Table I. Asymmetric Cross-Coupling of **1** with **2** Catalyzed by Chiral Ferrocenylphosphine–Nickel Complexes[a]

Chiral ligand	$1/2^b$	Reaction temp (°C)	Yield[c] (%)	$[\alpha]^{22}D^d$ (neat)	% optical purity con-figuration)
(R)-(S)-PPFA	4	−20	99	+4.04	63 (S)
(S)-(R)-PPFA	4	0	99	−3.75	59 (R)
(S)-(R)-PPFA	2	0	97	−3.58	56 (R)
(S)-(R)-PPFA	2^e	0	98	−3.62	57 (R)
(S)-(R)-PPFA	1	0	83	−3.32	52 (R)
(S)-FcPN	4	0	98	+3.82	60 (S)
(R)-EPPF	4	0	86	+0.27	4 (S)

[a] Ratio $[Ni]^*/2 = 5 \times 10^{-3}$. [b] Concentration of **1** in ether was 1.5 M unless otherwise noted. [c] Yields based on **2** used were determined by GLC. [d] Optically pure (R)-(−)-3-phenyl-1-butene has $[\alpha]^{22}D$ −6.39° (neat); D. J. Cram, J. Am. Chem. Soc., **74**, 2141 (1952). [e] **1** of 0.5 M was used.

Grignard reagent, the optical purity of **3** was not largely affected by the **1/2** ratio, indicating that the inversion of the Grignard reagent **1** is relatively fast as compared with the coupling reaction. The high ability of PPFA and FcPN ligands to cause asymmetric induction is apparent by comparing the present results with 7–13% optical purity[8] obtained with [Ni{(−)-DIOP}Cl₂] as a catalyst where DIOP refers to 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.[1f] Secondly, (S)-FcPN ligand, which is analogous to (R)-(S)-PPFA but has only planar chirality, showed asymmetric induction of comparable efficiency to the PPFA ligand. The result demonstrates that ferrocene planar chirality plays an important role in the present asymmetric reaction rather than the carbon central chirality. Finally, a dramatic decrease in the asymmetric induction was observed with EPPF as a ligand which contains no dimethylamino group. Thus, the dimethylamino group on chiral ferrocenylphosphines is the first requisite for the high stereoselectivity in the present asymmetric cross-coupling reaction.

The important role of the amino group may be visualized by its strong ability to coordinate with the magnesium atom in the Grignard reagent. Thus, according to the mechanism proposed for the nickel–phosphine complex-catalyzed Grignard cross-coupling reaction,[7a,d] it is most probable that the configuration of the coupling product has already been determined before the chiral carbon–nickel bond is formed. The magnesium atom in the Grignard reagent must be coordinated with the dimethylamino group and such a complexation should increase the stereoselectivity via the enhanced steric interactions.[9]

Now we are in a position to be able to design new chiral phosphine ligands of higher ability for asymmetric induction.

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Mechanisms of Photochemical Reactions in Solution. 80.[1] Photochemical Oxidation of Tris(2,2′-bipyridyl)ruthenium(II) by Molecular Oxygen

Sir:

The cation, tris(2,2′-bipyridylruthenium(II) (**1**), is a useful prototype for study of intermolecular interactions of excited states having the MLCT configuration because the ion shows an easily monitored luminescence, believed to arise from a closely grouped manifold of excited states.[2] A number of studies of quenching of the luminescence have been reported.[3-11] Quenching may involve electronic excitation transfer,[3-6] electron transfer with production of Ru(III)[3,6-9,11] or both. Experimental separation of the two processes is not easy although Natarajan and Endicott[6] claim to have done so in a study of quenching by Co(III) complexes using scavenging techniques. Their argument was later questioned by Navon and Sutin.[9] Bock, Meyer, and Whitten[7] showed that in quenching by trans-1,2-bis(N-methyl-4-pyridyl)ethylene both energy transfer and electron transfer occurred with the latter being predominant. In cases where both processes are energetically feasible it is not at all clear as to what micromechanistic events precede separation to give products of energy or charge transfer. One can conceive of the two processes as being paths for decay of a single excited state complex (exciplex) but this is by no means required. We wish to report evidence that involvement of a third species, a proton, can influence the decay of a quench complex formed from **1** and molecular oxygen.

Demas and co-workers[5] have shown that quenching of **1** by oxygen in ·methanol leads to production of singlet oxygen. Although quantum yields were apparently high, absolute values were not determined. We have observed that on irradiation of acidic aqueous solutions containing **1**, Fe²⁺, and oxygen, oxidation of iron(II) to iron(III) occurs.[12] Quantum yields for production of Fe³⁺ were determined by measurement of Fe³⁺ absorbance and by the quenching of emission of **1** by Fe³⁺. The quantum yields were insensitive to sensitizer concentration and were independent of Fe²⁺ concentration (±15%) for 1.9×10^{-4} to 1.8×10^{-2} M, but did depend on oxygen pressure.[12] Figure 1 shows that there is a linear relationship between quantum yield for oxidation and the fraction of emission of **1** ($1 - I/I^0$), quenched by O₂. The quantum
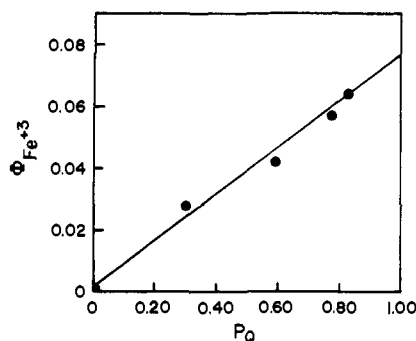
Figure 1. The dependence of Fe^{3+} appearance quantum yield on the fraction of $Ru(bpy)_3^{2+}$ excited states quenched by O_2 in 0.05 F H_2SO_4 at 26 ± 2 °C, irradiation at 313 nm, ferrioxalate actinometry, $[Fe^{2+}] = 7 \times 10^{-3}$ M.
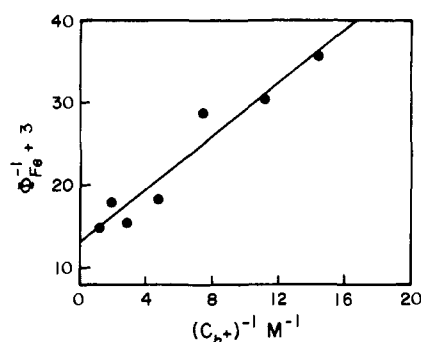
Figure 2. Functional dependence of inverse oxidation quantum yield on effective hydrogen ion concentration.[13] Air-saturated solutions at room temperature, 313 and 436 nm irradiation, $[Fe^{2+}] = 6 \times 10^{-3}$ M.

yields under fixed oxygen pressure also varied with the hydrogen ion concentration.[12] As shown in Figure 2, reciprocal quantum yield was linearly correlated with values of $(C_{h+})^{-1}$ calculated from Hammett acidity functions of the solutions.[13] Determined by least-squares analysis, the best fit straight line had slope of 1.6 einstein mol^{-1} M^{-1} and intercept of 13 einstein mol^{-1}, with correlation coefficient of 0.96. Addition of 0.9 N sodium sulfate to solutions 0.1 N in sulfuric acid led to no change in quantum yield indicating that the effects are due to changes in acidity rather than changes in ionic strength.[12]
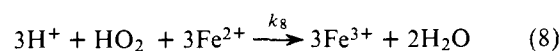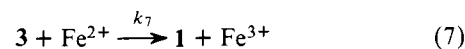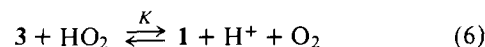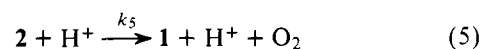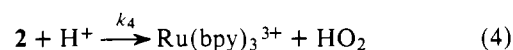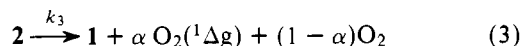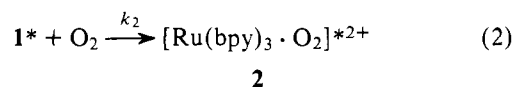
From a Stern–Volmer plot of emission quenching against oxygen pressure and our measured value of the emission lifetime[12] (0.60×10^{-6} s) in 0.05 F sulfuric acid we derive a value of 3.5×10^9 M^{-1} s^{-1} for the quenching rate constant in good agreement with other reports.[4,5] Incidentally, we did not observe the curious decrease in absorption of the complex in oxygen free solution (10^{-4} to 10^{-5} M) that was recently reported by Van Houten and Watts.[14]

Apparently interaction of O_2 with the emitting state of **1** produces an oxidant. At first we believed the oxidant to be either singlet oxygen or superoxide ion which might subsequently be protonated to produce the perhydroxyl radical. However, neither intermediate provides a good explanation of the effect of hydrogen ion concentration on quantum yield. Superoxide should be nearly completely protonated over the entire acid range of our experiments since perhydroxyl radical has a pK_a of 4.5.[15] Perhydroxyl oxidations of Fe^{2+} are pH invariant in the range studied.[16] On the other hand we would not expect singlet oxygen to be appreciably basic although protons might effect changes in stoichiometric pathways in secondary steps of singlet oxygen mechanisms.

The issue was really settled by demonstration that $Ru(bpy)_3^{3+}$ is also produced by oxygen quenching of **1*** and has a detectable lifetime in oxygenated solutions containing no Fe^{2+}. In 0.05, 0.5, and 1.0 F iron free acid saturated with

O_2, visible irradiation of 10^{-4} M **1** resulted in bleaching at 450 nm which decayed in the dark to regenerate the initial absorbance within a few percent. The decay rate decreased with increasing acidity. In 9 F H_2SO_4 bleaching was irreversible, as would be expected,[17] and high conversions of **1** could be obtained, resulting in the characteristic green color of-$Ru(bpy)_3^{3+}$. Subsequent addition of Fe^{2+} resulted in quantitative regeneration of **1**. No bleaching occurred on irradiation of oxygen free solutions.

Oxygenated solutions of 10^{-4} M **1** in 0.5 F H_2SO_4 were examined by flash spectroscopy, using 10 ns pulses from a Molectron UV 1000 N_2 laser for excitation. By monitoring the 450-nm absorption of **1** it was discovered that complete ground state depletion as well as fractional chemical bleaching was a consequence of excitation. At 300 ns after the laser pulse, fluorescence was negligible, at which time a new absorption baseline was established, and attributed to conversion of Ru(II) to Ru(III). The quantum yield of this chemical bleaching of **1** was 0.035 ± 0.012. Extrapolation of the Fe^{3+} quantum yields in Figure 2 to the same conditions of oxygen pressure and acidity gives a calculated quantum yield of 0.17 for the oxidation of Fe^{2+} to Fe^{3+}. This result is, within experimental error, equal to the factor of four difference between the quantum yields of **3** production and Fe^{3+} production predicted by the following mechanism.

$$1 \xrightarrow{h\nu} 1^* \xrightarrow{-h\nu'} 1 \tag{1}$$

$$1^* + O_2 \xrightarrow{k_2} [Ru(bpy)_3 \cdot O_2]^{*2+} \tag{2}$$
$$\mathbf{2}$$

$$2 \xrightarrow{k_3} 1 + \alpha\,O_2(^1\Delta g) + (1 - \alpha)O_2 \tag{3}$$

$$2 + H^+ \xrightarrow{k_4} Ru(bpy)_3^{3+} + HO_2 \tag{4}$$

$$2 + H^+ \xrightarrow{k_5} 1 + H^+ + O_2 \tag{5}$$

$$3 + HO_2 \underset{}{\overset{K}{\rightleftarrows}} 1 + H^+ + O_2 \tag{6}$$

$$3 + Fe^{2+} \xrightarrow{k_7} 1 + Fe^{3+} \tag{7}$$

$$3H^+ + HO_2 + 3Fe^{2+} \xrightarrow{k_8} 3Fe^{3+} + 2H_2O \tag{8}$$

Reaction 5 provides for the possibility that hydrogen ion quenching of **2** may proceed concurrently with protonation. If eq 7 and 8 are the only important paths for the destruction of the products of reaction 4, the overall stoichiometric factor for oxidation of iron(II) would be four in agreement with the laser data. However, reaction 6 and possibly oxidation of other species such as hydrogen peroxide by **3** may reduce the efficiency of oxidation at low Fe^{2+} concentrations.

In the presence of sufficient Fe^{2+}, sequence 1–8 predicts that

$$\frac{1}{\phi_{Fe^{3+}}} = \frac{1}{4\phi_2} \cdot \frac{k_4 + k_5}{k_4} \left(1 + \frac{k_3}{k_4 + k_5} \cdot \frac{1}{C_{h+}}\right) \tag{9}$$

which is the functional dependence on C_{h+} shown by the system in Figure 2. In air saturated solution at 25 °C, $\phi_2 = 0.33$ since 33% emission quenching of **1*** occurs. From the slope and intercept of Figure 2, $k_4/(k_4 + k_5) = 0.058$ and $k_3/(k_4 + k_5) = 0.12$.

We have no firm basis for assigning an electronic structure to **2**. We infer that it decays in large part to give singlet oxygen and reacts with protons to give perhydroxyl. This behavior is consistent with the assumption that **2** is a cage-complex of **3** and superoxide ion since it has been shown that oxidation of

superoxide produces singlet oxygen ($^1\Delta$g).[18,19] Exciplex structures involving less complete charge transfer could also be used to rationalize the behavior.

Singlet oxygen has been hypothesized to oxidize Fe^{2+} in 0.8 N H_2SO_4[20] as well as pH 5 $HClO_4$.[21] In the latter case, oxidation efficiency was found to increase with pH in contrast to the results here. The extent of involvement of singlet oxygen in our system, if any, must await more precise data correlating 3 formation with measured yields of Fe^{3+}. Similarly, more detailed investigation might reveal that oxidants other than singlet oxygen were involved in the earlier studies since the proposed mechanisms were based on reasonable inference rather than rigorous proof.

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A Novel Rearrangement of Angularly Fused Cyclobutanone. Stereospecific Syntheses of Intermediates to the Diterpene Alkaloids and the C_{20} Gibberellins[1]

Sir:

Recently we have developed[2] a simple efficient synthetic route to a few angularly fused polycyclic cyclobutanones **3a,b** and **4a,b** through intramolecular C-alkylations of the easily accessible β,γ-unsaturated diazomethyl ketones **1a,b** and **2a,b** and their stereocontrolled hydrogenation to the saturated cyclobutanones **5a,b** and **6a,b**. We now report a remarkable stereospecific rearrangement of these saturated cyclobutanones to the respective bridged ketones **7a,b** and **8a,b**. The importance of **7b** relating to the synthesis of *Garrya* and *Atisine* groups of the diterpene alkaloids and the C_{20}-gibberellins has already been established.[3] We also report here the transformations of the tetracyclic ketones **8a** and **8b** to some key hydrofluorene synthons **9a** and **9b** towards the C_{20}-gibberellins.[4]

Scheme I
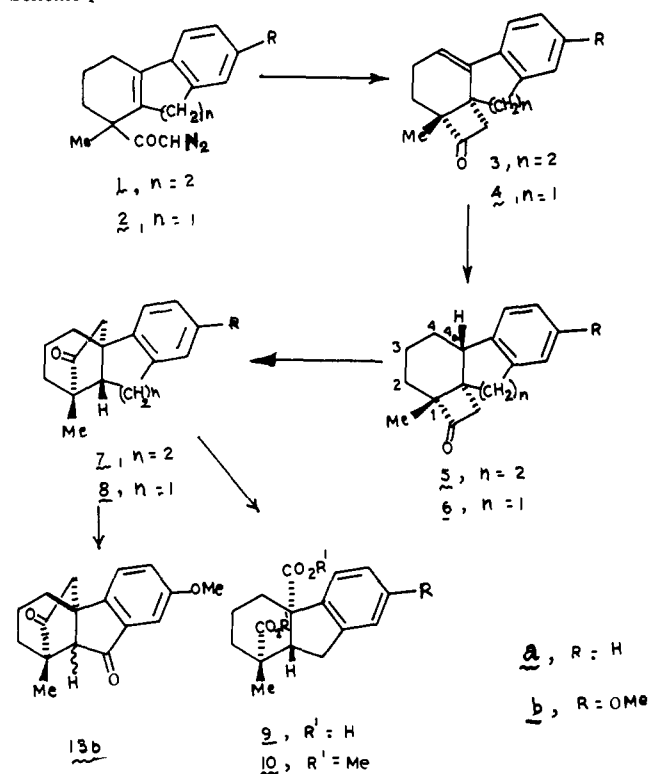
Thus, treatment of the strained[5] cyclobutanone **5a** with an excess (20–25 mole equiv) of triethyloxonium fluoborate[6] in anhydrous methylene chloride under dry nitrogen for 12–16 h afforded the known[3] bridged-tetracyclic ketone **7a** in 90–95% isolated yield. The corresponding methoxy analogue **5b** under the same sequence produced **7b**[3] in 90% yield. The intramolecular nature of this rearrangement has been established from the results of the reaction of **5a**-*4,4a-d2*[7] with triethyloxonium fluoborate, which showed a pronounced isotope effect and required ca. 6 days at room temperature for complete conversion of the cyclobutanone to the cyclopentanone (monitored by ir). The rearranged ketone **7a**,[8] isolated in 85% yield, showed >99% of d_2 in the mass spectrum.

It may be mentioned that the reaction of the cyclobutanone **5a** with concentrated H_2SO_4 in benzene at ice-salt bath temperature (ca. −10 to −5°) produced the unsaturated methyl ketone **11a**[9] in excellent yield, as has been reported[11] in a similar case.

The triethyloxonium fluoborate catalyzed rearrangement of the major isomer[2] **6a** from the catalytic hydrogenation of the unsaturated hydrofluorene ketone **4a**[12] required somewhat longer reaction time (24 h) and afforded the liquid five-membered bridged ketone **8a**,[13] bp 135–140° (0.3 mm) (bath temp) (*m/e* 226; ν_{max} 1730 cm^{-1}; δ (CCl$_4$) 0.70 (3 H, s), 1.2–3.5 (11 H, complex mm), 7.06 (4 H, s)) in 90–95% yield; semicarbazone mp 235–238° dec. The corresponding methoxy analogue **6b**,[14] under identical conditions gave the respective rearranged ketone **8b**, bp 120–125° (0.1 mm) (bath temp)

Scheme II

Communications to the Editor