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LETTERS

Bidentate planar chiral η^6-arene tricarbonyl chromium(0) complexes: ligands for catalytic asymmetric alkene hydrosilylation

Immo Weber and Graham B. Jones*

Bioorganic and Medicinal Chemistry Laboratories, Department of Chemistry, Northeastern University, Boston, MA 02115, USA

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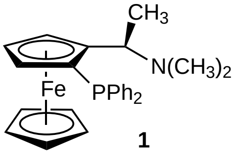
Abstract—S_EAr-type reactions of various heterocycles with *ortho*-substituted (1′*S*,*P*)-tricarbonyl[(1-chloroethyl)-η^6-benzene]chromium(0) derivatives lead to a family of novel planar chiral bidentate and pseudo-bidentate ligands. Two members of this family (1′*S*,*P*)-2-[1′-tricarbonyl-η^6-((2″-*P*,*P*-diphenylphosphino)phenyl)-chromium(0))ethyl] furan and thiophene show high activity and enantioselectivity in the Pd-catalyzed hydrosilylation of styrenes. © 2001 Published by Elsevier Science Ltd.

The catalytic hydrosilylation of alkenes with trichlorosilane provides a powerful method for the in situ conversion of olefins to alcohols via oxidation of the alkyltrichlorosilane, complementing hydroboration protocols.[1] Of significance, Pd-catalyzed hydrosilylation reactions require much lower catalyst loadings (ca. 0.01–0.1 mol%) than conventional Rh-catalyzed hydroborations (ca. 1.0 mol%). The first enantioselective Pd-catalyzed hydrosilylation of olefins was reported by Hayashi using chiral ferrocenyl phosphine ligand **1**.[2] Further improvements were obtained with the less basic analogue **2**,[3] and the substituted heterocycle **3**.[4] The use of ferrocenyl catalysts in asymmetric synthesis is now a maturing field,[5] and has prompted the search for additional planar chiral templates including analogous η^6-arene chromium(0) derivatives.[6] A prerequisite for such templates in Pd-catalyzed hydrosilylations is the presence of one strongly coordinating and one weakly coordinating functional group, dissociation of the labile group providing the necessary coordination site for the substrate olefin. Viable templates include **4** and **5**, where the coordinative ability of heteroatoms (X, Y) are modulated by the tricarbonyl chromium tripod. A number of such ligands have been synthesized, though application in asymmetric hydrosilylation has not been reported.[7] Although numerous ligand candidates could be envisioned, the principle drawback lies in a lack of suitable chiral pool templates, which thus requires either resolution or diastereoselective synthesis. An attractive possibility for the latter lies in the use of the complex **6**, derived from (*S*)-phenethylamine, which is known to undergo highly selective *O*-metallation.[8] Given our ongoing interest in the development of related η^6-arene chromium(0)-based catalysts,[9] we therefore elected to develop a series of bidentate planar chiral complexes containing heterocyclic pendant groups. Given the flexibility for heterocycle functionalization, such systems would be expected to offer considerable advantages for subsequent and systematic ligand optimization.



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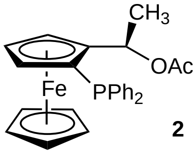

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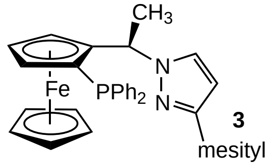

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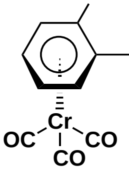

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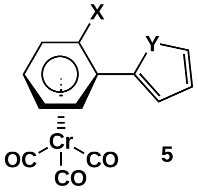

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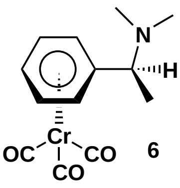

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* Corresponding author.

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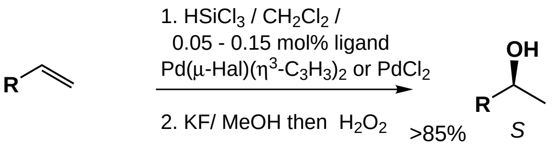
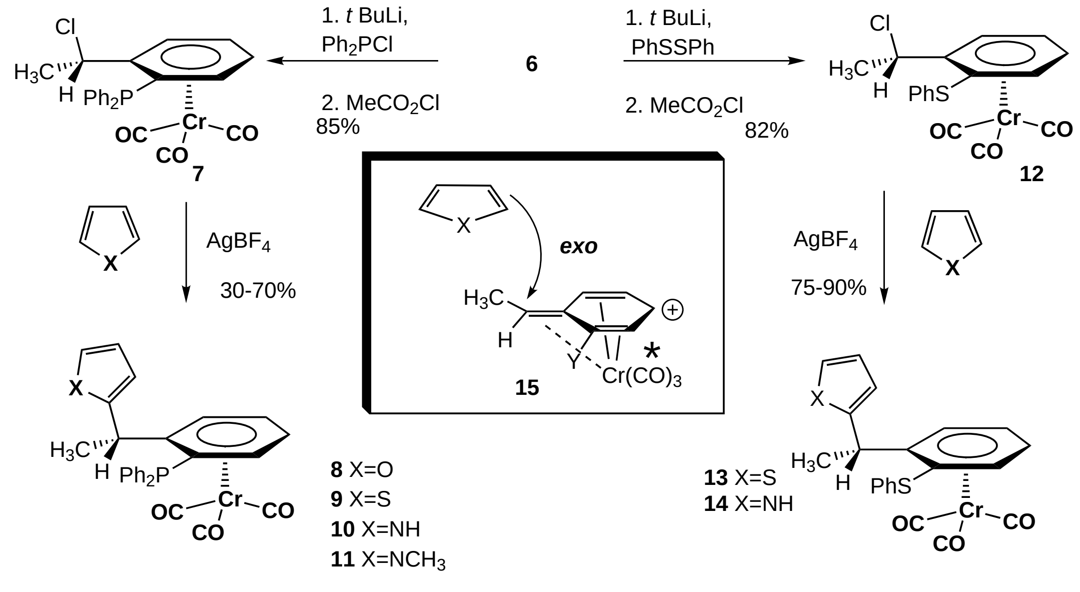
Synthesis commenced from **6**, which was subjected to diastereoselective metallation, quenched with the appropriate electrophile, followed by chlorination, to give **7** or **12**, respectively (Scheme 1).[10] Silver mediated coupling of **7** with furan, thiophene, pyrrole, or *N*-methyl pyrrole gave products **8** through **11**, respectively. Alternatively, thiophenyl substrate **12** gave adducts **13** and **14** in good yield. Of significance, the heterocycle adducts were formed as single diastereomers, retention of stereochemistry (precedented on the basis of *exo* attack on the intermediate benzylidene **15**[11]) confirmed in the case of **8** by X-ray crystallography.[12] While many applications of these ligands could be envisioned, we elected to study the Pd-catalyzed hydrosilylation of olefins as a test case since this reaction has yet to be successfully addressed with a planar chiral η^6-arene chromium-based catalyst.

Hydrosilylation was conducted using a variety of substituted styrene substrates (Scheme 2). Reaction end points were determined by NMR (typically involving incubation for up to 48 h), then followed by in situ addition of fluoride and immediate oxidation, which in each case gave good yields of the corresponding (*S*) product alcohols (85–90% isolated yields on a 10 mmol scale), with moderate to high enantioselectivity (Table 1).

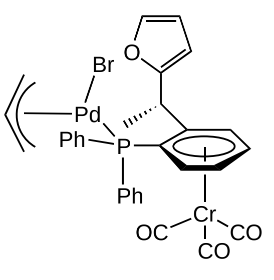
As can be seen, a temperature dependence for enantioselectivity exists, providing high levels of control at −50°C (entry 7) though poor solubility precludes reaction below this temperature. No discernable electronic trend emerged from the substrates examined, though it is interesting to note that the major product enantiomer was *S* with all substrates examined, in contrast to results obtained with related catalysts.[4] In the absence of solvent, catalysts derived from **8** and **9** also proved to be extremely *reactive*. At ambient temperature and with a catalyst loading of only 0.04 mol% the hydrosilylation of styrene is complete within 2 min, equivalent to a turnover rate of 60,000 h^{-1} yet still returning a product e.e. of >50% (entry 19). Results were identical either using in situ formation of the allyl–Pd complex, or with a pre-formed admix, e.g. **16**, which proved more practical on a smaller scale. For comparison ligand **17** was prepared from **7** (MeOH, THF), and its poor selectivity (entry 20) supports our use of the heterocyclic template. Based on the ready availability of **8** and **9**, coupled with their promising activity (Table 1), we believe that this new class of ligand will be of broad interest. It is well precedented that modifications on the phosphine groups of related catalysts results in strong improvements in enantioselectivity.[4] This, coupled with the potential for introduction of modulating substituents on the heterocycle ring itself may give rise to highly discriminating catalysts for use in numerous asymmetric transformations.



Scheme 2. Catalytic hydrosilylation–oxidation of alkenes.



Scheme 1. Preparation of bidentate planar chiral η^6-arene tricarbonyl chromium(0) ligands.



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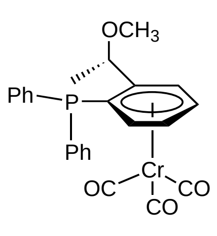

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Table 1. Catalytic enantioselective hydrosilylation using planar chiral ligands[a]

Entry	Ligand	Pd species	Equiv.	R	Temp. (°C)	% e.e.[b]
1	**8**	$PdCl(\eta^3\text{-}C_3H_5)$	0.05	C_6H_5	25	47
2	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.05	C_6H_5	−25	86
3	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.25	C_6H_5	−40	87
4	**9**	$PdCl_2$	0.05	C_6H_5	−25	82
5	**9**	$PdCl_2$	0.25	C_6H_5	−40	87
6	**9**	$PdCl_2$	0.25	C_6H_5	−50	87
7	**9**	$PdBr(\eta^3\text{-}C_3H_5)$	0.25	C_6H_5	−50	**92**
8	**11**	$PdBr(\eta^3\text{-}C_3H_5)$	0.05	C_6H_5	−40	65
9	**13**	$PdBr(\eta^3\text{-}C_3H_5)$	0.05	C_6H_5	25	No reaction
10	**14**	$PdBr(\eta^3\text{-}C_3H_5)$	0.05	C_6H_5	25	No reaction
11	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.15	$p\text{-}CH_3(C_6H_4)$	−25	83
12	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.10	$p\text{-}CH_3O(C_6H_4)$	−25	77
13	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.05	$p\text{-}F(C_6H_4)$	−25	82
14	**9**	$PdCl_2$	0.10	$p\text{-}CH_3(C_6H_4)$	−25	77
15	**9**	$PdCl_2$	0.05	$p\text{-}F(C_6H_4)$	−25	76
16	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.05	$p\text{-}Cl(C_6H_4)$	−25	83
17	**9**	$PdCl_2$	0.05	$p\text{-}Cl(C_6H_4)$	−25	73
18	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.25	$p\text{-}CF_3(C_6H_4)$	−25	86
19[c]	**8**	$PdBr(\eta^3\text{-}C_3H_5)$	0.04	C_6H_5	25	52
20	**17**	$PdCl(\eta^3\text{-}C_3H_5)$	0.05	C_6H_5	25	17

[a] Reactions conducted in CH_2Cl_2 or $CDCl_3$ for 48 h. Product configuration (*S*) determined by optical rotation.

[b] Determined by GC [Supelco β-DEX].

[c] Reacted in the absence of solvent for 2 min.

In summary a new class of heterocyclic planar chiral catalysts has been developed, and applied to the first example of highly enantioselective alkene hydrosilylation using a η^6-arene chromium catalyst. The scope and versatility of this family of catalysts will be reported in due course.

Acknowledgements

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12. Weber, I.; Krawiec, M.; Pennington, W. T.; Jones, G. B., manuscript in preparation. Compound **8**: yellow solid; mp 140–142°C; ^{13}C NMR (75 MHz, $CDCl_3$): δ 232.33 (*C*O), 155.79 (*C*(2)furyl), 140.98 (*C*(5)furyl), 134.96–133.07 (series of d, *C*(PPh_2)), 129.77–128.21 (series of d, *C*(PPh_2)), 120.22 (d, $J_{CP}=22.1$, *C*(2)-η^6-PhCr), 109.71 (*C*(4)furyl), 106.12 (*C*(3)furyl), 104.00 (d, $J_{CP}=22.1$, *C*(1)-η^6-PhCr), 97.3 (d, $J_{CP}=2.6$, *C*(3)-η^6-PhCr), 93.78 (*C*(6)-η^6-PhCr), 90.89 (*C*(4)-η^6-PhCr), 89.67 (*C*(5)-η^6-PhCr), 34.43 (d, $J_{CP}=24.4$, *C*H(CH_3)), 19.86 (CH(*C*H_3)); ^{31}P NMR (300 MHz, $CDCl_3$): −14.75 (s, 1P); $[\alpha]_D^{20}=+341.5$ (*c* 0.1, $CHCl_3$).