# Unprecedented Enantioselectivity in a Cluster-Based Catalytic System

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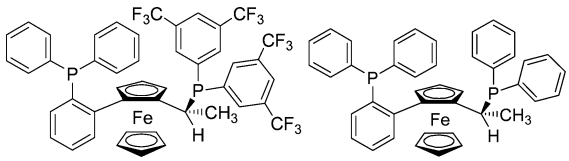
*Summary: Catalytic systems based on the clusters [$H_4Ru_4(CO)_{10}$-{$\mu$-1,2-(P−P)}] and [$H_4Ru_4(CO)_{10}${1,1-(P−P)}] (P−P = (R)-(R)-$Ph_2PPhFcCHCH_3PR_2$; Fc = ferrocenyl; R = 3,5-$CF_3$Ph (W001), Ph (W002)) have been used successfully in asymmetric hydrogenation of prochiral α-unsaturated carboxylic acids under mild conditions. Enantiomeric excesses of 42−92% and conversion rates in excess of 99% were observed.*

There has been considerable interest in the use of transition metal carbonyl clusters as catalysts for various chemical reactions of industrial relevance.[1] Such clusters are often thermally stable, and the presence of more than one metal in a catalyst offers, in principle, new pathways for the activation of molecules and regioselectivity in reactions due to differentiated metal binding of a substrate molecule (reactant).[2] It has indeed been found that metal carbonyl clusters can function as efficient catalysts (or catalyst precursors) for several chemical reactions,[1] but cluster-based catalysis has not yet proven to be commercially viable.

Using para-hydrogen as a label, Duckett, Dyson, and co-workers[3] have used NMR spectroscopy to show that phosphine-substituted triruthenium clusters can function as catalysts for the hydrogenation of alkynes (diphenylacetylene); it was found that the trinuclear clusters were the most active catalysts, but that fragmentation to form mononuclear ruthenium complexes with catalytic properties also occurs. Hydride-containing trinuclear and tetranuclear ruthenium carbonyl cluster anions have been shown to be effective catalysts/catalyst precursors for hydroformylation,[4] hydrosilylation,[5] and reductive coupling[6] reactions as well as the water-gas shift reaction.[7] In pioneering systematic studies, Matteoli and co-workers have shown that clusters of the general formula [$H_4Ru_4(CO)_{12-2x}(P-P)_x$] ($x$ = 1, 2; P−P = chiral diphosphine) are good catalysts for asymmetric isomerization,[8] hydroformylation,[9] and hydrogenation reactions.[10] The best enantiomeric excesses reported thus far for cluster-based asymmetric catalysis are approximately 45% in the case of hydrogenation of tiglic acid ((*E*)-2-methyl-2-butenoic acid) by [$H_4Ru_4(CO)_{10}$(1,1-bdpp)] (bdpp = (2*R*/*S*,4*R*/*S*)-2,4-bis(diphenylphosphino)pentane).[11] The catalysis was found to take place under relatively mild conditions, and strong chiral induction was indirectly shown by the fact that the chirality of the predominating enantiomer of the product (2-methylbutyric acid) was dependent on the chirality of the bdpp ligand.[11] Here, we demonstrate the importance of the chiral ligand for enantioselective cluster-based catalysis: the use of tetraruthenium cluster catalysts containing the Walphos[12] ligands (*R*)-1-[(*R*)-2-(2′-diphenylphosphinophenyl)ferrocenyl]ethyldi-(bis-3,5-trifluoromethylphenyl)phosphine (W001) or (*R*)-1-[(*R*)-2-(2′-diphenylphosphinophenyl)ferrocenyl]ethyldiphenylphosphine (W002, Figure 1) has led to unprecedented enantioselectivities for cluster-based catalysis, with ee's exceeding 90% in the hydrogenation of prochiral α-unsaturated carboxylic acids (Scheme 1).




W001 W002

**Figure 1.** Schematic depiction of the ligands W001 and W002.

The new tetranuclear carbonyl hydrido clusters [$H_4Ru_4(CO)_{10}$-{$\mu$-1,2-(*R*)-W001}] (**1**), [$H_4Ru_4(CO)_{10}${1,1-(*R*)-W001}] (**2**), [$H_4Ru_4(CO)_{10}${$\mu$-1,2-(*R*)-W002}] (**3**), and [$H_4Ru_4(CO)_{10}${1,1-(*R*)-W002}] (**4**) were prepared by literature methods[11,13] and have been characterized by IR and NMR spectroscopy, mass spectrometry, and X-ray crystallography.[14] The crystal structures of **1** and **3** (Figure 2) reveal that in both clusters the four hydrides bridge metal−metal bonds, and (in the solid state) these hydrides

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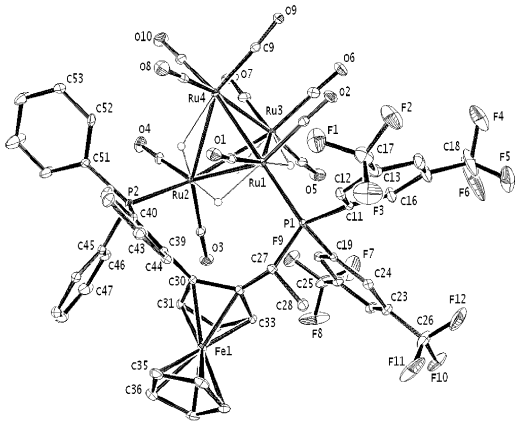
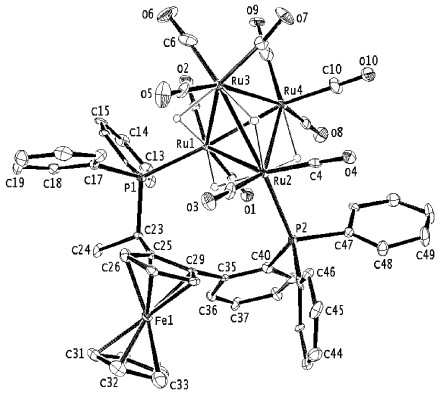


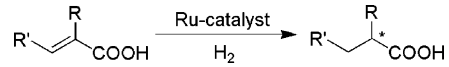
**1**



**3**

**Figure 2.** ORTEP plot of the molecular structure of $[H_4Ru_4(CO)_{10}\{\mu\text{-}1,2\text{-}L\}]$ [L = W001, **1**; L = W002, **3**]. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2) 3.028(1) (**1**) 3.003(2) (**3**); Ru(1)−Ru(3) 2.922(1) (**1**), 2.921(1) (**3**); Ru(1)−Ru(4) 2.764(1) (**1**), 2.777(1) (**3**); Ru(2)−Ru(3) 3.028(1) (**1**), 3.029(2) (**3**); Ru(2)−Ru(4) 2.999(1) (**1**), 2.953(2) (**3**); Ru(3)−Ru(4) 2.779(1) (**1**), 2.790(2) (**3**); Ru(1)−P(1) 2.325(1) (**1**), 2.369(3) (**3**); Ru(2)−P(2) 2.360(1) (**1**), 2.355(3) (**3**); P(1)−Ru(1)−Ru(2)−P(2) 82.73(3) (**1**), 74.70(1) (**3**); Ru(2)−Ru(1)−P(1)−C(23) −65.6(1) (**1**); Ru(2)−Ru(1)−P(1)−C(27) −49.5(5) (**3**); Ru(1)−Ru(2)−P(2)−C(40) −10.7(1) (**1**), −15.4(5) (**3**); Ru(1)−Ru(2)−P(2) 108.23(3) (**1**), 107.15(9) (**3**); Ru(2)−Ru(1)−P(1) 116.28(3) (**1**), 120.7(1) (**3**); Ru(1)−P(1)−C(23) 116.2(1) (**1**); Ru(1)−P(1)−C(27) 118.1(4) (**3**); Ru(2)−P(2)−C(40) 115.8(1) (**1**), 120.0(4) (**3**).

**Scheme 1. General Scheme for the Catalytic Hydrogenation Reactions Studied in This Paper**




are located in a structural pattern that has been observed previously for $[H_4Ru_4(CO)_{10}(\mu\text{-}1,2\text{-diphosphine})]$ clusters.[11,15]

The spans ("bites") of the above-mentioned diphosphine ligands are so large that it is not possible to coordinate both phosphorus atoms in the same relative positions on the triangular metal faces to which both phosphorus atoms are coordinated (nine-membered "dimetallacycles" are formed). Therefore, one phosphorus atom on the ligand occupies an "equatorial" position, while the second is coordinated in an "axial" position of the specific triangular face. To our knowledge, this coordination mode of two phosphine moieties on the tetrahedral $H_4Ru_4$ framework has not been observed previously, with the exception of the dimeric cluster $[\{H_4Ru_4(CO)_{10}(1,2\text{-DIOP})\}_2]$ (DIOP = (4*R*,5*R*)-2,2-dimethyl-4,5-bis((diphenylphosphino)methyl)-1,3-dioxolane), where two diphosphine ligands form bridges between two tetraruthenium units so that each $H_4Ru_4$ unit is coordinated by two phosphorus atoms originating from two different diphosphine ligands.[16]

The coordination of a heterodidentate ligand in a 1,2-bridging coordination mode to a trinuclear (triangular) cluster framework leads to an intrinsically chiral framework unless there is complete planarity,[17] and the coordination of the enantiomerically/diastereomerically pure diphosphine ligands used in this investigation to a triangular face of the $Ru_4$ tetrahedron may thus yield mixtures of diastereomers. However, the X-ray structures and, more importantly, the NMR spectra of the clusters indicate that only one diastereomer is formed except in the case of **3**, where the low value of the Flack parameter suggests the possibility of the presence of a diastereomer in the solid-state structure (although there is no evidence of such a diasteromer in the NMR spectrum of the cluster). The structure was therefore refined with an 86:14 mixture of two diastereomers, which led to a slight improvement of the *R*-factor. While there was no evidence of the presence of more than one diastereomer for the other clusters, the presence of minute quantities of a second diastereomer cannot be entirely ruled out.

The catalytic activities of **1**−**4** were examined in asymmetric hydrogenations of tiglic acid (**5**), (*E*)-α-methylcinnamic acid (**6**), (*E*)-α-phenylcinnamic acid (**7**), and (*E*)-2-methyl-2-pentenoic acid (**8**) (Figure 3). In a typical experiment, a mini-bench reactor (total volume of 100 mL) fitted with a glass liner was charged with solvent (toluene/EtOH, 1:1 (v/v), 5 mL), substrate, and catalyst ($n_{substrate}/n_{catalyst}$ 250/1 to 500/1) and finally pres-

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(14) Selected spectroscopic and analytical data: **1**: IR $\nu$(CO)/cm$^{-1}$, ($CH_2Cl_2$): 2073ms, 2053ms, 2028vs, 2013s, 1998w, 1965w. $^1$H NMR ($CDCl_3$, 293 K): $\delta$ hydride signals −16.4 ppm (m, br), −16.7 ppm (d, $J$ = 7.3 Hz), −17.6 ppm (td, $J$ = 11 Hz, $J$ = 2.4 Hz), −18.5 (dm, br, $J \approx$ 30 Hz). $^{31}$P{$^1$H} NMR ($CDCl_3$, 293 K): $\delta$ 45.9 ppm (m), 39.1 ppm (m). MS (FAB$^+$): 1620 ($M^+$). Anal Calcd for $C_{56}H_{36}O_{10}F_{12}P_2FeRu_4 \cdot 1/2C_6H_{14}$: C, 42.60; H, 2.59. Found: C, 42.50; H, 2.83. **2**: IR $\nu$(CO)/cm$^{-1}$, ($CH_2Cl_2$): 2078ms, 2049s, 2027vs, 2003ms, 1986mw, 1965w, 1949w. $^1$H NMR ($CDCl_3$, 293 K): $\delta$ hydride signals −15.7 ppm (s, br), −16.0 ppm (t, $J$ = 7.8 Hz), −16.5 ppm (m, br), −16.9 (s, br), −17.5 (s, br), −17.8 (s, br). $^{31}$P{$^1$H} NMR ($CDCl_3$, 293 K): $\delta$ 43.3 ppm (m), 4.3 ppm (m). **3**: IR $\nu$-(CO)/cm$^{-1}$, ($CH_2Cl_2$): 2075s, 2055s, 2020vs, 2010ms, 1995mw, 1965w. $^1$H NMR ($CDCl_3$, 293K): $\delta$ hydride signals −16.70 ppm (s, br), −16.77 ppm (d, $J$ = 4.9 Hz), −16.98 ppm (td, $J$ = 10.4 Hz, $J$ = 1.6 Hz), −17.82 (br), −17.82 (br), 18,02 (br). $^{31}$P{$^1$H} NMR ($CDCl_3$, 293 K): $\delta$ 42.3 ppm (m), 35.2 ppm (m). **4**: IR $\nu$(CO)/cm$^{-1}$, ($CH_2Cl_2$): 2074ms, 2045s, 2021vs, 2000m, 1983mw, 1961w. $^1$H NMR ($CDCl_3$, 293 K): $\delta$ hydride signals −16.8 ppm (s, br), −17.0 ppm (m, br), −17.8 ppm (s, br). $^{31}$P{$^1$H} NMR ($CDCl_3$, 293K): $\delta$ 45.7 ppm (m), 38.5 ppm (m). Selected crystallographic data: **1**: $C_{62}H_{50}F_{12}FeO_{10}P_2Ru_4$; a red plate of dimensions 0.26 × 0.23 × 0.08 mm$^3$ gave a monoclinic space group *C*2, $a$ = 44.368(9) Å, $b$ = 10.745-(2) Å, $c$ = 14.356(3) Å, α = 90°, $\beta$ = 103.65°, $\gamma$ = 90°, $V$ = 6651(2) Å$^3$, $T$ = 100(2) K, $Z$ = 4, $\rho_{calcd}$ = 1.703 Mg/m$^3$, $2\theta_{max}$ = 55.00°, Mo Kα $\lambda$ = 0.71073 Å. All structures were solved and refined with convergence on $F^2$ (SHELXS and SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany, 1997). CCDC 652265 and 652266 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. $R_1$ = 0.0280 (for 13 849 reflections with $I > 2\sigma(I)$), $wR_2$ = 0.0659, and $S$ = 1.015 for 793 parameters and 15 198 unique reflections. Minimum/maximum residual electron density −0.770/0.946 e Å$^{-3}$. **3**: $C_{52}H_{40}FeO_{10}P_2Ru_4$; a red plate of dimensions 0.19 × 0.16 × 0.09 mm$^3$ gave an orthorhombic space group $P2_12_12_1$, $a$ = 10.836(2) Å, $b$ = 14.243-(3) Å, $c$ = 32.129(6) Å, α = 90°, $\beta$ = 90°, $\gamma$ = 90°, $V$ = 4958.9(17) Å$^3$, $T$ = 120(2) K, $Z$ = 4, $\rho_{calcd}$ = 1.804 Mg/m$^3$, $2\theta_{max}$ = 55.08°, Mo Kα $\lambda$ = 0.71073 Å, $R_1$ = 0.0702 (for 8623 reflections with $I > 2\sigma(I)$), $wR_2$ = 0.1830, and $S$ = 1.123 for 624 parameters and 10 239 unique reflections. Minimum/maximum residual electron density −1.898/1.488 e Å$^{-3}$.

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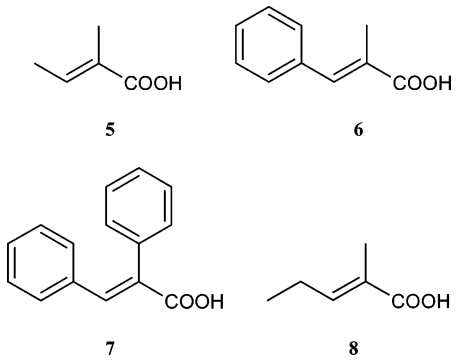


**5** **6** **7** **8**

**Figure 3.** Drawings of the substrates used in catalytic experiments: (*E*)-2-methyl-2-butenoic acid (tiglic acid) (**5**), (*E*)-α-methylcinnamic acid (**6**), (*E*)-α-phenylcinnamic acid (**7**), and (*E*)-2-methyl-2-pentenoic acid (**8**).

**Table 1. Summary of Catalytic Asymmetric Hydrogenation Reactions**

| entry | catalyst | substrate | conversion[a] (%) | selectivity[b] (%) | ee (%) | config[c] |
|---|---|---|---|---|---|---|
| 1 | **1** | **5** | 99 | 99 | 82 | *S* |
| 2 | **1** | **6** | 100 | 91 | 75 | *S* |
| 3 | **1** | **7** | 99 | 90 | 66 | *R* |
| 4 | **1** | **8** | 100 | 99 | 68 | *S* |
| 5 | **1**/Hg[d] | **5** | 100 | 100 | 87 | *S* |
| 6 | **2** | **5** | 100 | 100 | 93 | *S* |
| 7 | **2** | **6** | 100 | 74 | 89 | *S* |
| 8 | **2** | **7** | 100 | 65 | 83 | *R* |
| 9 | **2** | **8** | 100 | 100 | 68 | *S* |
| 10 | **3** | **5** | 100 | 100 | 58 | *S* |
| 11 | **3** | **6** | 100 | 89 | 69 | *S* |
| 12 | **3** | **7** | 100 | 83 | 63 | *R* |
| 13 | **3** | **8** | 100 | 99 | 42 | *S* |
| 14 | **3**/Hg[d] | **5** | 100 | 100 | 62 | *S* |
| 15 | **4** | **5** | 100 | 100 | 63 | *S* |
| 16 | **10** | **5** | 100 | 85 | 68 | *R* |
| 17 | **11** | **5** | 100 | 79 | 30 | *S* |

[a] The amount of substrate consumed in the catalytic experiment, assessed by $^1$H NMR. [b]The carboxylate of the substrate was found to react with solvent (ethanol) to form an ester. [c]Favored enantiomer. [d]Mercury poison test.

surized with dihydrogen gas (50 bar). The autoclave was heated at 100 °C for 24 h and allowed to cool to ambient temperature before it was opened. The enantiomeric excess of the product was determined by converting the hydrogenated carboxylic acid with (*S*)-methyl mandelate and analyzing the diastereomeric mixture by NMR, as previously described in detail by Tyrell et al.[18] and by us[11] (cf. Supporting Information). The catalysis results are summarized in Table 1. We have noted that tetraruthenium clusters containing ferrocenyl-based diphosphine ligands consistently give high conversion in hydrogenation reactions of α-unsaturated carboxylic acids,[19] and this is also the case when the present Walphos ligands are used. Thus, the conversion and selectivity of the hydrogenation reactions in this study are excellent (cf. Table 1), while the enantioselectivity is very good and significantly better than any other cluster-based catalytic system,[10,11,19] especially in the case of reduction of tiglic acid by **1** or **2**.

In experiments where **1** and **3** were used as catalysts, approximately 70% of the specific catalyst could be recovered upon separation of products after a completed catalytic experiment; this is virtually a quantitative recovery of the catalyst/catalyst precursor when the small amount of cluster used (10 mg) is taken into consideration. Spectroscopic measurements (IR, $^1$H/$^{31}$P NMR, cf. Supporting Information) and mass spectrometry (and, in the case of **1**, X-ray crystallography) showed no signs of changes in the clusters after catalytic runs. In order to assess whether colloidal material is formed during the reaction and may be responsible for the catalytic effect, a mercury poisoning test[20] was performed. Hydrogenation of substrate **5** by clusters **1** and **3** was undertaken in the presence of an approximate 2000-fold excess of liquid mercury. The addition of Hg(0) led to moderately *improved* catalytic results with complete conversion and selectivity in the hydrogenation and an increase of the enantiomeric excess by 4−5 percentage units (cf. Table 1, entries 1 vs 5 and 10 vs 14). While these results may lie within the margins of experimental error, we have consistently detected a discrepancy toward improved conversion/selectivity/enantioselectivity when Hg(0) is present in catalytic runs involving **1**, **3**, and closely related clusters. Our interpretation of these results is that fragmentation of the cluster and formation of colloids does take place during the catalysis under the conditions used, but that the catalytic effect of this colloidal material is of minor importance.

It is reasonable to assume that any hydrogenation by colloids formed in these experiments results in very little or no stereoselective discrimination. On the other hand, the formation of mononuclear chiral diphosphine complexes might lead to effective and enantioselective hydrogenation. It is possible that Noyori-type catalysts of the general formula [Ru(II)(P−P)($O_2$-CR)$_2$][21] may be formed, as all "ingredients" for the formation of such a complex are present in the reaction systems (although oxidation of the metal is required). In order to investigate this possiblility, we prepared the ruthenium complexes [Ru(II)(*R*-BINAP)(OAc)$_2$] (**10**) (*R*-BINAP = (*R*)-(+)-2,2′-bis(diphenylphosphino)-1−1′-binaphthyl) and [Ru(II)(*R*-W001)(OAc)$_2$] (**11**) using the synthetic route described by Noyori et al.[21] The hydrogenation of tiglic acid by **10** and **11** was studied under the same reaction conditions as for the cluster-based catalysts. While **10** and **11** both showed a high activity with varying amounts of byproducts, the enantioselectivities obtained for these mononuclear catalysts (cf. Table 1, entries **16** and **17**) were significantly different from those obtained when the tetraruthenium clusters with the same diphosphine ligands were used in the catalytic systems. Catalyst **10** yielded an enantiomeric excess of 68% (*R*), exceeding the ee's reported for [$H_4Ru_4(CO)_{10}$(*S*-BINAP)] under similar reaction conditions by more than 40 percentage units. [Reaction conditions used for the cluster (cf. ref 10b): temperature = 100 °C; duration = 93 h; solvent =20 mL (ethanol/toluene, 1:1 v/v); pressure $H_2$ = 130 bar; molar ratio substrate/catalyst = 2000 mol/mol. Results obtained: conversion = 90.5%, optical purity = 28.5% (*R*).] On the other hand, **11** was found to be a considerably poorer catalyst than **1** (and **10**) under the conditions used, yielding an enantiomeric excess of 30% (*S*). These results indicate that mononuclear Noyori-type catalysts are not the catalytically active species in the cluster-based reactions; however, it should be noted that the possibility still exists that other mononuclear complexes, e.g., [Ru(CO)$_3$(P−P)] (cf. ref 3), are the active catalysts.

Our experimental setup has precluded sampling during the reaction, but in an attempt to establish turnover number (TON) for catalyst **1** a molar substrate:catalyst:Hg ratio of 10000:1:16000 was used, and the reaction was heated for 96 h. $^1$H/$^{31}$P NMR and IR analyses showed no other cluster species than **1** present in the reaction mixture upon completion of the experiment. The substrate/product ratios were assessed by $^1$H NMR and gave the following result: tiglic acid (0.5%), 2-methylbutanoic acid (87%), and ethyl 2-methylbutanoate (12.5%); the

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TON can thus be considered to be >9900. The enantiomeric excess of the isolated product 2-methylbutyric acid was determined to 87% (*S*). The results from this experiment show that the enantioselectivity in this catalytic system is retained even when quite high substrate/catalyst ratios are used (cf. entry 5, Table 1).

In the cluster-based hydrogenation effected by $[H_4Ru_4(CO)_{10}(\mu\text{-}1,2\text{-}(R,R \text{ or } S,S)\text{-bdpp})]$,[11] it was found that these clusters, which contain a bridging diphosphine ligand, were converted to the analogous clusters $[H_4Ru_4(CO)_{10}(1,1\text{-}(R,R \text{ or } S,S)\text{-bdpp})]$ (chelating diphosphine) during the catalytic reactions. The opposite interconversion is observed during catalytic experiments with clusters **2** and **4**; that is, the "chelating" isomers **2** and **4** are converted to the analogous "bridging" isomers **1** and **3.** No remnants of **2** or **4** could be detected after the catalytic reactions, but when **2** was used as a starting material, a second cluster—tentatively identified as $[H_4Ru_4(CO)_8(W001)_2]$—could be detected in addition to **1**. It thus appears unlikely that **2** and **4** are active catalysts for the hydrogenation reactions.

It is evident that in these catalytic systems the coordinated chiral ligand strongly affects the outcome of hydrogenation, in terms of both conversion and enantioselectivity, and that cluster-based catalytic systems can give enantioselectivities approaching (but not yet matching) those of mononuclear catalysts. We have noted that for the type of tetraruthenium clusters discussed here there appears to be a correlation between the barrier to hydride fluxionality and enantioselectivity in hydrogenation, with a high barrier resulting in good enantioselectivity. Thus, while hydrides in derivatives of $[H_4Ru_4(CO)_{12}]$ usually are fluxional at room temperature, the hydrides of $[H_4Ru_4(CO)_{10}(P-P)]$ (P−P = 1,1-bdpp; $\mu$-1,2-W001; $\mu$-1,2-W002) exhibit sharp resonances in the $^1$H NMR spectra at ambient temperature. Similar $[H_4Ru_4(CO)_{10}(\text{chiral diphosphine})]$ clusters that exhibit complete hydride fluxionality at room temperature, e.g., $[H_4Ru_4(CO)_{10}(\mu\text{-}1,2\text{-}(R,R)\text{-dipamp})]$, give practically no enantioselectivity and have low turnover frequency in the hydrogenation of tiglic acid.[16] The hydride resonances in the NMR spectrum of **1** were assigned on the basis of COSY, EXSY, and $^{31}$P spectra, and the fluxional behavior of the hydrides under high temperature and an $H_2$ pressure of 20 bar was examined by $^1$H NMR spectroscopy in $d_8$-toluene. It was found that three hydrides become fluxional on the NMR time scale as the temperature is raised, while, somewhat surprisingly, the fourth hydride, which bridges the Ru−Ru edge to which both phosphine moieties are coordinated, remains fixed even at a temperature of 80 °C, and in a separate experiment it was found that the above-mentioned hydride remains fixed on the NMR time scale at 110 °C in $d_8$-toluene under ambient atmosphere and pressure (Figure 4). It is possible that the transfer of this (fixed) hydride to the substrate is the origin of the enantioselectivity in the reaction/catalysis. Furthermore, high-pressure IR spectroscopy of **1** in a toluene/ethanol mixture or cyclohexane under 50 bar of $H_2$ pressure and temperatures varying from ambient temperature to 100 °C revealed no changes in the spectrum.[22]

The above-mentioned observations suggest that in the case of **1** and **3** it is the cluster that is the active catalyst during the hydrogenation reaction or that the starting cluster is the immediate precursor to a cluster catalyst and that the starting cluster is re-formed (quantitatively) after completion of the reaction. Clusters **2** and **4** appear to be precursors to the active catalysts. While the only unambiguous proof of a cluster being an active catalyst may be asymmetric catalysis effected by a cluster that is formed from achiral building blocks,[23] a kinetic study by Doi et al.[24] has shown that the parent cluster $[H_4Ru_4(CO)_{12}]$ hydrogenates ethene in heptane at 72 °C, and the investigation provides compelling evidence for the cluster being the catalyst; the evidence includes first order-dependence of the catalytic rate on the cluster concentration and the absence of any lag phase in the catalytic hydrogenation. Catalytic cycles/reaction schemes for hydrogenation of alkenes by $[H_4Ru_4(CO)_{12}]$ and its phosphine derivatives have been proposed.[11,24,25] The suppression of catalysis by addition of CO[24,25] suggests initial decarbonylation of the cluster and formation of $[H_4Ru_4(CO)_{11}(\text{alkene})]$ and, subsequently, $[H_3Ru_4(CO)_{11}(\text{alkyl})]$ species.[11,24] We have attempted catalytic reduction of tiglic acid by **1** under the conditions used by Doi et al.[24] but failed to detect any conversion after 14 h.

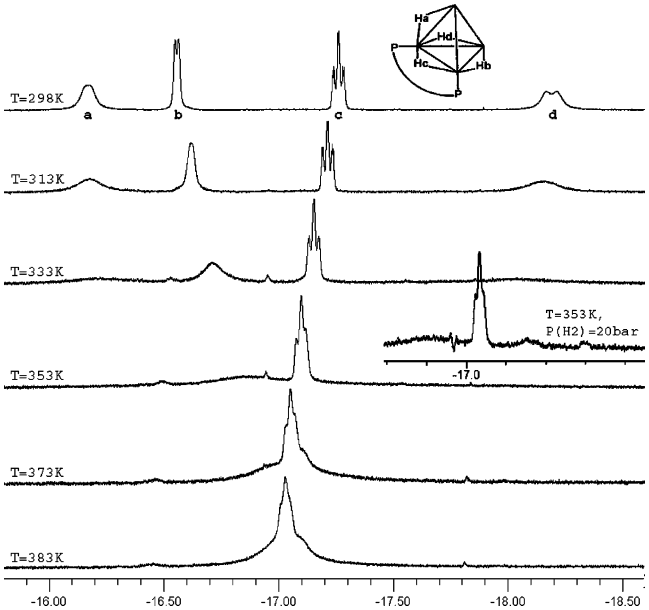


**Figure 4.** $^1$H NMR spectra of the hydride region of **1** recorded at 298 (top) and 383 K (bottom). Inset: $^1$H NMR spectrum of the hydride region of **1** recorded at 353 K under 20 bar of $H_2$ pressure.

The excellent conversion rates, high selectivities, and relatively good enantioselectivities that have been found for the present tetraruthenium cluster-based catalytic systems make clusters **1**−**4** viable catalysts/catalyst precursors for asymmetric hydrogenation of α-unsaturated carboxylic acids. Advantages of using these cluster-based catalytic systems include the facts that the clusters are stable with respect to both high temperatures and exposure to air/oxygen and that low catalyst/substrate ratios may be used.

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**Supporting Information Available:** Synthetic procedures and analytical data for **1**−**4**. IR, $^1$H and $^{31}$P NMR, and mass spectra for complex **1** before and after catalytic experiments. Experimental details for the catalytic investigations. This material is available free of charge via the Internet at http://pubs.acs.org.

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