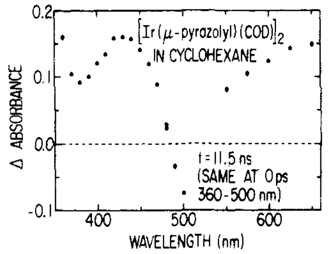

Figure 3. Transient difference spectrum of $[Ir(\mu\text{-}pz)(COD)]_2$ in cyclohexane solution (4.4×10^{-4} M) recorded 11.5 ns after 532-nm laser excitation. An identical spectrum in the 360–500-nm region results immediately after laser excitation (t = 0 ps). For $\lambda > 600$ nm, stimulated emission interferes with difference spectrum measurements during the lifetime of the singlet excited state.

$[Ir(\mu\text{-}pz)(COD)]_2(Ir_2)$ in Cyclohexane. The luminescent $^3B_2$ state in Ir_2 lives 250 ns in acetonitrile at room temperature and has an emission quantum yield (Φ_{em}) of 8×10^{-3}.[1d] The $^1B_2$ state in Ir_2 is much shorter-lived with an emission quantum yield of 1×10^{-4} in acetonitrile at room temperature. If the radiative rates for the $^1A_{2u}$ state of $Rh_2(TMB)_4^{2+}$ and the $^1B_2$ state of Ir_2 are similar, the 460-fold lower Φ_{em} for Ir_2 would imply a 2-ps lifetime for the $^1B_2$ state of Ir_2. The ΔA kinetics data at 440 nm for Ir_2 in cyclohexane (Figure 2) show that the 20–25-ps temporal response of our laser system is too slow to observe the $^1B_2$ to $^3B_2$ relaxation process. Figure 3 presents the ΔA spectrum of the $^3B_2$ state from 350 to 650 nm. There is no change in this spectrum from 0 ps to 11.5 ns after photoexcitation in the 360–500-nm region. Stimulated emission beyond 500 nm interferes with ΔA measurements during photoexcitation (t = 0). The spectrum in Figure 3 was recorded 11.5 ns after excitation and is free of stimulated emission artifacts.

$[Ir(\mu\text{-}pz)(COD)]_2(Ir_2)$ in DCE. Earlier work by Caspar and Gray[2] showed that single-photon excitation of Ir_2 effected the two-electron reduction of DCE shown in eq 1. In this solvent

$$Ir_2 \xrightarrow[DCE]{h\nu} [Ir(Cl)(\mu\text{-}pz)(COD)]_2 + C_2H_4 \qquad (1)$$

the luminescence of the $^3B_2$ state is quenched 40%, while that of the $^1B_2$ state is quenched 30% relative to their luminescence yields in cyclohexane. The bimolecular rate constant for $^3B_2$ quenching by DCE is in agreement with that expected for a one-electron-transfer mechanism (DCE: $E_{1/2} = -2.1$ V vs. SSCE, $k_q = 7.3 \times 10^5$ M^{-1} s^{-1}).[2] The more negative reduction potential for the $^1B_2$ state (−2.1 V vs. SSCE for $^1B_2$; −1.8 V vs. SSCE for $^3B_2$) should lead to a faster one-electron-transfer reaction from the singlet state (estimated $k_q = 2 \times 10^6$ M^{-1} s^{-1}). In view of the very different lifetimes of these states in cyclohexane, the question arises whether the quenching of the two excited states proceeds by different reaction mechanisms.

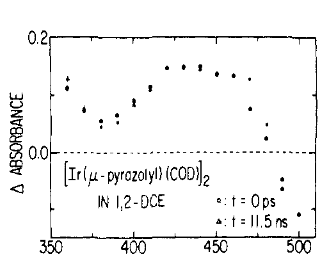

Figure 4. Transient difference spectra of $[Ir(\mu\text{-}pz)(COD)]_2$ in 1,2-dichloroethane solution (4.6×10^{-4} M) recorded immediately after (○) and 11.5 ns after (△) 532-nm laser excitation.

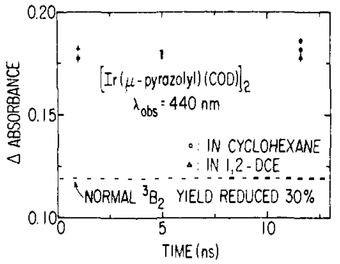

Figure 5. Relative yields of $^3B_2$ states of $[Ir(\mu\text{-}pz)(COD)]_2$ in cyclohexane (○) and 1,2-dichloroethane (△) solutions (4.5×10^{-4} M in each) at various times after 532-nm laser excitation. The dashed line indicates the relative yield of the $^3B_2$ state that would result if the fluorescence quenching in 1,2-dichloroethane were due to photochemistry or enhanced radiationless decay to the ground state.

Figure 4 presents the ΔA spectra for Ir_2 in DCE at t = 0 ps and 11.5 ns after photoexcitation. The striking result is that there is almost no difference between these two spectra. The small disparities encountered are consistent with an expected 7% reaction of the $^3B_2$ state during the first 11.5 ns of its lifetime. No photochemical products resulting from reaction of the $^1B_2$ state appear to evolve during the first 11 ns.

If the quenching of the $^1B_2$ state's luminescence in DCE signals photochemical reaction, there should be a reduced yield of formation of the $^3B_2$ state. This would occur even if there were a rapid back reaction, since such a process would most likely produce ground-state Ir_2 rather than the $^1B_2$ or $^3B_2$ states. In order to determine the yield of the $^3B_2$ state in DCE relative to that in cyclohexane, two samples with identical concentrations of Ir_2 were prepared. One contained DCE and the other cyclohexane. The results of exciting these samples with 532-nm pulses of the same energy are shown in Figure 5. The dashed line indicates the ΔA increase expected at 440 nm in DCE if 30% of the $^1B_2$ state were diverted from producing the $^3B_2$ state. Not only is the $^3B_2$ yield in DCE not reduced by 30% but its yield is identical with that found in cyclohexane, within the accuracy of this experiment.

The most probable explanation for the lack of spectral evidence for photochemical reaction (see Figure 4) and the unchanged $^3B_2$ yield in reactive vs. nonreactive solvent (see Figure 5) is that no significant oxidative addition chemistry proceeds from the extremely short-lived $^1B_2$ state. The reduced fluorescence yield could be due to solvent perturbation of the $^1B_2$ radiative constant. However, the $^1A_1 \rightarrow {}^1B_2$ absorption cross section does not vary between cyclohexane and DCE, indicating quite similar radiative decay rates in the two solvents. A more likely explanation is enhanced $^1B_2$ to $^3B_2$ intersystem crossing in DCE.

Discussion

The $^1A_{2u}$ state of $Rh_2(TMB)_4^{2+}$ was found to have an 820-ps lifetime. This appreciable lifetime accords with the robust 4.6×10^{-2} fluorescence quantum yield of this state.[7] The corresponding $^1B_2$ state of Ir_2 has a fluorescence yield of 1×10^{-4} [1d] and a lifetime much shorter than 20 ps. It is worth noting that the ratio of fluorescence quantum yields for these two complexes implies a 2-ps singlet lifetime for Ir_2 if both complexes have similar

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(9) This argument is based on the assumption that $\Delta E(S_n - T_n) = \Delta E(S_1 - T_1)$. For $Rh(TMB)_4^{2+}$, $\Delta E(S_1 - T_1) = 3100$ cm^{-1}.[10a] In fact, singlet-triplet splittings for transition metals vary with the type of excited state. Some of the largest splittings are found for ligand-field states, where the values range from 6000 to 9000 cm^{-1} for $[Rh(NH_3)_5X]^{n+}$ complexes.[10b] Much smaller values are found for MLCT states in ruthenium(II) poly(pyridine) complexes, where they range from 2000 to 3000 cm^{-1}.[10c] Our wavelength observation window of 360–750 nm allows us to observe $T_1 \rightarrow T_n$ absorptions which would correspond to $\Delta E(S_n - T_n)$ splittings ranging from 0 to 12 500 cm^{-1}. The ΔA spectrum of the $^3A_{2u}$ state in Figure 1 shows that no strong absorptions occur in this wavelength range. Thus, it is highly unlikely that the terminal S_n state (see text) has a corresponding terminal T_n state.

radiative rates from their $^1(d\sigma^*p\sigma)$ states.

The strong ΔA increase at 440 nm for the $^1A_{2u}$ state of $Rh_2(TMB)_4^{2+}$ is expected for a $^1(d\sigma^*p\sigma)$ electronic configuration. The strength of the 440-nm band and its shape are very similar to those of related complexes, all of which exhibit intense $d\sigma^* \rightarrow p\sigma$ absorptions. That this $d\sigma^* \rightarrow p\sigma$ transition in the $^1A_{2u}$ state of $Rh_2(TMB)_4^{2+}$ is to the blue of its location in the ground state ($^1A_{1g} \rightarrow {}^1A_{2u}$, $\lambda_{max} = 515$ nm) may be due to spin-pairing and electronic polarization differences between these two states. In particular, the $d\sigma^* \rightarrow p\sigma$ transition in $Rh_2(TMB)_4^{2+}$ unpairs two electrons, creating half-filled $d\sigma^*$ and $p\sigma$ orbitals, while the $d\sigma^* \rightarrow p\sigma$ transition in the $^1A_{2u}$ state both pairs two electrons in the $p\sigma$ orbital and leaves an empty $d\sigma^*$ orbital at lower energy. Importantly, the strong 440-nm band in the ΔA spectrum of the $^1A_{2u}$ state of $Rh_2(TMB)_4^{2+}$ does not have a counterpart in the spectrum of the $^3A_{2u}$ state. The formation of a $^1(p\sigma)^2$ electronic configuration as a result of a $d\sigma^* \rightarrow p\sigma$ transition should be much less allowed from the $^3A_{2u}$ state. Thus, the spectral results on $Rh_2(TMB)_4^{2+}$ are consistent with prior assignments of the two lowest-energy excited states in d^8–d^8 complexes.[1]

The unobservably short lifetime ($\tau < 20$ ps) of the $^1B_2$ state of Ir_2 accords with its low fluorescence quantum yield but contrasts with the 820-ps lifetime of the $^1A_{2u}$ state of $Rh_2(TMB)_4^{2+}$. This trend is consistent with the greater spin–orbit coupling expected for the iridium dimer,[11] but a quantitative comparison is not feasible because of the significant structural differences between the two Rh and Ir complexes.

Although the fluorescence quantum yield of the $^1B_2$ state of Ir_2 decreases by 30% in DCE relative to its yield in nonreactive cyclohexane, the yield of the $^3B_2$ state is the same in these two solvents. Additionally no evidence of photochemical reaction as a result of $^1B_2$ quenching is seen in the 360–500-nm difference spectrum during the first 11 ns after photoexcitation. Reasonable conclusions are that (1) there is *no* significant oxidative addition photochemistry proceeding from the $^1B_2$ state and (2) the reduced fluorescence yield in DCE is due to slightly more rapid intersystem crossing in this solvent than in cyclohexane. This is not likely to be due to an external heavy-atom effect as is commonly found for organic molecules; rather it more likely reflects a solvent-specific interaction. Since DCE modifies neither the absorption nor the emission spectrum of Ir_2, the interaction between the metal complex and the chlorinated hydrocarbon solvent is likely to be weak. Inasmuch as Ir_2 has two vacant coordination sites and haloalkanes are known to be weak bases,[12] a weak Lewis acid–base pairing of the two molecules is plausible. This interaction could sufficiently perturb the electronic and vibrational structure of Ir_2 to produce a 30% increase in the rate of intersystem crossing in haloalkanes vs. alkanes.

This work has shown that the $^3B_2$ state of Ir_2 is populated extremely rapidly, indicating that photochemistry from upper excited states is not likely. Similarly, extraneous energy losses from nonreactive, nonradiative processes also appear to be insignificant prior to the formation of the $^3B_2$ state. The observation that a decrease in $^1B_2$ fluorescence in DCE relative to cyclohexane did not produce a change in the yield of the $^3B_2$ state suggests that the quantum yield for formation of this state is near unity.

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Registry No. $Rh_2(TMB)_4^{2+}$, 73367-41-6; $[Ir(\mu\text{-pz})(COD)]_2$, 80462-13-1.

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Rhenium Carbonyl Biradicals. Formation, Recombination, and Halogen Atom Transfer[1]

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Abstract: The organometallic biradicals $\cdot(OC)_4Re\overset{\frown}{L\,L}Re(CO)_4\cdot$ ($\overset{\frown}{L\,L} = R_2P(CH_2)_nPR_2$; R = Me, Ph, Cy; n = 2–6 or *cis*-$Ph_2PCH{=}CHPPh_2$) have been observed as transient species following laser flash photolysis of the bridging ligand substituted dirhenium octacarbonyls, in which homolytic metal–metal bond cleavage is a dominant primary photoprocess and CO dissociation is negligible. The intramolecular recombination of these biradicals follows simple first-order kinetics. The rate constants for recombination show a slight solvent dependence probably related to viscosity and the sizes of solvent molecules. The rate constants are affected by steric requirements of the substituents on phosphorus atoms and geometry in the ligand backbone. The rate constants for halogen atom transfer to the biradicals, determined either by laser flash photolysis or by continuous photolysis, are characteristic of mononuclear rhenium carbonyl radicals with similar substituent environments. The metal-centered biradicals thus show typical monoradical behavior in their reactions such as recombination, halogen atom transfer, and electron transfer.

In recent years there has been much interest in transition-metal-centered radicals generated by flash photolysis. Various metal carbonyl dimers including $M_2(CO)_8L_2$ (M = Mn, Re; L = CO, PR_3, AsR_3) are known to undergo both metal–metal bond homolysis and CO dissociation following irradiation at wavelengths corresponding to a $\sigma \rightarrow \sigma^*$ or $d\pi \rightarrow \sigma^*$ transition.[2-12] The radicals

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