Asymmetric homogeneous hydrogenation of olefins catalyzed by alkylphosphine complexes of rhodium(I)

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The cationic rhodium(I) complexes of the optically active ferrocenes, $C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][ER_2]$-1,2, catalyze the asymmetric hydrogenation of acetamidoacrylic acid derivatives, itaconic acid and styrene, when ER_2 is $P(C_6H_5)_2$ or $P(C(CH_3)_3)_2$. The configuration of the product is reversed on substituting C_6H_5 for $C(CH_3)_3$ groups. The catalyst with the *tert*-butyl groups can afford higher optical yields and is faster overall. The rhodium(I) complexes of the arsenic derivatives $ER_2 = As(C_6H_5)_2$ or $As(CH_3)_2$ do not catalyze the hydrogenation reactions. The nmr spectrum of the arsenic complex ($ER_2 = As(C_6H_5)_2$) is temperature dependent which seems to be due to a process involving the making and breaking of the Rh—N bond. The unsuccessful use of the MEM group (β-methoxyethoxymethyl) to protect an alcohol function α to a ferrocene ring is described. The hydrogenation results are discussed in the light of models which are currently used to predict the results of rhodium(I) catalyzed reactions but which are inapplicable to this work.

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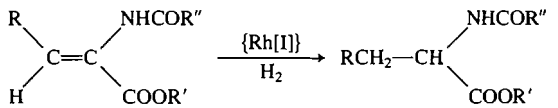
Les complexes cationiques du rhodium(I) avec des ferrocènes optiquement actifs du type $C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][ER_2]$-1,2, catalysent l'hydrogénation asymétrique des dérivés de l'acide acétamidoacrylique, de l'acide itaconique et du styrène lorsque le groupe $ER_2 = P(C_6H_5)_2$ ou $P(C(CH_3)_3)_2$. On observe une inversion de la configuration du produit lorsqu'on remplace le groupe $C(CH_3)_3$ par le groupe C_6H_5. Le catalyseur portant un groupe *tert*-butyle conduit à des rendements optiques plus élevés et agit d'une façon plus rapide. Les complexes du rhodium(I) des dérivés de l'arsenic $ER_2 = As(C_6H_5)_2$ ou $As(CH_3)_2$ ne catalysent pas les réactions d'hydrogénation. Le spectre de rmn du complexe de l'arsenic ($ER_2 = As(C_6H_5)_2$) dépend de la température et ceci semble être dû à un processus impliquant la formation et la rupture d'une liaison Rh—N. On décrit un essai qui n'a pas porté fruit d'utiliser le groupe MEM (β-méthoxyéthoxyméthyle) pour protéger la fonction alcool en α du cycle du ferrocène. On discute des résultats de l'hydrogénation en se basant sur les modèles couramment utilisés pour prédire les résultats de la catalyse par le rhodium(I) mais qui ne peuvent pas s'appliquer à ce travail.

[Traduit par le journal]

Introduction

The spectacular success in achieving nearly 100% enantiomeric excess in the homogeneous hydrogenation of α-acetamidoacrylic acids, using cationic rhodium(I) complexes of chelating ligands as catalysts, eq. [1], has generated considerable interest (1–15). One mechanism of the reaction, based on studies of the commonly used substrates and catalysts, appears to be as depicted in eqs. [2]–[5] (3). However, as discussed below, this need not apply to all systems.

The source of the stereospecificity in these reactions is of particular importance. On the basis of the crystal structures of several catalyst precursors, all of which have ditertiary phosphines as ligands, Knowles and co-workers (6, 7) have suggested that the absolute configuration of the amino acid product can be predicted in terms of a model which requires the square planar intermediate **1** to have the structure shown in **4**. Here the COOH group (R′ = H) is located above the *face* of a phenyl group on the ligand.[1]

[1] 

[2] $[Rh(L\text{-}L')(solvent)_2]^+ + substrate \leftrightarrows [Rh(L\text{-}L')substrate]^+$ **1** $+ 2\ solvent$

[3] $[Rh(L\text{-}L')(substrate)]^+ + H_2 \rightarrow [Rh(H)_2(L\text{-}L')(substrate)]^+$ **2**

[4] $[Rh(H)_2(L\text{-}L')(substrate)]^+ \rightarrow (Rh(H)(L\text{-}L')(Hsubstrate)]^+$ **3**

[5] $Rh(H)(L\text{-}L')(Hsubstrate) \rightarrow [Rh(L\text{-}L')(solvent)_2]^+ + (H)_2substrate$

Halpern and co-workers (3, 4) have recently determined the structure of two square planar intermediates **4** (L-L′ = $Ph_2P(CH_2)_2PPh_2$, $Ph_2P\overset{*}{C}HMeCH_2PPh_2$, R′ = Me, R = Ph). The olefin is bound as indicated but in both solids the COOR group lies over an *edge* of a phenyl ring. This, in the case of the optically active complex, hydrogenation would give the amino acid product of opposite configuration to that actually observed. These and other results led to the suggestion that the discrimination arises because of differences in the rates of reaction of the diasterotopic complexes **1** (or **4**) (eq.

[1] The four aromatic groups bound to phosphorus on the ditertiary phosphine, (L-L′), in **1** (or **4**) are "seen" by the incoming substrate as an alternating set of edge-on or face-on rings.

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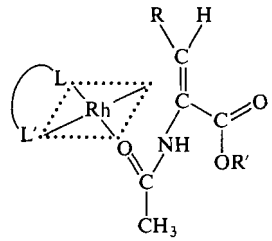
TABLE 1. Analytical data for new ligands and complexes[a]

	Complex	Found (%) C	Found (%) H	Found (%) N	Calcd. (%) C	Calcd. (%) H	Calcd. (%) N
7	$C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][As(C_6H_5)_2]$-1,2	64.37	5.93	2.86	64.43	5.82	2.89
8	$C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][As(CH_3)_2]$-1,2	52.47	6.73	3.95	53.21	6.70	3.88
9	$C_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][P(C(CH_3)_3)_2]$-1,2	65.64	8.85	3.41	65.84	8.97	3.49
10	$C_5H_5FeC_5H_3[CH(CH_3)OCOCH_3][P(C_6H_5)_2]$-1,2	68.27	5.67	—	68.44	5.52	—
11	$C_5H_5FeC_5H_3[CH(CH_3)OH][P(C_6H_5)_2]$-1,2	69.62	5.90	—	69.58	5.60	—
12	$C_5H_5FeC_5H_4CH(CH_3)OCH_2OC_2H_4OCH_3$	60.29	6.96	—	60.34	6.97	—
13	$\{C_7H_8RhC_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][As(C_6H_5)_2]$-1,2$\}ClO_4$[b]	50.32	4.93	1.78	50.83	4.65	1.79
14	$\{C_7H_8RhC_5H_5FeC_5H_3[(CH(CH_3)N(CH_3)_2][As(CH_3)_2]$-1,2$\}ClO_4$[c]	37.34	5.21	2.00	37.92	4.70	1.92
15	$[C_7H_8RhC_5H_5FeC_5H_3[CH(CH_3)N(CH_3)_2][P(C(CH_3)_3)_2]$-1,2$\}ClO_4$	50.08	6.82	2.00	50.06	6.37	2.01

[a]All derivatives are orange-red oils except for **7**, **13–15** which are orange-red solids.
[b]Cl Found: 4.90; calcd.: 4.55.
[c]CH_2Cl_2 solvate.

[3]). It should be noted that these rate differences could arise because of steric effects in the 6-coordinate *cis* hydride intermediate (13). In this connection Knowles *et al.* (7) have implied that the rate of subsequent reactions of **1** is a function of the flexibility of the ligand.



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This paper describes some further studies with complexes of some ferrocenylphosphines **6–9**. The results indicate that some of the currently accepted models are not applicable to these systems. In particular, unexpectedly high optical yields are achieved using complexes of the bulky phosphine **9**.

Experimental

Air sensitive reagents and products were manipulated in a nitrogen or argon atmosphere. Optical rotations were monitored on a Perkin Elmer 141 polarimeter. A cell length of 10 cm was used and the light source was the sodium D line (589 nm). *N,N*-dimethyl-α-ferrocenylethylamine **5** was prepared and resolved using (*R*)-(+)-tartaric acid as previously described (16). Microanalyses were done by Mr. Peter Borda, Chemistry Department, University of British Columbia. Data are given in Table 1.

Preparation of the Group V derivatives ***7–9***

The procedure for the preparation of **7–9** from **5** is essentially the same as that described for the preparation of **6** (13) (eq. [6]).

The resolved amine (or the racemic mixture) (0.01 mol) was placed in a Schlenck tube together with 15 mL of dry diethyl ether. The solution was treated with *n*-butyllithium (0.01 mol) and stirred for 1.5 h. The reaction is exothermic. The appropriate halide XER_2 ($ClAs(C_6H_2)_2$, $IAs(CH_3)_2$, $ClP(C(CH_3)_3)_2$) (0.01 mol) was added slowly and the solution stirred a further 3 h. An aqueous slurry of sodium bicarbonate (5 g in 10 mL) was added and the mixture was stirred for a further 1 h before it was filtered. The precipitate was washed with ether and the filtrate and washings were washed with water (2 × 30 mL). The organic layer, dried over K_2CO_3, was evaporated to leave an oily residue which was purified by recrystallization from absolute ethanol (**7**, 56% yield) or chromatography on an alumina column. Both **8** (40% yield) and **9** (40% yield) were eluted with 40:60 petroleum ether/diethyl ether; the first band was the desired product.

*Preparation of the rhodium(I) perchlorate complexes (**13–15**)*

The perchlorate salts of the ligands **7–9** were prepared essentially using the procedure of Schrock and Osborn (17) as described by Cullen *et al.* (13). Recrystallization required very little solvent. Thus at the ~1 m*M* scale the first formed cationic perchlorate salt was dissolved in ~1.5 mL of dichloromethane and treated with 5 mL of ethanol and 0.1 mL of diethyl ether to give crystals.

*Preparation of the acetate, **10***

The amine, **5**, (0.0125 mol) was sealed in a Carius tube with acetic anhydride (0.025 mol). The tube was heated to 100°C for 12 h. The reaction mixture was treated with K_2CO_3 (15 g in 50 mL of water) and extracted with diethyl ether. The ether extract was washed with dilute HCl (5%), K_2CO_3 (5%), and water, and dried over K_2CO_3. Evaporation of the solvent gave a 93% yield of **10**.

*Preparation of the alcohol, **11***

The acetate **10** in diethyl ether was treated with a slight excess of butyllithium and the mixture was stirred for 1 h. Water was added and the ether layer separated, washed with water, and dried over K_2CO_3. Removal of the solvent gave a 100% yield of **11**. The product can be recrystallized from heptane.

*Preparation of the MEM derivative of ferrocenylethanol, **12***

Ferrocenylethanol (11.7 g, 0.05 mol) was dissolved in dry dichloromethane (50 mL). To this solution was added diisopropylethylamine (9.7 g, 0.075 mol) and MEM chloride (9.35 g, 0.075 mol) was slowly added to the cooled stirred mixture (0°C). The temperature was slowly raised to 20°C (4 h). The resulting reaction mixture was washed with 5% HCl (2 × 50 mL), water (50 mL), and dried over K_2CO_3. Removal of solvent gave a brown liquid, **12**, in 88% yield. The liquid decomposed on distillation.

Hydrogenation reactions

A standard gas uptake apparatus was used for all hydrogenation reactions (13). The appropriate conditions are given in Table 3.

TABLE 2. The ^1H nmr spectra of new compounds[a]

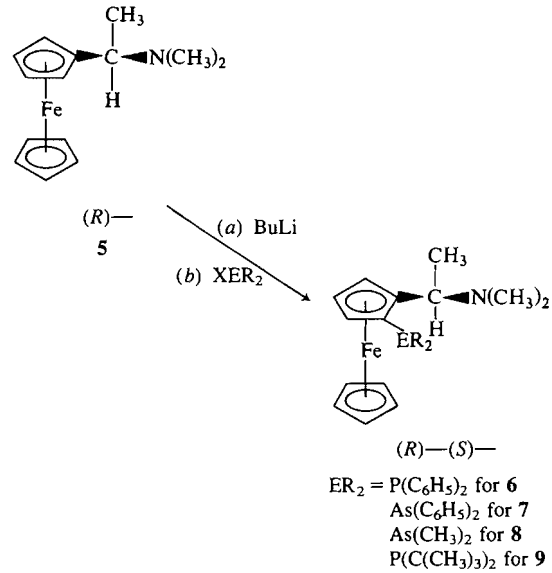
Compound	$CH(CH_3)(J(H,CH_3))$	$N(CH_3)_2$	C_5H_5	Other
7	1.21 (7)	1.78	3.97	—
8	1.28 (6)	2.11	4.10	1.22 (s), 1.03 (s), $(As(CH_3)_2)$
9	[b]	2.14	4.14	1.45(d), 0.88(d), $J(P,H) = 11$, $(P(C(CH_3)_3)_2)$
10	1.60 (6)	—	4.03	1.15 $(C(O(CH_3)$
11	1.20 (7)	—	4.24	1.10(d) (C—OH), 5.6 (qd)(C—H)
12	1.56 (6.5)	—	4.12	4.12(s)(OCH_3), 4.78(2)(—O—CH_2—O—), 3.6(m)(—O—CH_2CH_2—OCH_3), 3.4(m)(—O—CH_2CH_2—OCH_3)
13	1.74 (6)	2.78	3.65	See Fig. 1

[a] Principal features only at ambient temperature. Chemical shifts are given in ppm downfield from TMS. Coupling constants are in Hz.
[b] Under $C(CH_3)_3$ signals.

Results and discussion

The lithiation of optically pure **5** is almost stereospecific (18), which allows the preparation of disubstituted derivatives **6–9** in reasonable yield. The products have the (*R,S*)-configurations as shown in eq. [6]. The (*S*)-isomer of **5** affords (*S,R*)-products. The phosphine **6** has been described previously (13, 15, 19) but the other derivatives **7–9** are new. The analytical results, Table 1, and the nmr spectra, Table 2, confirm their formulation. In particular, all show the singlet at about 4 ppm characteristic of an unsubstituted C_5H_5 ring. The most interesting feature of these spectra is the appearance of two signals for the alkyl groups in the $—P(C(CH_3)_3)_2$ and $—As(CH_3)_2$ derivatives. This could be due to inter- or intramolecular complex formation with the amine acting as a donor, however, since the $—N(CH_3)_2$ signal is a singlet this explanation seems unlikely. Probably the doubling arises because the groups are diastereotopic. The spectrum of the corresponding $—P(CH_3)_2$ derivative is reported to show inequivalent methyl groups (doublets at 1.08 and 1.31 ppm) (19).

[6]

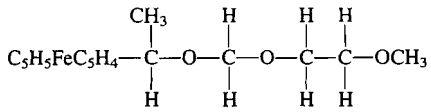


ER_2 = $P(C_6H_5)_2$ for **6**
$As(C_6H_5)_2$ for **7**
$As(CH_3)_2$ for **8**
$P(C(CH_3)_3)_2$ for **9**

The action of acetic anhydride in the amine **6** affords the acetate **10**. This compound has been prepared by others, also in high yield, using essentially the same conditions (19) and the spectroscopic data are in good agreement. The acetate **10** is readily converted to the alcohol **11** by reaction with butyllithium, a procedure which has been used to prepare this and related derivatives (19). The nmr spectrum of **11** is different from that previously described. The OH absorption is actually a doublet due to coupling with the C—H proton which itself is shifted downfield to 5.6 ppm and, because of the approximate equality of the couplings $J(CH_3,H)$ and $J(HO,H)$, it is seen as a sextet (a quartet of doublets).

In order to extend the chemistry of the phosphine **11** it was desirable to be able to protect the alcohol function. The β-methoxyethoxymethyl (MEM) group described by Corey *et al.* (20) seemed to offer many advantages, so preliminary experiments were carried out on α-ferrocenylethanol.

The MEM derivative, **12**, is formed easily from MEM chloride and the alcohol in the presence of diisopropylethylamine as described in the literature (20) (other suggested procedures involving, for example, butyl lithium are less desirable).



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A number of unsuccessful experiments were attempted to establish if the MEM group would direct lithiation in ferrocene derivatives. Typically when **12** is treated with 1 equivalent of TMEDA and 1 equivalent of butyllithium a dark solution is obtained. Nuclear magnetic resonance investigation of the product following hydrolysis of this solution with D_2O shows no lithiation reaction

takes place. Seemingly the MEM derivative complexes with the butyllithium. If excess butyllithium is used (three equivalents), cleavage occurs and an 80% yield of $C_5H_5FeC_5H_4C(CH_3)HOD$ can be isolated following treatment of the reaction mixture with D_2O.

Thus it seems that the MEM group is not as useful in ferrocene chemistry as could be hoped and no attempts were made to investigate the MEM derivative of **11**.

Cationic rhodium(I) complexes

The phosphines and arsines **6–9** all form derivatives $[(L\text{-}L')RhNBD]^+CO_4^-$ (L-L′ = bidentate ligand, and NBD=norbornadiene). The analytical results in Table 1 confirm the formulation of the new derivatives of **7–9**, however, the nmr spectra of the complexes are not straightforward. Some spectra of the perchlorate derivative of the arsine **7** are shown in Fig. 1. At ambient temperature, the phenyl region of the spectrum is more spread out than usual indicating that the two rings are in different environments and are, perhaps, held in a fixed orientation relative to each other. This difference in orientation is obvious in the crystal structure of the similar cation obtained from the $—P(C_6H_5)_2$ analogue **6** (13). The spectrum (Fig. 1) also shows a broad signal for the $N(CH_3)_2$ group which collapses and becomes the expected two singlets on cooling. The separation between the two signals is 72 Hz at −30°C. At this temperature the specturm is very similar to that of the analogous complex of **6** measured at ambient temperature.

It is difficult to account for this temperature effect by any simple exchange process such as conformational averaging because the methyl groups will always be inequivalent if the ring structure is preserved. The steps which seem to be necessary are as follows. (*i*) The Rh—N bond breaks. (*ii*) Rotation about the $C—N(CH_3)_2$ bond and inversion at nitrogen occurs. (*iii*) The Rh—N bond reforms.

A number of investigators have been attracted to work with ligands containing both hard and soft donor atoms in the hope that their metal complexes might show bond lability. This result could be the first clear demonstration of this expectation.

Work is now in progress to establish the validity of these proposals and hopefully the results will also enable an interpretation of the nmr spectra of complexes **15** and **16** which show similar features.

Hydrogenation studies

The results of a number of catalyzed hydrogenation reactions are given in Table 3.

The two phosphine derivatives **6** and **9** form

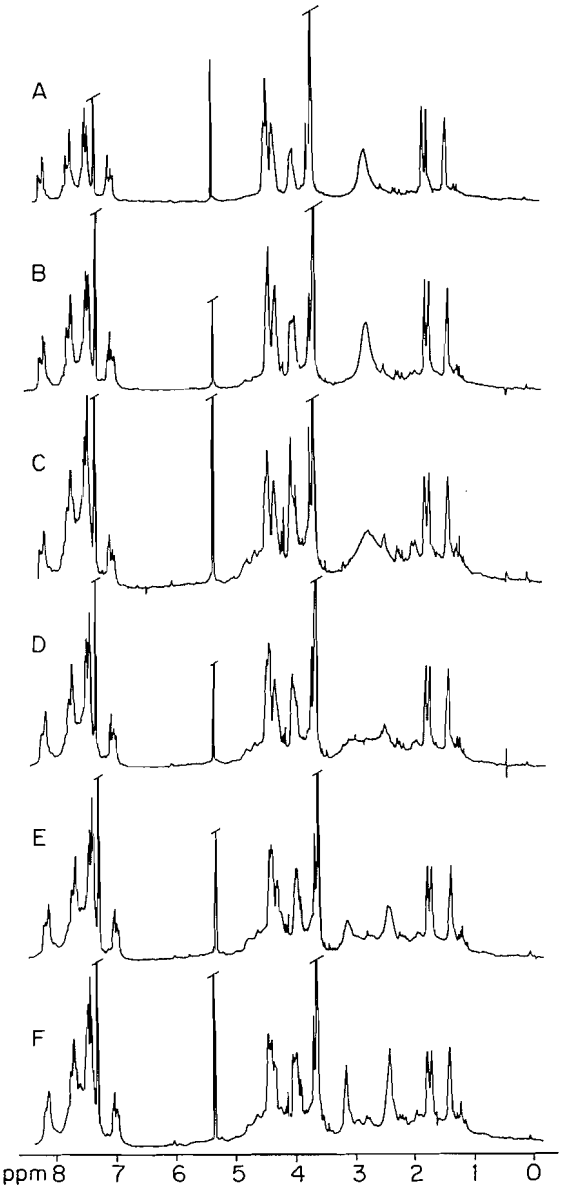


FIG. 1. The ^1H nmr spectrum of the arsine complex **13** (100 MHz). A, at ambient temperature; B, 10°C; C, 0°C; D, −10°C; E, −20°C; F, −30°C.

rhodium complexes which are catalyst precursors but the arsine analogues **7** and **8** do not. Furthermore, the arsines **7** and **8** do not give catalytically active solutions when mixed with $[Rh(1,5\text{-}COD)Cl]_2$ (COD = cyclooctadiene).

The failure of the arsines to afford catalytic systems is yet a further example of the unpredictability of experiments of this type and no good rationalization is available. Thus, in related work, the rhodium(I) complexes (produced *in situ*) of the

TABLE 3. Homogeneous hydrogenation of some olefins catalyzed by [Rh(L-L')(NBD)]$^+$ ClO_4^-[a]

L-L' of the catalyst precursor	Substrate	Time (h)	Optical yield (%)	Configuration
9	Acetamidocinnamic acid	16	84	*S*
	Acetamidoacrylic acid	12	24	*S*
	Itaconic acid	16	43	*R*
	Styrene	6	—	—
6	Acetamidocinnamic acid	24	76	*R*
	Acetamidoacrylic acid	18	49	*R*
	Itaconic acid[b]	72	33	*S*
	Styrene	12	—	—

[a]Reactions were carried out at 1 atm H_2 and 30°C. The concentration of the catalyst was 5×10^{-4} *M* and the substrate 5×10^{-2} *M*. Optical yields are based on the rotation of the isolated products. All reductions were quantitative (by nmr or gas chromatography) except [b] which was only 21% completed after 72 h.

arsenic analogue of DIOP (**16**, $ER_2 = As(C_6H_5)_2$) catalyze reductions such as shown in eq. [1]. The rates are slower than with phosphine based catalysts (21, 22) and the optical yields are low. The products also have the opposite configuration. The same *in situ* catalyst can also be used for the reduction of ketones via hydrosilylation. The yields, chemical and optical, are similar to those obtained from DIOP based catalysts but this time no reversal of product configuration is found.

In the case of the unsymmetrical ligands **17** ($ER_2 = P(C_6H_5)_2$ or $As(C_6H_5)_2$, $R' = CH_3$), *in situ* rhodium(I) catalysts prepared from the phosphine give high chemical and optical yields for the hydrosilylation of ketones, with the optical yields being higher than those obtained from DIOP (**16**) based catalysts in some cases. However, even though the arsine **17** ($ER_2 = As(C_6H_5)_2$, $R' = CH_3$) affords an *in situ* catalyst for the hydrosilylation reaction the optical yields are very low or zero in spite of very similar chemical yields.[2]

The catalyst precursor based on **6** has a known crystal structure and, using this as model, it is apparent that in an intermediate like **1** the two, and only two, phenyl rings would have an edge-on face-on arrangement with respect to the bound substrate (13). The face-on ring is adjacent to the cyclopentadiene rings and from models its motion appears to be restricted.

As mentioned in the Introduction, Knowles and co-workers (6, 7) have pointed out that the absolute configuration of the products from reactions of this type can be predicted by requiring the intermediate **1** to have a structure with the COOR group lying above the face of an aromatic ring attached to phosphorus. If this model is applied to the present results (L-L' = **6**) then the opposite configuration to that actually obtained is predicted.

[2]N. C. Payne and D. W. Stephan. Personal communication.

It is worth noting that using ligands like **6** with P and N donor atoms the Knowles requirement would ensure that the olefin C=C bond would have to be *trans* to the nitrogen in **4** ($L' = N(CH_3)_3$). This apparently is a favourable situation for binding since the crystal structure of (P-N)Ir(CO)Cl, when P-N is the closely related ligand *o*-diphenylphosphino-*N*,*N*-dimethylaniline, (**17**, $ER_2 = P(C_6H_5)_2$, $R' = H$) shows that the CO group is *trans* to N and that the Ir—(CO) and Ir—P bonds are unusually short and presumably strong (23).

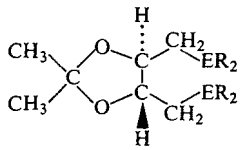
A further striking feature of these new results (Table 3) is that changing the $-P(C_6H_5)_2$ group to $-P(C(CH_3)_3)_2$ results in an effective hydrogenation catalyst which gives products of the opposite absolute configuration. Furthermore, the reactions go to completion in a shorter time and, in one case, a higher optical yield is obtained. Clearly, aromatic rings on the ligand donor atom are not needed to achieve good optical yields and fast rates can be obtained in spite of the bulk of the *tert*-butyl groups. (The noteworthy reversal of product configuration should be considered with the same effect caused by changing the ER_2 group in **16** from $P(C_6H_5)_2$ to $P(C_6H_4OCH_3\text{-}o)_2$ (24).)

There are only a few reports of asymmetric catalysis by metal complexes of aliphatic phosphines. Thus, Kumada and co-workers (25) showed that a closely related ferrocene derivative to **6–9** in which the ER_2 group is $P(CH_3)_2$ can be used to prepare an *in situ* rhodium(I) catalyst for the hydrosilylation of ketones. The optical yields are moderate (~50%). This same reaction and reactions such as [1] are reported (26) to be catalyzed by rhodium(I) complexes of ditertiary phosphines related to DIOP (**16**, $ER_2 = P(alkyl)_2$). It should also be mentioned that alkyl sulfoxides with the DIOP skeleton (**16**, $ER_2 = S(O)CH_3$) form ruthenium complexes which catalyze hydrogenations like [1]. However, the optical yields are low (27).

The hydrogenations reported by Otsuka (26) appear to proceed via a hydride intermediate $[(L\text{-}L)Rh(H)_2\ (solvent)_x]^+$ rather than the simple solvate **1** described in eq. [2]. Brown *et al.* (28) also described cationic rhodium hydrides which have phosphines such as $(C_6H_5)_2P(CH_2)_5P(C_6H_5)_2$ as ligands. Thus it is certainly possible that the pathway of some of the reactions described in Table 3 also involves the formation of a stable hydride. This will be checked by kinetic and spectroscopic measurements.

When itaconic acid is the substrate (Table 3) the hydrogen uptake is slower than observed for the other substrates. The optical yields are in the same range reported for similar catalyzed hydrogenations. It seems that the hydrogen bonding in the acid needs to be disrupted in some way before high optical yields are achieved (29).

Kumada and co-workers have found that rhodium(I) complexes of the amine and alcohol **18** (R = OH or $N(CH_3)_2$) are excellent hydrogenation catalysts (15, 19, 30, 31). In view of the result that the closely related **6** gives complexes which are as effective, it was of interest to establish if the same would hold for the alcohol **11**. The results of a number of experiments can be summarized as follows. For olefin reductions (eq. [1]) reaction is slow and optical yields are low. Thus acetamidocinnamic acid is 25% reduced after 3 days at 30°C (1 atm H_2). The optical yield is 17%. Ketones are not reduced under the same conditions.



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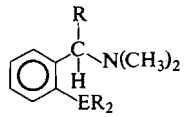
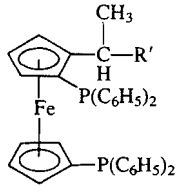
DIOP $ER_2 = P(C_6H_5)_2$



17

These results could well be due to lack of chelate formation by **11**. Both P and N are bound in complexes of **6** (13) and both P atoms are bound in complexes of **18** ($R' = N(CH_3)_2$).[3]



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[3]W. R. Cullen and T.-J. Kim. Unpublished results.

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