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Chiral 1,1′-Diphosphetanylferrocenes: New Ligands for Asymmetric Catalytic Hydrogenation of Itaconate Derivatives**

Ulrich Berens, Mark J. Burk,* Arne Gerlach, and William Hems

The attainment of both high catalytic efficiency and high enantioselectivity remains a formidable challenge in asymmetric catalysis.[1] Bidentate ligands composed of *trans*-2,5-disubstituted phospholane groups have been shown to be useful in asymmetric catalytic hydrogenation reactions.[2] Despite high enantioselectivities, practical application of this technology frequently requires enhancement of catalyst activity and productivity. To augment the turnover frequencies of catalysts bearing bis(phospholane) ligands, we introduced more flexible backbones (for example, 1,3-propandiyl and 1,1′-ferrocene bridges).[3] Whereas catalytic rates were greatly improved in these systems, enantioselectivities were found to plummet. We now have found that the combination of efficiency and selectivity may be realized through use of phosphetanes. Here we outline the synthesis of new 1,1′-diphosphetanylferrocene ligands (**1**; FerroTANE)[4] and demonstrate the superiority of these ligands over known systems in the highly efficient and enantioselective Rh-catalyzed hydrogenation of itaconate derivatives.

The first optically active phosphetanes previously were described in seminal reports by Marinetti and Ricard.[5] More recently, we[6] and the group of Marinetti and Genêt[7] have independently prepared and examined enantiomerically pure 2,4-disubstituted phosphetanes for use as ligands in asymmetric catalysis. The chiral 2,4-disubstituted phosphetane moiety may be constructed from readily available enantiomerically pure 1,3-diols. The requisite 1,3-diols were prepared conveniently through asymmetric hydrogenation of 1,3-diketones using well-documented procedures involving biaryldiphosphane – Ru catalysts.[8] Subsequently, the diols were converted to 1,3-diol cyclic sulfates **3** through treatment with thionyl chloride followed by Ru-catalyzed oxidation with sodium periodate.[6, 7] As shown in Scheme 1, the reaction between the cyclic sulfates **3** and the known diphosphanylferrocene **2**[3b] provided facile access to the desired ligands **1a** – **e**, which were isolated as yellow to orange crystalline solids in moderate to good overall yields. A wide range of different 2,4-disubstituted FerroTANE ligands may be obtained through this procedure. The facility with which ligand **1e** (R = *t*Bu) was formed is particularly surprising considering

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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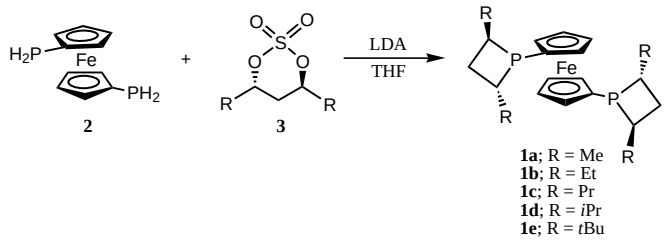


Scheme 1. Preparation of FerroTANE ligands.

that assembly required four independent neopentylic nucleophilic substitution reactions.

The new ligand series **1** initially was surveyed for relative utility in the Rh-catalyzed asymmetric hydrogenation of the standard olefinic substrate dimethyl itaconate **4**. The results of these studies (Table 1) reveal that cationic catalysts bearing

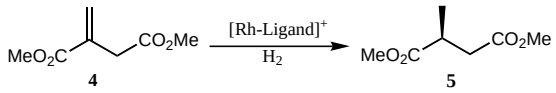


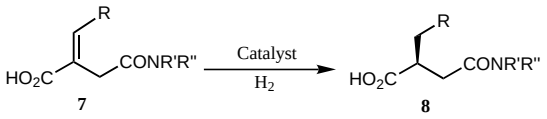
Table 1. Asymmetric hydrogenation of dimethyl itaconate **4**.[a]

Entry	Ligand	*ee* [%][b] (config.)[c]
1	(*R*,*R*)-Me-FerroTANE, **1a**	91 (*S*)
2	(*S*,*S*)-Et-FerroTANE, **1b**	98 (*R*)
3	(*R*,*R*)-Pr-FerroTANE, **1c**	97 (*S*)
4	(*S*,*S*)-*i*Pr-FerroTANE, **1d**	78 (*S*)
5	(*S*,*S*)-*t*Bu-FerroTANE, **1e**	1 (*S*)
6	(*S*,*S*)-**6a**	70 (*S*)
7	(*S*,*S*)-**6b**	66 (*S*)

[a] All reactions were performed in MeOH (1M in **4**) at 20 °C, S/C = 200, and 0.55 MPa H_2 using the catalyst precursors [Rh(Ligand)(cod)]BF_4 (cod = 1,5-cyclooctadiene). All reactions were complete after 1 h reaction time. [b] Enantiomeric excess was determined by chiral GC chromatography using a Chiraldex G-TA column. [c] Absolute configuration was ascertained by comparison of sign of optical rotation of product with that reported for configurationally assigned (*R*)-**5**: $[\alpha]_D^{20} = +6.11$ (neat). See reference [10].

the Et-FerroTANE and Pr-FerroTANE ligands (**1b** and **1c**, respectively), are very effective for this transformation, affording the product **5** with enantioselectivity comparable to that achieved with the Et-DuPHOS-Rh catalyst (97% *ee*).[11] Striking is the difference observed between results achieved with the FerroTANE ligands **1a**–**e** and the structurally analogous 1,1′-bis(2,5-dialkylphospholanyl)ferrocene derivatives[3b] **6a** (alkyl = Me) and **6b** (alkyl = Et) (entries 6–7). The advantages conferred by the phosphetane ligands are evident, although the reason for such a significant increase in selectivity upon moving from a five- to a four-membered phosphorus heterocycle is unclear at present.

Specifically protected succinamide derivatives of type **8** have been shown to serve as versatile peptidomimetic intermediates in the design of active drugs.[12] We envisaged that asymmetric catalytic hydrogenation of the monoamido itaconates **7** could provide direct and economic access to a diverse array of valuable analogues. Despite the attractiveness of this approach, little success has been reported thus far. No general catalyst has yet been developed and shown to furnish a range of peptidomimetics **8** through efficient hydrogenation of substrates of type **7** [Eq. (1)].[13, 14]



(1)

Initially, we examined the effectiveness of numerous cationic rhodium catalysts for asymmetric hydrogenation of the known substrate **9**.[15] Screening studies were performed under a standard set of conditions (1M MeOH solution, 0.55 MPa (80 psi) H_2, substrate–catalyst ratio (S/C) = 1000, 1 h). We selected the Et-FerroTANE-Rh catalyst for comparison against other cationic rhodium catalyst systems.[16] Ruthenium catalysts, such as Ru-BINAP, previously have been shown inadequate for hydrogenation of monoamido itaconate substrates analogous to **9** (BINAP = 2,2′-Bis(diphenylphosphanyl)-1,1′-binaphthyl).[13c] The results of our screening experiments are shown in Table 2.

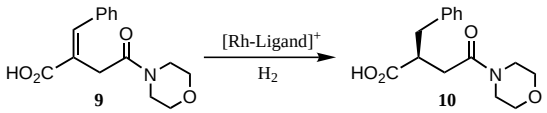


Table 2. Asymmetric hydrogenation of amido itaconate **9**.[a]

Entry	Ligand	Conv. [%][b]	*ee* [%][c] (config.)[d]
1	(*S*,*S*)-Et-FerroTANE, **1b**	100	98 (*R*)
2	(*S*,*S*)-Et-DuPHOS	5	85 (*R*)
3	(*R*,*R*)-**6b**	55	70 (*S*)
4	(*R*,*R*)-DIPAMP	10	87 (*R*)
5	(*S*,*S*)-BPPM	75	79 (*S*)
6	(*S*)-Tol-BINAP	11	43 (*S*)
7	(*S*)-PHANEPHOS	60	62 (*S*)

[a] All reactions were performed in MeOH (1M in **9**) at 20 °C, S/C = 1000, and 0.55 MPa H_2 using the catalyst precursors [Rh(Ligand)(cod)]BF_4. [b] Conversion after 1 h reaction time. [c] Enantiomeric excess was determined by SFC chromatography using a Chiralpak AD HPLC column. [d] Absolute configuration was ascertained by comparison of sign of optical rotation of product with that reported for configurationally defined **10**. See reference [12f].

The data demonstrate that the Et-FerroTANE-Rh catalyst is far superior to all other catalysts tested for hydrogenation of substrate **9**, both in terms of rate as well as enantioselectivity. In fact, under the conditions described using the Et-FerroTANE-Rh catalyst, hydrogen uptake ceased within 15 min reaction time (see also Table 3). No other catalyst was found to effect complete conversion under these conditions. Moreover, enantioselectivities achieved were significantly lower with all other catalysts in comparison with that observed with the Et-FerroTANE-Rh catalyst (98% *ee*). The BPPM-Rh and analogous catalysts previously were considered the best available for this transformation.[13c] Surprisingly, the Et-DuPHOS-Rh catalyst, which is so effective for hydrogenation of a wide range of Stobbe-derived itaconate derivatives,[11] was

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found relatively unavailing for substrate **9**. In general, impracticably low rates were observed with the Et-DuPHOS-Rh catalysts in hydrogenation of substrates of type **7**.

To explore the scope of the Et-FerroTANE-Rh catalyst, we have examined a variety of substrates **7** possessing different β-substituents and a morpholine-derived amido group. The results of these studies are shown in Table 3. As can be seen,

Table 3. Asymmetric catalytic synthesis of amido succinates **8**.[a]

Entry	R in **8**	t [min][b]	*ee* [%][c]
1	Ph	3 h[d]	98[d]
2	*p*-FC_6H_4	10	96
3	*p*-BrC_6H_4	30	95
4	*p*-$MeSC_6H_4$	15	97
5	thienyl	30	97
6	*n*Bu	30	92
7	*i*Pr	30	94
8	*t*Bu	60	99

[a] All reactions were performed in MeOH (0.2 – 0.5 M in **7**) at 20 °C, S/C = 1000, 0.55 MPa H_2, using the catalyst precursor [Rh((*S*,*S*)-**1b**)(cod)]BF_4. [b] Reaction time allowed for complete conversion. [c] Enantiomeric excesses were determined by either SFC chromatography using a Chiralpak AD HPLC column or by chiral GC using a CP-Chirasil L-Val column. [d] Reaction was performed at S/C = 20000.

the Et-FerroTANE-Rh catalysts were found to be very effective for rapid enantioselective synthesis of multifarious monoamido succinates **8**. High enantioselectivities were achieved in the hydrogenation of substrates **7** bearing assorted β-aryl groups, as well as linear and branched β-alkyl substituents. Importantly, the practical utility of the Et-FerroTANE-Rh catalyst is demonstrated effectively in entry 1, where complete conversion to **10** was achieved over 3 h at S/C = 20000 (turnover frequency = 7000 cycles h^{-1}). Enantioselectivity was found to be independent of catalyst loading.

In our final analysis, we have surveyed the effect of varying the amide functionality. Different amide groups may be incorporated readily into substrates **7** through direct reaction between a cyclic itaconic anhydride and a primary or secondary amine.[15] Accordingly, we have prepared a range of secondary and tertiary amide derivatives analogous to morpholine amide **9** (Table 4). Preliminary results achieved upon using the Et-FerroTANE-Rh catalyst suggest broad tolerance to the nature of the amide functionality, and indicate that a diverse selection of monoamido itaconates may be hydrogenated very efficiently and with high enantioselectivities using this catalyst system. Of particular interest is the hydroxamic acid derivative (entry 5), as enantiomerically pure hydroxamic succinates are widely employed as intermediates for production of collagenase and metalloproteinase inhibitors.[17]

Table 4. Asymmetric catalytic synthesis of monoamido succinates **8** (R = Ph).[a]

Entry	Amide group in **8**	t [min][b]	*ee* [%][c]
1	piperidine	20	98
2	pyrrolidine	20	88
3	benzylamine	60	97
4	cyclohexylamine	60	97
5	O-Bn-hydroxylamine	60	96

[a] All reactions were performed in MeOH (0.2 – 0.4 M in **7**) at 20 °C, S/C = 1000, 0.55 MPa H_2, using the catalyst precursors [Rh((*S*,*S*)-**1b**)((cod)]BF_4. [b] Reaction time allowed for complete conversion. [c] Enantiomeric excesses were determined by SFC chromatography using Chiralpak AD or OD HPLC columns.

Overall, we have highlighted the design and synthesis of a new family of 1,1′-diphosphetanylferrocene (FerroTANE) ligands **1**.[4, 18] Further uses of these ligands and catalysts will be reported in due course.

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[18] The FerroTANE ligands and rhodium catalysts are available for both research and commercial use through Chirotech Technology Ltd.

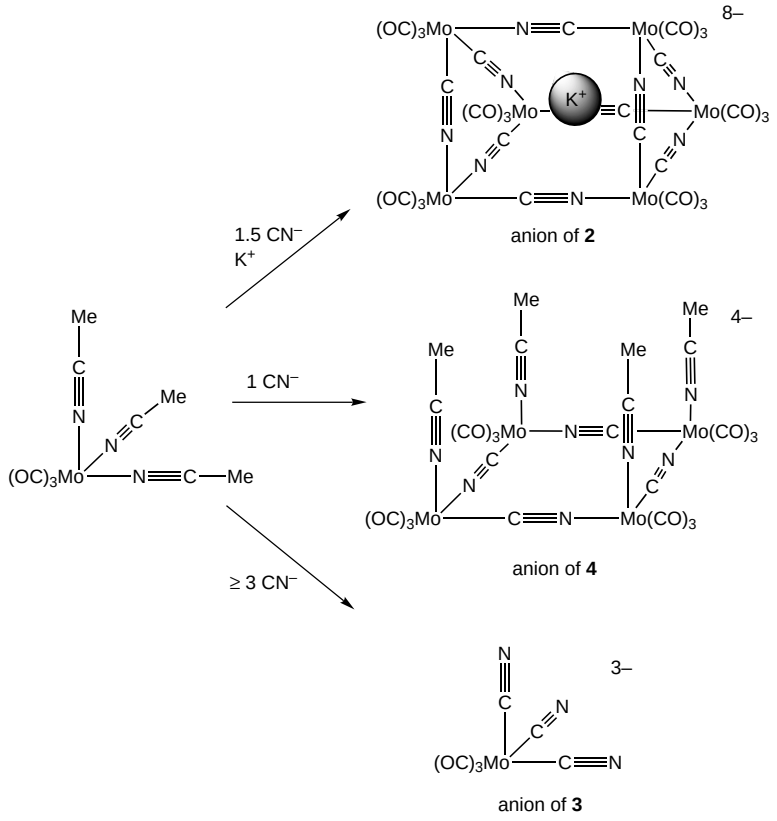
$\{K \subset [Mo_6(\mu\text{-}CN)_9(CO)_{18}]\}^{8-}$: A Trigonal-Prismatic Cyanometalate Cage**

Stephen M. Contakes and Thomas B. Rauchfuss*

Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday

The preeminent cyanometalate is Prussian Blue. Prussian Blue and its many analogues feature cubic or incomplete cubic arrays of metals linked by μ-CN units.[1, 2] The Prussian Blue motif is the basis of a new generation of high T_c magnets,[3, 4] molecular bowls and boxes[5, 6] with novel ion-binding properties,[7] and unusual coordination polymers.[8] Isoelectronic analogies between $[L_nFe^{II}CN]$ and $[L_nMo^0CN]$ suggest that it should be possible to prepare families of cages based on Prussian Blue employing cyano derivatives of the Group 6 metal–carbonyl complexes $[M(CO)_6]$.[9] Relevant to this plan is the well-recognized ability of cyanide to accomodate high negative charge, for example $[Ni(CN)_4]^{4-}$.[10, 11]

We have examined the reaction of $(Et_4N)CN$ in MeCN with $[Mo(Mes)(CO)_3]$ (**1**, Mes = mesitylene = 1,3,5-$Me_3C_6H_3$), the latter serving as a convenient source of $[Mo(CO)_3(MeCN)_3]$.[7] When solutions of **1** and $(Et_4N)CN$ in MeCN are combined in a 6:9 ratio in the presence of KPF_6, one obtains $(Et_4N)_8\{K \subset [Mo_6(\mu\text{-}CN)_9(CO)_{18}]\}$ (**2**) as yellow microcrystals in quantitative yield (Scheme 1). Crystallographic



Scheme 1. Synthesis of **2**–**4**.

analysis reveals that **2** consists of a trigonal-prismatic $Mo_6(CN)_9$ cage with idealized D_{3h} symmetry (Figure 1). Eight Et_4N^+ ions are evident in the asymmetric unit. At the center of the cage lies a potassium cation. The potassium is formally 18-coordinate, but the K···C/N bonding is ionic. The potassium atom is 3.37 and 3.20 Å from the C/N atoms of the triangular and square faces, respectively. The Mo centers are octahedral with all OC-Mo-CO angles of about 84° and C/N-Mo-CO of about 96°. The average C/N-Mo-C/N angle within the square faces is 85°, and within the triangular faces it is 80°. The ring strain associated with the 60° Mo···Mo···Mo angles is also responsible for the acute Mo-C-N/Mo-N-C angles of 169° observed for the triangluar faces (versus 178° for the square faces). Because of disorder between the C and N sites, the Mo–C/N distance of 2.23 Å represents an average of Mo–N(C) and Mo–C(N) distances. In similar compounds, the $(CO)_3Mo^0$–$[\mu\text{-}NC]_3$ distance is about 2.2 Å.[7] This implies that Mo–CN and Mo–NC distances are similar, especially in view of the small thermal parameters for C/N atoms. The Cs^+ analogue of **2** was also crystallographically characterized,

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