the μ-O···H distance, bond angle, and O--O distance.[16]

In Figure 2 are shown plots of effective monomer per molecule versus temperature in an applied field of 10.00 kG. Data for complex **3** are readily fit to a Heisenberg exchange Hamiltonian of the form $\mathbf{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ with $g = 2.00$ and $J = -134$ cm^{-1}; contributions from TIP and the paramagnetic impurity were held fixed at 3.00×10^{-4} cgsu and 0.002, respectively.[18] This value for J is typical for an oxo-bridged Fe$^{III}_2$ complex[5] and is in fact identical to that found in N$_3$metHr. The data for complexes **1** and **2**, however, show a dramatic change in the magnitude of the pairwise exchange interaction as evidenced by both the larger effective moments and as well larger values of $\partial\mu_{eff}/\partial T$ at low temperature. The data for complex **2** can be fit reasonably well to the above Hamiltonian for $g = 2.00$ and $J = -26$ cm^{-1} (impurity = 0.008; TIP as above). The data for complex **1**, however, *cannot* be fit to a simple Heisenberg expression. It is our opinion that the J values for both complexes **1** and **2** are temperature dependent. This conclusion was reached on the basis of attempts to fit the data for complex **1** in different temperature regions. If only the data below 100 K are considered, a value of $J \approx -30$ cm^{-1} is obtained, obviously similar to that for complex **2**. However, the resulting theoretical curve substantially overshoots the experimental data at higher temperatures. Conversely, a consideration of the high temperature data (i.e., $T \geq 150$ K), affords $J \approx -70$ cm^{-1}, but such a value undershoots the low-temperature data. Similar results are found for complex **2**, but since the variation with temperature is much less pronounced ($\Delta J \approx 10$ cm^{-1}), a presentable fit assuming a temperature-independent J term can be obtained. Regardless of the details of the data fitting, it is quite clear that the antiferromagnetic exchange interactions in complexes **1** and **2** are considerably weaker than that in complex **3**.

We suggest that the temperature dependence of J is a result of the hydrogen-bonding interaction of the solvate with the μ-oxo bridge. As temperature is increased, the increase in available thermal energy and resultant expansion of the crystal are expected to weaken hydrogen bonds. Weakening of the hydrogen bond to the oxo-bridge leads to an increase in the magnitude of the antiferromagnetic exchange interaction between the Fe^{III} ions as the bridge loses its μ-O···H character, resulting in a smaller moment (i.e., larger J value) at higher temperatures. The more pronounced effect seen for complex **1** versus complex **2** can be explained by considering the nature of the bridging carboxylates in the two compounds. The benzoate bridges of complex **1** will, in general, produce a lattice which is more susceptible to thermal expansion/contraction than that for the acetate complex. The lattice characteristics will affect the strength of the hydrogen bond, resulting in a larger temperature coefficient for the exchange parameter in the case of complex **1**. These data are further evidence of the importance of this subtle hydrogen-bonding interaction in determining the magnetic properties of these molecules. There is one other example in the literature where exchange interactions propagated by hydrogen-bonding contacts have shown a pronounced temperature dependence.[19]

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Supplementary Material Available: Tables of positional parameters and bond distances and angles for complexes **1** and **3** and tables of magnetic data for complexes **1–3** (18 pages). Ordering information is given on any current masthead page.

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Photosubstitution of Fe(CO)$_5$ with PEt$_3$ in Cyclohexane: Fe(CO)$_4$PEt$_3$ and Fe(CO)$_3$(PEt$_3$)$_2$ as Single-Photon Products

The photochemistry of Fe(CO)$_5$ has proven to be very complex, and even though it was one of the first organometallic compounds to be studied, it is still actively investigated.[1-5] In the gas phase, UV photolysis of metal carbonyls (M(CO)$_n$) leads to multiple, stepwise CO dissociations since the energy of a UV photon is in excess of two or more of the metal–CO bond energies.[6] The number of CO's lost and the distribution of M(CO)$_x$ formed (x varies) depends on the wavelength.[6] In contrast, it is generally believed that UV photolysis of metal carbonyls in condensed phases results in only one CO dissociation since further CO dissociation is not expected to compete with vibrational relaxation of M(CO)$_{n-1}$.[6-8] This is supported by the photochemistry of group VI metal carbonyls where only monosubstitution of the metal carbonyl is observed in solution.[9,10] When disubstitution has been detected, it has been rationalized as the result of secondary photolysis (i.e., photolysis of primary photoproducts, eqs 1 and 2). This was the case in a recent study of Fe(CO)$_5$ photosubstitution by (E)-cyclooctene in n-hexane, where the authors reported a quantum yield of 0.8 for monosubstitution.[2,11] Only once has the quantum yield for disubstitution as a primary photoprocess been published.[12,13] In that account, the photolysis of Fe(CO)$_5$

$$\mathrm{M(CO)}_n \xrightarrow{h\nu,\,-\mathrm{CO}} \mathrm{M(CO)}_{n-1} \xrightarrow{+\mathrm{L}} \mathrm{M(CO)}_{n-1}\mathrm{L} \tag{1}$$

$$\mathrm{M(CO)}_{n-1}\mathrm{L} \xrightarrow{h\nu,\,-\mathrm{CO}} \mathrm{M(CO)}_{n-2}\mathrm{L} \xrightarrow{+\mathrm{L}} \mathrm{M(CO)}_{n-2}\mathrm{L}_2 \tag{2}$$

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Table I. Quantum Yields for Photosubstitution of $Fe(CO)_5$ with PEt_3 in Cyclohexane at 25 °C[a]

$[Fe(CO)_5]$, mM	$[PEt_3]$, mM	Φ	
		$Fe(CO)_4(PEt_3)$	$Fe(CO)_3(PEt_3)_2$
10	90	0.32	0.45
10	30	0.38	0.46
10	10	0.38	0.42
10	10	0.54	0.28[b]
10	1.0	0.68	0.07[b]
10	neat[c]	0.34	0.40

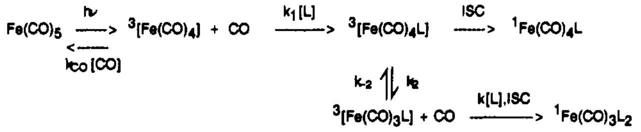
[a] λ = 337 nm; Φ errors are 0.03 or less. [b] CO-saturated solution: [CO] = 9 mM at 25 °C (Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1). [c] $P(n\text{-}Bu)_3$; CO stretching frequencies for $Fe(CO)_4(n\text{-}PBu_3)$ and $Fe(CO)_3(n\text{-}PBu_3)_2$ were at 1929 and 1868 cm^{-1}, respectively.

with triphenylphosphine in isooctane led to the formation of $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ in a three-to-one ratio. In the current investigation of the photosubstitution of $Fe(CO)_5$ with PEt_3, we find that, although $Fe(CO)_4(PEt_3)$ (**1**) is formed, $Fe(CO)_3(PEt_3)_2$ (**2**) is also a primary photoproduct and is formed in a greater yield than **1**. Our results indicate that **2** is a single-photon product and that **2** may be formed via CO substitution of triplet $Fe(CO)_4PEt_3$.

Phosphines and $Fe(CO)_5$ were vacuum distilled in subdued light and stored under N_2 or Ar prior to use. Cyclohexane was distilled after refluxing overnight with potassium. Reagents were transferred in a glovebag under N_2 or Ar. The same results were obtained when cannulas and syringes were used for transfers. Actinometric samples in a septum-sealed cuvette (Wilmad No. 110CQ) were irradiated with a high-pressure 150-W xenon lamp. The light was passed through a 10-cm water filter and a 337-nm interference filter (Corion P10F). The beam cross section at the sample cuvette was about 0.5 cm^2. Part of the light was focused on a diode that was calibrated at the beginning and end of a day of experiments. To ensure consistency, the diode was calibrated with more than one chemical actinometer (fulgide, azobenzene, dimethylanthracene/O_2).[14-16] The production of **1** and **2** was quantified using a Mattson Polaris or Galaxy FTIR instrument. The spectrometers were calibrated with authentic samples of **1** and **2** (CO stretching frequencies used were at 1935 and 1874 cm^{-1}, respectively)[17,18] synthesized by established procedures.[19,20] Spectra were found not to change up to 3 h after photolysis, and all quantum yield measurements were obtained within 3 h of sample photolysis. Irradiated samples were transferred to an IR cell (NaCl, 0.1 mm) for measurement. Quantum yields showed no dependence on light intensity ($(5-15) \times 10^{-10}$ Einstein s^{-1}) and did not change for 1-10% conversion of $Fe(CO)_5$. The extinction coefficients of $Fe(CO)_5$ (ϵ_{Fe}) and **1** (ϵ_1) at 337 nm are 340 and 300 M^{-1} cm^{-1}, respectively. The quantum yield results are summarized in Table I.

The quantum yield for **2** formation significantly exceeds that of **1** in the absence of added CO. Since **2** is in excess of **1** even after 1% conversion of $Fe(CO)_5$ and $Fe(CO)_5$ absorbs essentially all of the light ($\epsilon_{Fe}[Fe(CO)_5] \gg \epsilon_1[\mathbf{1}]$), **2** must be formed in a single-photon process. We believe reactions with multinuclear species (such as $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$) are not responsible for formation of **2** since we see no IR peaks, precipitation, or color changes associated with these species.[21] Furthermore, multinuclear species would require the reaction of $Fe(CO)_5$ with $Fe(CO)_4$ (or some other intermediate), and hence, $Fe(CO)_5$ would have to compete with PEt_3 for $Fe(CO)_4$. If $Fe(CO)_5$ were competing with PEt_3, the **1**/**2** ratio should change as the $Fe(CO)_5/PEt_3$ ratio changes, yet this is not the case, even with neat phosphine (Table I).[22]

Scheme I



A simple explanation for the formation of **2** would be via stepwise dissociation of two CO's from $Fe(CO)_5$ to generate $Fe(CO)_3$ followed by reaction with two phosphines. A recent report of the strength of the $Fe(CO)_3$–CO bond energy (27.9 ± 8.8 kcal/mol) indicates this mechanism is unlikely.[23,24] After dissociation of the first CO from $Fe(CO)_5$, $Fe(CO)_4$ will not have enough excess vibrational energy for the rate of CO dissociation to compete with the rate of vibrational relaxation in solution. Previous studies of metal carbonyl compounds indicate that vibrational relaxation of metal carbonyls in solution occurs in about 100 ps,[25,26] while the lifetime for the second CO dissociation after 351-nm photolysis is in the ns–μs range.[8,27,28] The strength of the $Fe(CO)_3$–CO bond also rules out the possibility of simple CO dissociation from $Fe(CO)_4$ after vibrational relaxation since the rate of this reaction would be too slow to be significant on the time scale of our experiments. Regardless of the magnitude of the bond strength, the formation of **2** via $Fe(CO)_3$ is inconsistent with the dependence of the **1**/**2** ratio on ligand structure (vide infra).

In the absence of added CO, the independence of the **1**/**2** ratio on $[PEt_3]$ indicates that the product-determining steps for the formation of **1** and **2** are a competition between two unimolecular processes. This might suggest that the steps do not involve ligand, yet the ratio of $Fe(CO)_4L/Fe(CO)_3L_2$ changes considerably with ligand structure. With pyridine we observe no $Fe(CO)_3(C_5H_5N)_2$, and in agreement with a previous study, we obtained a three-to-one ratio of $Fe(CO)_4PPh_3/Fe(CO)_3(PPh_3)_2$ with triphenylphosphine.[12] Substitution with cyclooctene is reported to yield about a ten-to-one ratio of $Fe(CO)_4(c\text{-}C_8H_{14})/Fe(CO)_3(c\text{-}C_8H_{14})_2$.[13] Clearly the ligand effects the partitioning between products. On the time scale of the experiments, $Fe(CO)_4PEt_3$ is thermally stable in the presence of free PEt_3; hence, the results suggest an intermediate reacting with PEt_3 forms **1** and **2** via two competing processes.[29]

A mechanism that accounts for these results is shown in Scheme I (ISC = intersystem crossing). It is generally believed that the ground state of $Fe(CO)_4$ in solution is a triplet.[6] Addition of L would lead initially to the formation of $^3Fe(CO)_4L$. A different L will result in different triplet–singlet energy differences and thus different intersystem crossing rates. Likewise, the rate of CO dissociation from $^3Fe(CO)_4L$ will be dependent on the structure of L. In agreement with the results, this mechanism indicates

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the product distribution will be dependent on the structure of L but independent on the concentration of L.[30]

The mechanism is also consistent with the results observed when CO is added. Increasing CO decreases **2** and increases **1**. In CO-saturated solutions, the total quantum yield ($\Phi_1 + \Phi_2$) does not decrease, within experimental error, and is the same as the yield previously obtained for substitution of $Fe(CO)_5$ by (*E*)-cyclooctene.[2] The independence of $\Phi_1 + \Phi_2$ on [CO] suggests that $k_1 \gg k_{CO}$ since in one experiment $[CO]/[PEt_3] = 9$. Therefore PEt_3 adds to $Fe(CO)_4$ faster than does CO.

Further studies with other ligands and solvents are underway. We conclude that the formation of a disubstituted product is a single-photon process and that the relative rates of intersystem crossing and CO dissociation for $^3Fe(CO)_4L$ may determine the relative yields of mono- and disubstituted products.

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Supplementary Material Available: A figure showing IR spectra (1 page). Ordering information is given on any current masthead page.

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(30) An alternative mechanism might involve $Fe(CO)_4$(solvent) in equilibrium with $Fe(CO)_4$ where the different reactivities of the two intermediates determine the distribution of products. This alternative seems unlikely since at 20 K both $Fe(CO)_4$ and $Fe(CO)_4$–methane are formed (Poliakiff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2279). Since all the $Fe(CO)_4$ is not trapped, it may be that the $Fe(CO)_4$–alkane interaction is very weak and at room temperature the formation of $Fe(CO)_4$–alkane is not significant.

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Unusual Stabilization of Trans 2,2′-Bipyridine Ligands in a Rhenium(V) Phenylimido Complex

The majority of bis(2,2′-bipyridine) complexes possess cis geometries. In those few instances where the 2,2′-bipyridine (bpy) ligands are trans, extraordinary steric or electronic factors result in abnormal kinetic or thermodynamic stability. Some notable examples include $Pd^{II}(bpy)_2^{2+}$,[1] *trans*-$Ru^{III}(bpy)_2(H_2O)(OH)^{2+}$,[2] *trans*-$Os^{II}(bpy)_2(PPh_2Me)_2^{2+}$,[3] *trans*-$Os^{VI}(bpy)_2O_2^{2+}$,[4] and *trans*-$Ru^{II}(bpy)_2(py)_2^{2+}$.[5]

During our studies of the photochemistry of complexes with metal–nitrogen multiple bonds,[6] we have developed synthetic routes to new Re(V) imido complexes of the type $[PhNRe(chelate)_2X]^{2+}$ where the chelate contains nitrogen or phosphorus donors. For example, a displacement reaction can be used to prepare the new complex *trans*-$PhNRe(dppe)_2Cl^+$ as depicted in eq 1 (dppe =

$$trans\text{-}mer\text{-}PhNRe(PPh_3)_2Cl_3 + dppe \xrightarrow{\text{EtOH, }\Delta} trans\text{-}PhNRe(dppe)_2Cl^{2+} + 2Cl^- \tag{1}$$

1,2-bis(diphenylphosphino)ethane).[7] We also attempted to prepare complexes containing two bipyridine ligands, with the expectation that they would adopt structures similar to that of the isoelectronic nitride *cis*-$NTc(bpy)_2Br^+$.[8] The synthesis was designed to follow the two-step procedure shown in eqs 2 and 3.

$$mer\text{-}ORe(bpy)Cl_3 + PhNH_2 \xrightarrow{\text{xylene, }\Delta} mer\text{-}PhNRe(bpy)Cl_3 + H_2O \tag{2}$$

$$mer\text{-}PhNRe(bpy)Cl_3 + bpy \xrightarrow{\text{EtOH, }\Delta} cis\text{-}PhNRe(bpy)_2Cl^{2+} + 2Cl^- \tag{3}$$

Unexpectedly, the product was not *cis*-$PhNRe(bpy)_2Cl^{2+}$, as shown in eq 3, but *trans*-$PhNRe(bpy)_2(OEt)^{2+}$, where an ethoxide group had replaced chloride in the coordination sphere. The PF_6^- salt was characterized by ^1H NMR and UV–visible spectroscopies, cyclic voltammetry, elemental analysis, and a structure determination by X-ray diffraction.[9]

The crystal structure of *trans*-$PhNRe(bpy)_2(OEt)^{2+}$ shown in Figure 1 reveals a pseudooctahedral coordination sphere about Re with the bpy ligands distorted in a "concerted-canted" fashion so as to minimize steric interactions between the 6 and 6′ protons on adjacent bpy ligands. The main distortions from ideal octahedral symmetry are due to the rather small bite angles of the bpy ligands (75.3 (2) and 74.9 (2)°) and to the asymmetric apical ligands. A closer look at the bond parameters shows the Re–N(bpy) lengths vary between 2.134 (6) and 2.163 (6) Å. These are notably shorter than the 2.210- and 2.203-Å Re–N(bpy) bond lengths found in the d^2 dioxo complex *cis*-$Re^VO_2(bpy)(py)_2^+$.[10] The (Ph)N–Re–O(Et) angle is nearly, but not quite, linear (174.8 (3)°). Probably the most striking features are Re–N(Ph) and Re–O(Et) bond lengths of 1.740 (6) and 1.895 (5) Å, which are in the range of multiple bonds for both interactions. This is aptly illustrated by a Re–N distance of 1.726 (6) Å in *mer-trans-*

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(7) Preparation of *trans*-$[Re(NPh)(Cl)(dppe)_2](PF_6)_2$: A mixture of $ReNPhCl_3(PPh_3)_2$ (0.2 g, 0.22 mmol), dppe (0.35 g, 0.88 mmol), and EtOH (200 mL) was refluxed for 2 days. The resulting reaction mixture was allowed to cool to room temperature and filtered. The yellow filtrate was evaporated to dryness. The resulting brown residue was dissolved in CH_3CN, and the solution was loaded into a neutral alumina column. The column was washed with CH_2Cl_2 and CH_3CN, and finally a brown fraction was eluted with ethanol. The ethanol solution was reduced in volume, NH_4PF_6 (0.3 g, 1.8 mmol) was added, and the mixture was stirred at room temperature for 1 h. A brown solid was filtered off, washed with ethanol, hexanes, and diethyl ether, and dried. Yield: 0.15 g (48%). Anal. Calcd for $C_{58}H_{53}ClF_{12}NP_6$: C, 49.78; H, 3.80; Cl, 2.54; N, 1.00. Found: C, 50.37; H, 3.72; Cl, 2.18; N, 0.77. UV–visible spectrum (CH_3CN; λ, nm (ε): 540 (160), 476 (2584), 339 (12 488), 254 (50 330), 236 (64 516). ^{13}P NMR spectrum (CD_3CN): a singlet at $\delta = +11.65$ ppm due to the diphosphine and a septet at $\delta = -142$ ppm due to the hexafluorophosphate anion.

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(9) Preparation of *trans*-$[Re(NPh)(OEt)(bpy)_2](PF_6)_2$: A mixture of $ReNPhCl_3(bpy)$ (0.2 g, 0.37 mmol), bpy (0.23 g, 1.48 mmol), and EtOH (200 mL) was refluxed for 4 days. The resulting reaction mixture was filtered. The brown filtrate was evaporated to dryness. The brown residue was dissolved in CH_3CN, and the solution was loaded into a neutral alumina column. The column was washed with CH_2Cl_2 and CH_3CN, and finally a brown fraction was eluted with ethanol. The ethanol solution was reduced in volume, NH_4PF_6 (0.3 g, 1.80 mmol) was added, and the mixture was stirred at room temperature for 1 h. A brown solid was filtered off, washed with ethanol, hexanes, and diethyl ether, and dried. Yield: 0.15 g (44%). Anal. Calcd for $C_{28}H_{26}F_{12}N_5OP_2Re$: C, 36.37; H, 2.74; N, 7.57. Found: C, 36.42; H, 2.74; N, 7.53. UV–visible spectrum (CH_3CN; λ, nm (ε): 525 (424), 421 (3467, sh), 364 (9535, sh), 316 (23 114), 221 (43 339). ^1H NMR spectrum (CD_3CN): δ 9.25 (d, bpy, 2 H), 8.70 (t, bpy, 2 H), 8.50 (t, bpy, 2 H), 7.95 (t, bpy, 2 H), 7.32 (t, Ph, 1 H), 7.18 (t, Ph, 2 H), 6.95 (t, Ph, 2 H), 3.25 (q, OEt, 2 H), 0.35 (t, OEt, 3 H). Crystal data for *trans*-$[PhNRe(bpy)_2(OEt)](PF_6)_2$ ($C_{28}H_{26}F_{12}N_5OP_2Re$): $M_r = 924.7$, monoclinic, space group $P2_1/n$, with $a = 11.032$ (3) Å, $b = 8.848$ (2) Å, $c = 34.642$ (6) Å, $\beta = 98.32$ (2)°, $V = 3208.6$ (13) Å^3, $F(000) = 1800$, $Z = 4$, and $D_c = 1.914$ mg/m^3. Final $R = 0.0332$ and $R_w = 0.0367$ from 3704 observed reflections. The data were collected with a Siemens R3m/v diffractometer employing Mo Kα radiation and using ω scans. The structure was solved via Patterson methods and refined by least-squares techniques.

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