

quasi-neutrality of the dioxygen ligand). A similar conclusion has been reached on the basis that the "picket fence" porphyrin is a good model for myoglobin but lacks the possibility of hydrogen bonding.²⁰

Finally the results of Table I point to: (i) a barrier to the rotation of the dioxygen ligand about the Fe–O bond of 5.6 kcal/mol in FePO₂; (ii) a linear structure for the Fe–C–O unit. This latter result is in agreement with a preliminary report of structural analysis for a picket fence carbonyl complex¹ but disagrees with the bent structure proposed on the basis of Mossbauer spectra and extended Huckel calculations.⁹ The computed binding energy for the carbonyl ligand is equal to 16 kcal/mol, to be compared to an experimental value of 10 kcal/mol for the binding to deoxymyoglobin.²¹

A more detailed account of this work will be presented elsewhere.^{23,24}

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- The LCAO–MO–SCF calculations were carried out with the Asterix system of programs¹¹ using Gaussian basis sets (10,6,4) for Fe, (7,3) for first-row atoms, and (3) for hydrogen contracted to a minimal basis set (except for the 3d functions which are split). The following geometries were used: for the iron-porphyrin core, the experimental geometry of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrinatoiron(II),¹² for the Fe–O₂ moiety the experimental values for the dioxygen complex of the "picket-fence" porphyrin,¹ for the "proximal" NH₃ ligand the experimental geometry of NH₃¹³ with an Fe–N bond length of 2.12 Å, for the CO ligand a C–O bond length of 1.16 Å and an Fe–C bond length of 1.77 Å.¹⁴ The nitrogen atom of the "distal" NH₃ ligand was positioned according to the x-ray data reported in ref 15. For the perpendicular structure of the Fe–O₂ unit we retained the same Fe–O and O–O bond lengths used for the bent structure with the two Fe–O bond lengths equal. The porphyrin plane is the *xOy* plane with the nitrogen atoms along the *x* and *y* axis, the Fe–O axis is the *z* axis and the O–O axis projects along a bisector of *xOy*.
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- Note Added in Proof. Similar calculations for the FePO₂Im system yield orbital and atomic populations very close to the ones of Table II for FePO₂(NH₃).²³ The two conformations of FePO₂Im with the Fe–O–O plane either parallel or perpendicular to the imidazole plane differ in energy by less than 5 kcal/mol. A double-zeta type calculation for a model-

Fe(N₆C₄H₈)ImO₂ of the synthetic oxygen carrier of Baldwin and Huff (*J. Am. Chem. Soc.*, **95**, 5757 (1973)) yields conclusions very similar to the above ones (such as the quasi-neutrality of the dioxygen ligand).

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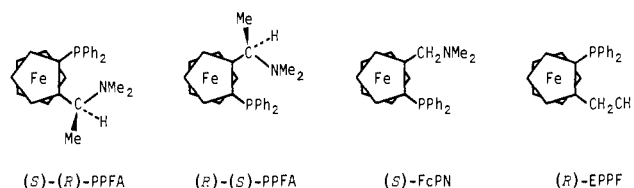
High Stereoselectivity in Asymmetric Grignard Cross-Coupling Catalyzed by Nickel Complexes of Chiral (Aminoalkylferrocenyl)phosphines

Sir:

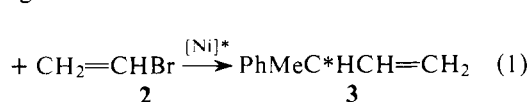
We report here that chiral (aminoalkylferrocenyl)phosphines are effective ligands for the nickel-phosphine catalyzed asymmetric Grignard cross-coupling to form an optically active hydrocarbon, with the aminoalkyl side chain being essential for the high asymmetric induction.

In recent years, catalytic asymmetric reactions have received much attention to obtain chiral molecules efficiently and considerable efforts have been devoted to developing new chiral phosphine ligands.^{1,2} Yet, the experimental results so far obtained have told us little about structural features of a ligand which will bring about the highest stereoselectivity in a given reaction.

The chiral (aminoalkylferrocenyl)phosphines, which we have recently prepared starting with Ugi's chiral α -dimethylaminoethylferrocene³ and used successfully for the asymmetric hydrosilylation² and hydrogenation,⁴ are quite unique in that they contain both planar and central elements of chirality, and also an amino group that can interact attractively with an appropriate substrate. These phosphines also offer an advantage over others in permitting one to estimate separately the role which each element of chirality and the functionality plays in an asymmetric reaction by appropriate structural modifications. Thus, (*S*)- α -[(*R*)-2-diphenylphosphinoferrocenyl]ethyl dimethylamine² (PPFA) contains all three features mentioned above, (*S*)-1-dimethylaminomethyl-2-diphenylphosphinoferrocene^{5,6} (FcPN) lacks the central chirality, and (*R*)-1-diphenylphosphino-2-ethylferrocene² (EPPF) possesses the planar chirality only.



Using these chiral phosphines as ligands, the nickel-catalyzed cross-coupling⁷ of the 1-phenylethyl Grignard reagent (**1**) with vinyl bromide (**2**) was examined (eq 1). A 1:2 mixture PhMeCHMgCl



of anhydrous NiCl₂ and each chiral phosphine was used as a catalyst precursor. The coupling reaction occurred smoothly at –20 to 0° within several hours to give optically active 3-phenyl-1-butene (**3**) in higher than 83% chemical yields. Results summarized in Table I contain three significant features. Firstly, the coupling product of highest optical purity (52–63%) was obtained with PPFA and FcPN. Although the present asymmetric reaction is due to kinetic resolution of the *sec*-alkyl

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 (%)	[α] ^{22D} ^d (neat)	% optical purity configuration
(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 × 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 [α]^{22D} -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 purity⁸ obtained with [Ni](-)-DIOPCl₂ 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'-bipyridyl)ruthenium(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 Endicott⁶ 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 Whitten⁷ 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-workers⁵ 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/I⁰), quenched by O₂. The quantum