of 53 kcal and a Pd–CH$_3$ bond energy of 40 kcal. The critical geometries are shown in Figure 1, where we see that each methyl group leads to a substantial increase (8 to 12 kcal) in the barrier for reductive coupling. As indicated above, the origin of this increase is the directionality of the orbital for the alkyl groups that prevents the carbon atom from simultaneously forming strong C–H and C–C bonds while retaining a strong Pd–C bond in the transition state. This idea is supported by the orbital plots shown in Figure 2. Further support for this idea is that the Pd–H bond stretches only by 2% (1.51 to 1.55 Å) in going to the transition state for reductive elimination of H$_2$ from PdH$_2$, while the Pd–CH$_3$ bond stretches by 10% (1.96 to 2.20 Å) for reductive elimination of C$_2$H$_6$ from Pd(CH$_3$)$_2$. The calculated barriers for reductive elimination suggest an activation energy of $\sim$10 kcal/mol for each Pd–C bond and $\sim$1 kcal/mol for each Pd–H bond. Therefore the barrier for a concerted reductive coupling of C–C bonds should be twice as high as the barrier for coupling C–H bonds.

For Pd + H$_2$, we also find a 4.4-kcal well for an H$_2$ adduct in which the H–H bond is not activated (R_{HH} = 0.81 Å, $\angle$HPdH = 26°, R_{PdH} = 1.83 Å). This represents an η^2-H$_2$ Lewis base–Lewis acid complex to the Pd. This minimum at long Pd–H distances has previously been observed theoretically[2f,4] and may be compared with the M(CO)$_3$(PR$_3$)$_2$H$_2$ (M = Mo, W; R = Cy, i-Pr) complex studied experimentally by Kubas et al.[5a] and theoretically by Hay.[5b]

Previous theoretical studies[2f,4] of Pd(H)$_2$ did not find the local minimum corresponding to a Pd dihydride complex. These calculations did *not* include relativistic effects and consequently the d^{9}s^1 (^{3}D) state [important in the Pd(H)$_2$ complex] is 15 kcal/mol too high relative to the d^{10} state.[6] Since our calculated barrier is only 1.5 kcal/mol, it is not surprising that in the nonrelativistic calculations this minimum does not exist.

These results provide an explanation for the trends observed in reductive elimination from Pt(II) complexes. Halpern et al.[1d,e] and Michelin et al.[1f] have observed intramolecular reductive coupling from various hydridoalkylbisphosphineplatinum(II) complexes. However, reductive coupling from Pt(II) dialkyls prefer β-hydride elimination.[7,8] As has been reported elsewhere,[3] calculations on Pt(H)$_2$(PH$_3$)$_2$ and Pt(CH$_3$)$_2$(PH$_3$)$_2$ lead to average bond energies of 60 kcal for Pt–H and 36 kcal for Pt–CH$_3$, so that reductive coupling of H–C and C–C bonds is exothermic for both cases. Thus, the high intrinsic barrier ($\sim$22 kcal) for CC coupling vs. C–H coupling ($\sim$10 kcal) explains the observations.[7] On the other hand, for H–H coupling the Pd case is downhill 4 kcal, while the Pt(PH$_3$)$_2$ case is uphill 16 kcal. This is consistent with the fact that reductive elimination to form H–H bonds from Pt(H)$_2$L$_2$ (L = PMe$_3$ or PEt$_3$) has been observed[1q,r] to be very slow under vacuum and that PdL$_2$ complexes are unreactive with respect to H$_2$.[1r]

Calculational Details. At each point from reactants to products, we held the R–Pd–R angle fixed and optimized all other internal coordinates[9] (using a Hartree–Fock analytic gradient technique). This generated a potential curve as a function of the R–Pd–R angle. The energetics presented here were obtained from MCSCF calculations [RCI(4/8)*GVBCI(2/6)] on all points along this reaction path. This level of wavefunction was found adequate to describe the correlations between d electrons and the breaking of Pt–H bonds for reaction 1.[3]

The double ζ basis set and relativistic effective potential (including s, p, d, and f projections) used for Pd are those of Hay.[10] The carbon basis set was the Dunning[11] (9s5p/3s2p) valence double ζ contraction. Huzinaga's[11,12] four–Gaussian hydrogen basis scaled by a factor of 1.2 and contracted double ζ was used for the hydrogen atoms bound to the carbon atom throughout the reaction. Huzinaga's[12] six-Gaussian basis unscaled contracted triple ζ was used for hydrogens initially bound to the Pd atom.

(10) Hay, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 1390–1393.
(11) Dunning, T. H., Jr., Hay, P. J. In "Modern Theoretical Chemistry: Methods of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 1, pp 1–27.
(12) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293–1302.

Spin Polarization Conservation during the Excitation Energy Transfer in Fluid Solution

Kimio Akiyama, Shozo Tero-Kubota,[†] Yusaku Ikegami,* and Tsuneo Ikenoue

*Chemical Research Institute
of Non-Aqueous Solutions, Tohoku University
Katahira 2-1-1, Sendai 980, Japan*

The possibility of spin polarization conservation in the triplet–triplet energy-transfer process has been demonstrated in single-crystal[1] and glassy matrix.[2] However, there is no experimental study on the spin alignment conservation during energy-transfer process in fluid solution systems, in which the spin–lattice relaxation of excited triplet molecule is usually very fast. Since the generation of a radical from the excited triplet precursor gives all emission or enhanced absorption CIDEP (chemically induced dynamic electron spin polarization) spectrum,[3] similar pattern of the time-resolved ESR should be observed in the system produced by the triplet photosensitization, if the spin polarization is conserved during the excitation energy transfer. In this communication, we present the spin polarization conservation in triplet energy transfer between a pyridinyl radical dimer and aryl ketones with CIDEP observations.

The dimer of the 1,4-dimethylpyridinyl radical was prepared and purified by the method reported previously.[4] The dimer has a photosensitive absorption band at the near-UV region (λ_{max} = 353 nm, ϵ $\sim$5000 in toluene). Time-resolved ESR spectra were obtained with a dc detection (no field modulation) method, using a Varian E-109E EPR spectrometer. ESR signal from the preamplifier was amplified to +40 dB by a handmade wide-band amplifier. The signal was taken into a two-channel boxcar integrator (NF BX-531) at arbitrary times after the laser pulse. Nitrogen laser (5 mJ per pulse, 10-Hz repetition rate) was used as a source of the light pulse. Typical measurements were carried out using degassed toluene solutions containing 50 mM of the pyridinyl radical dimer.

(4) Bagatur'yants, A.; Anikin, N.; Zhidomirov, G.; Kazanskii, V. *Zh. Fiz. Khim.* **1981**, *55*, 2035–2039.
(5) (a) Kubas, R.; Ryan, R.; Swanson, B.; Vergamini, P.; Wasserman, H. *J. Am. Chem. Soc.* **1984**, *106*, 451–452. (b) Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466–469.
(6) Martin, R. L.; Hay, P. J. *J. Chem. Phys.* **1981**, *75*, 4539.
(7) (a) Whitesides, G.; Gaasch, J.; Stedronsky, E. *J. Am. Chem. Soc.* **1972**, *94*, 5258–5270. (b) McCarthy, R.; Nuzzo, R.; Whitesides, G. *Ibid.* **1981**, *103*, 1676–1678. (c) Nuzzo, R.; McCarthy, T.; Whitesides, R. *Ibid.* **1981**, *103*, 3404–3410. (d) McCarthy, T.; Nuzzo, R.; Whitesides, G. *Ibid.* **1981**, *103*, 3396–3403. (e) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, *1*, 1528–1536.
(8) Results for the reductive elimination of biphenyl from Pt(II) diaryls[1g] show a lower barrier (18.2 kcal/mol) than that for the measured barrier for reductive elimination of CH$_3$CF$_3$[1c] from Pt(H)(CH$_2$CF$_3$)L$_2$. These experimental results can be explained by the fact that the phenyl group may stabilize the transition state.[1g]
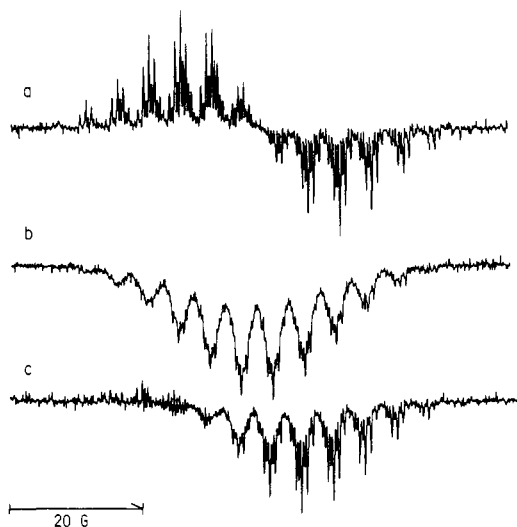(9) Rothman, M.; Lohr, L. *Chem. Phys. Lett.* **1980**, *70*, 405–409.

†Present address: Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

(1) El-Sayed, M. A.; Tinti, D. S.; Yee, E. M. *J. Chem. Phys.* **1969**, *51*, 5721. Clarke, R. H. *Chem. Phys. Lett.* **1970**, *6*, 413. Sharnoff, M.; Hurbe, E. B. *Phys. Rev. Lett.* **1971**, *27*, 576. Kim, S. S.; Weissman, S. I. *Rev. Chem. Intermed.* **1979**, *3*, 107.
(2) Weir, D.; Wan, J. K. S. *J. Am. Chem. Soc.* **1984**, *106*, 427.
(3) Wong, S. K.; Wan. J. K. S. *J. Am. Chem. Soc.* **1972**, *94*, 7197. Wong, S. K. Hutchinson, D. A.; Wan, J. K. S. *Ibid.* **1973**, *95*, 622; *J Chem. Phys.* **1973**, *58*, 985.
(4) Akiyama, K.; Tero-Kubota, S.; Ikenoue, T.; Ikegami, Y. *Chem. Lett.* **1984**, 903.

Figure 1. Transient ESR spectra of the 1,4-dimethylpyridinyl radical observed 1 μs after the laser pulse photolysis of the dimer at −45 °C in toluene: (a) without sensitizer, (b) in the presence of 2-acetonaphthone (0.1 M), and (c) in the presence of benzophenone (0.2 M).

The transient spectrum shown in Figure 1a was obtained by the laser photolysis of the pyridinyl dimer at −45 °C. In our previous paper,[4] a singlet radical pair precursor was proposed for the photolytic generation of the radical on the basis of the observation of A/E polarization. This proposal is supported by the subsequent results: (a) the CIDEP signal was clearly weakened by the addition of the singlet quencher, biacetyl (E_s = 272 kJ/mol),[5] and (b) oxygen showed no influence on the spin polarization. The dimer of the present radical has the lowest excited singlet state at about 330 kJ/mol above the ground state, as estimated roughly from the absorption spectrum, though no fluorescence spectrum has been observed.

Addition of 2-acetonaphthone, a triplet sensitizer, to the dimer solution caused a significant change of the CIDEP spectrum, as shown in Figure 1b. This sensitizer has a relatively long lifetime of the $\pi\pi^*$-phosphorescence (τ_p = 0.95 s)[6] and a large quantum yield of the intersystem crossing (ISC) (Φ_{ISC} = 0.84).[7] The complete emission spectrum of Figure 1b is essentially due to the 1,4-dimethylpyridinyl radical, though its hyperfine structure shows broadening. The half-life of the E polarization ($\tau_{1/2} \simeq 4$ μs) is longer than that of A/E polarization (1 μs) of Figure 1a. The observation of E spectrum suggests the participation of triplet mechanism in the process of the radical generation and it would be considered that the pyridinyl was generated by homolytic cleavage of excited state of the dimer formed through an energy transfer from the polarized triplet state of 2-acetonaphthone. In spite of the lower absorption coefficient of 2-acetonaphthone at 337 nm ($\epsilon_{337} \simeq 1600$) than that of the dimer ($\epsilon_{337} \simeq 4700$), triplet photosensitization occurred efficiently in the CIDEP. This is probably due to the higher possibility of photolytic cleavage of the dimer from the triplet state, as compared with that from the singlet state, and also to the large quantum yield of ISC of the excited 2-acetonaphthone. The E polarization also indicates that a highly spin-specific ISC to the triplet sublevel occurred in 2-acetonaphthone and the energy transfer was faster than the spin–lattice relaxation of the triplet state in this fluid system.

The effect of sensitizer was also examined by using benzophenone which has a nπ^* triplet of the first excited state. The quantum yield of ISC of the excited benzophenone is 1.0 and the ISC proceeds in highly spin-specific manner, while the half-life of the triplet state is very short (τ_p < 80 ms at 77 K).[8] Figure

1c shows the time-resolved ESR spectrum of the radical generated from the dimer in the presence of 0.2 M benzophenone observed 1 μs after the laser pulse irradiation. In this spectrum with an A/E* polarization, the absorption signal is compensated at the low field by the emission due to the sensitization by benzophenone. The complete E polarization was observed 3 μs after the photolysis in this system, because the E polarization due to triplet mechanism decayed slowly ($\tau_{1/2} \simeq 4$ μs). This result means that the triplet excitation transfer takes place in this system regardless of the short lifetime of the triplet state and the low absorption coefficient at 337 nm ($\epsilon_{337} \simeq 200$) of benzophenone. The mutual relation of the levels of excited states in the pyridinyl dimer and benzophenone makes double energy transfer possible, as demonstrated in the coumarine–benzophenone system,[9] that is, energy transfers from S_1 of the dimer to S_1 (320 kJ/mol) of benzophenone and then from T_1 (290 kJ/mol) of the latter to the dimer after the spin-specific ISC. During the ISC, the highest sublevel, P_+, of benzophenone is occupied with highest population at high magnetic field, because the zero-field parameter, D, is negative for the nπ^* state and the ISC rate into T_z is significantly larger than those into T_x and T_y (in which the z axis was chosen parallel to the C=O direction).

In contrast to the above results, fluorenone (E_T = 226 kJ/mol, $\pi\pi^*$) showed no effect on the CIDEP pattern of the radical, though the intensity decreased and the polarized signal diminished at high concentration (0.5 M) of fluorenone. The result is ascribed to that either the spin polarization conservation occurs less effectively or no energy transfer is caused because of the lower triplet energy of fluorenone compared with that of the pyridinyl dimer.

The present results clearly prove that the spin polarization is conserved during the triplet energy transfer in the system involving both $\pi\pi^*$ and nπ^* states, even in fluid solution. Therefore, the excitation transfer rate is faster than the triplet spin–lattice relaxation $1/T_1$. No T_1 value of benzophenone in fluid solution is available, while T_1 = 19 μs at 77 K.[10] Since the energy transfer proceeds with diffusion controlled rate, T_1 values of benzophenone and acetonaphthone would be larger than the order of nanosecond.

(9) Hammond, G. S.; Stout, C. A.; Lamola, A. A. *J. Am. Chem. Soc.* **1964**, *86*, 3103.
(10) Goncalves, A. N. P.; Gillies, R. *Chem. Phys. Lett.* **1980**, *69*, 164.

MCD–EPR Studies of Deoxy[Fe^{II},Fe^{II}]hemerythrin: Probes of Endogenous Bridging Ligands and Exogenous Ligand Binding

Richard C. Reem and Edward I. Solomon*

*Department of Chemistry, Stanford University
Stanford, California 94305*

Received August 27, 1984

The geometric structure of the binuclear nonheme iron active site in met[Fe^{III},Fe^{III}]hemerythrin[1] (Hr) is known to high resolution from crystallography[2] and is best described as two ferric ions bridged by a μ-oxo anion and the carboxylate side chains of glutamate and aspartate amino acid residues. In addition, one iron binds the imidazole groups from three histidines, while the other binds two histidines and the exogenous ligand.[3] The ex-

(5) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537.
(6) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.
(7) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.
(8) Pitts, J. N.; Johnson, H. W.; Kuwana, T. *J. Phys. Chem.* **1962**, *66*, 2456.

(1) (a) Klippenstein, G. L. *Am. Zool.* **1980**, *20*, 39. (b) Kurtz, D. M.; Shriver, D. F.; Klotz, I. M. *Coord. Chem. Rev.* **1977**, *24*, 145.
(2) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618. (b) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *Life Chem. Rep.* **1983**, *Suppl. 1*, 305.
(3) (a) Gay, R. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1978**, *100*, 1972. (b) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; Sanders-Loehr, J. *Nature (London)* **1981**, *281*, 263.