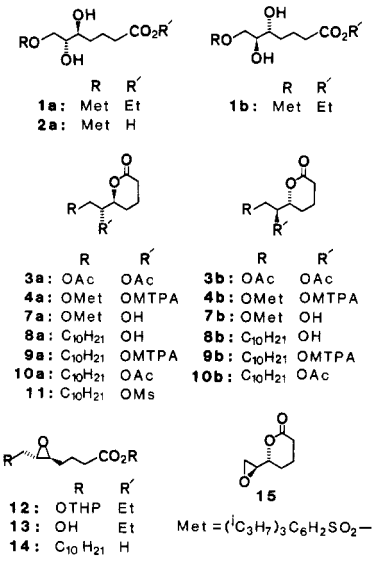
the isolated product had >98% ee, whereas the ee of product derived from the unprotected alcohol **13** was found to be only 68%. It is evident then that anhydrous conditions are essential in order to eliminate side reactions and to obtain high enantiomeric purity. Consequently the acid **2a**[10] was treated with freshly prepared NaOEt in anhydrous EtOH for 18 h, and the product was acetylated to afford the diacetate **3b** [88% yield, $[\alpha]_D$ −55° (*c* 0.9, $CHCl_3$)] whose optical purity was found to be >98% ee. Thus a simple procedure for effecting the inversion of configuration of two contiguous carbinol centers was achieved in high yield with high optical purity. This allows a direct access to the antipode of LTA_4[11] and a general entry to the synthesis of lipoxin A family of compounds in which the stereochemistry of the diol at C-5 and C-6 is critical for biosynthetic studies.[17]



This new methodology was also found to be useful for the synthesis of the oviposition attractant pheromone of the mosquito *Culex pipiens fatigans*, **10b**, and its enantiomer, **10a**,[12] from the same chiral starting material. Hydrolysis of the acetate **3b** with K_2CO_3/EtOH followed by sulfonylation (MetCl/pyr/0 °C) gave **1b** (91% yield). Heating this ester in THF containing 1 M HCl caused hydrolysis of the ester, which upon evaporation of the solvent lactonized to yield the lactone **7b** [78% yield, mp 131–132 °C $[\alpha]_D$ −30° (*c* 1, $CHCl_3$)]. Treatment of lactone **7b** with NaH in THF containing a catalytic amount of DMSO gave the epoxy lactone **15** [90% yield, $[\alpha]_D$ −41° (*c* 1, $CHCl_3$)] as an oil. Selective opening of the epoxide with $H_{21}C_{10}MgBr$ was achieved with 10 mol % of Li_2CuCl_4 as catalyst (THF, −78 °C, 20 min)[13] to afford the alcohol **8b** in 75% yield, which possessed similar physical data to that reported in the literature.[14] Finally, acetylation (Ac_2O/DMAP/CH_2Cl_2) gave the natural product **10b** in quantitative yield.[15,16]

Thus far the strategy involved inverting all the stereocenters of the starting material **2a** to give its enantiomer, which was then further elaborated to give the natural product. An alternative strategy would be to invert the two contiguous asymetric centers later in the synthetic sequence after all the structual elements of the desired compound are in place, for example the conversion of **8a** to **8b**. This variant of the approach would have the added attraction that both enantiomers **10a** and **10b** can be prepared in fewer steps. This would be particularly useful in cases where long syntheses are involved. Following the latter strategy, it was anticipated that mesylation of the masked vicinal diol **8a** followed by saponification should lead directly to its enantiomer **8b** via the epoxide **14** with carboxylate opening at C-5 of **14** competing favorably with random opening by hydroxide anion (cf. saponification of **12**).[9,17] Indeed, when the mesylate **11** was treated with aqueous NaOH followed by acidification with AcOH, **8b** was obtained in 82% yield and 98% ee.[18] Acetylation of the alcholol **8b** gave the natural product as before.[19]

In summary, the chemistry described represents a convenient way to invert the stereochemistry of vicinal hydroxyl groups in a diol and triol chain, thus affording the opposite enantiomer. Further studies on the scope of this methodology, including the effect of additional hydroxymethyl units, and the relative stereochemistry of hydroxy groups are in progress.

Acknowledgment. We thank Dr. Michael Bernstein for ^{19}F NMR measurements.

Supplementary Material Available: Experimental data for compounds **2a**, **3**, **4a,b**, **8**, **9a,b**, **10**, **11**, and **15** (2 pages). Ordering information is given on any current masthead page.

(9) Noyori described a similar reaction: Suzuki, M.; Morita, Y.; Yanakisawa, A.; Noyori, R. *J. Am. Chem. Soc.* **1986**, *108*, 5021.

(10) The acid **2a** was prepared by a slight variation of our published method[3] with $Ph_3P{=}CHCO_2CH_2Ph$ followed by hydrogenolysis.

(11) Compound **1b** was converted to the enantiomer of epoxide **13**, $[\alpha]_D$ +34° (*c* 0.9, $CDCl_3$) [lit.[3] $[\alpha]_D$ +35° (*c* 2.4, $CDCl_3$)], which has been converted (+)-LTA_4 methyl ester.[3]

(12) (a) Laurence, B. R.; Pickett. J. A. *J. Chem. Soc., Chem. Commun.* **1982**, *59*. (b) Mori, K.; Otsuka, T. *Tetrahedron Lett.* **1983**, *29*, 3267. (c) Quo-qiang, L.; Hai-jian, X.; Bi-chi, W. *Tetrahedron Lett.* **1985**, *26*, 1233. (d) Fuganti, C.; Grasselli, P.; Servi, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1285.

(13) The use of other catalysts required longer time and higher temperature and gave lower yields.

(14) Literature data:[12b] mp 67–68 °C, $[\alpha]^{20}_D$ −12.5° (*c* 5.4, $CHCl_3$); observed mp 68–69 °C, $[\alpha]^{20}_D$ −13.9° (*c* 0.4, $CHCl_3$).

(15) Literature data:[12b,c] $[\alpha]_D$ −38.5° (*c* 0.51, $CHCl_3$); observed $[\alpha]_D$ −38.1° (*c* 0.4, $CHCl_3$).

(16) The synthesis of the enantiomer of the natural product **10a** was achieved in a similar fashion by starting from the acid **2a** to yield **10a**, $[\alpha]_D$ +38.0° (*c* 1, $CHCl_3$) [lit.[12b,c] $[\alpha]_D$ +38.4° (*c* 1.41, $CHCl_3$)].

(17) Adams, J.; Fitzsimmons, B. J.; Girard, Y.; Leblanc, Y.; Evans, J. F.; Rokach, J. *J. Am. Chem. Soc.* **1985**, *107*, 464.

(18) ^1H NMR ($CDCl_3$) for OMe signals of (−)-MTPA derivatives: (**9b**) δ 3.51; (**9a**) δ 3.57. ^{19}F NMR ($CDCl_3$): (**9b**) δ 4.63; (**9a**) δ 4.69.

(19) $[\alpha]_D$ −37.5° (*c* 0.8, $CHCl_3$).

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Novel Amide-Directed Hydrocarbonylation and Double Carbonylation of *N*-Allylamides

Summary: The rhodium-catalyzed hydroformylation and palladium-catalyzed hydroesterification of *N*-allylamides give isoaldehyde (**1**) and isoester (**5**), respectively, with good regioselectivity through chelation control while the rhodium- and $Co_2Rh_2(CO)_{12}$-catalyzed reactions of an *N*-methallylamide give a novel double carbonylation product (**10**) and a pyrrolidine (**11**), respectively, with excellent selectivity.

Sir: Chelation-controlled regioselective and stereoselective reactions have extensively been studied in the field of

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Table I. Hydrocarbonylation of *N*-Allylacetamide[a]

entry	catalyst (mol %)	yield,[b] %	products ratio[b] 1	2	3	4
1	$[Rh(dppb)(NBD)]ClO_4$[c] (1.0)	78	71		5	24
2	$RhCl(PPh_3)_3$ (1.0)	80	65		7	28
3	$RhCl(CO)(PPh_3)_3$ (1.0)	79	66		7	27
4	$HRh(CO)(PPh_3)_3$ (1.0)	76	63	11	13	13
5	$Rh_4(CO)_{12}$ (0.25)	78	79	6	6	9
6	$Co_2Rh_2(CO)_{12}$ (0.5)	80	79		21	
7[d]		80	82		18	

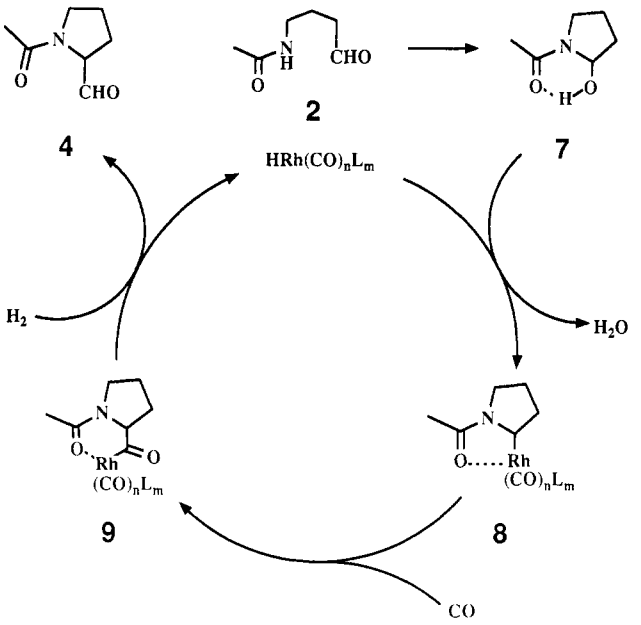
[a] All reactions were run with use of a Pyrex reaction vessel (50 mL) in a stainless steel autoclave (300 mL) with 1.50 mmol of *N*-allylacetamide in THF (3.6 mL) at 80 °C and 1200 psi of carbon monoxide and hydrogen (CO/H_2 = 1) for 18 h unless otherwise noted. The products were isolated by a column chromatography on silica gel and identified by ^1H and ^{13}C NMR, IR, and mass spectroscopies. [b] Determined by ^1H NMR and GLC analyses. [c] dppb = 1,4-bis(diphenylphosphino)butane. NBD = norbornadiene. [d] The reaction was carried out with 1.0 mol % of $Co_2Rh_2(CO)_{12}$ at 60 °C.

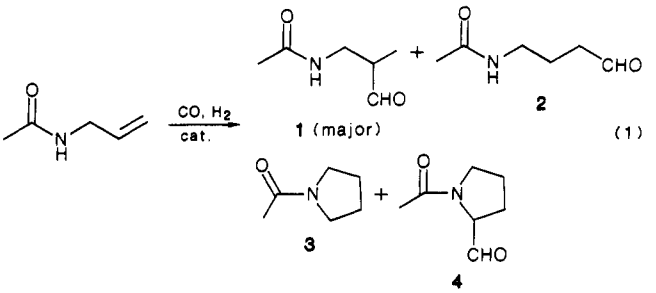
organometallics for organic synthesis. In catalysis field, the asymmetric hydrogenation of dehydroamino acids and dehydropeptides,[1] the asymmetric epoxidation of allylic alcohols,[2] and the asymmetric isomerization of allylamines[3] are excellent examples of the chelation-controlled methodologies to attain high stereoselectivity. However, to our best knowledge, no systematic studies have been performed on the application of chelation control to selective carbonylations. We describe here our preliminary results on the successful chelation control in hydrocarbonylations of *N*-allylamides catalyzed by rhodium, palladium, and Co–Rh mixed metal complexes and also other novel carbonylation reactions such as double carbonylation, which are found during the study.

The hydroformylation of *N*-allylacetamide was carried out with a variety of rhodium catalysts, i.e., $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $HRh(CO)(PPh_3)_3$,[4] $[Rh(dppb)(NBD)]ClO_4$, $Rh_4(CO)_{12}$, and a Co–Rh mixed metal complex, $Co_2Rh_2(CO)_{12}$. Typical results are summarized in Table I.

As Table I shows, the major product of the reaction is isoaldehyde (2-methyl-3-(acetylamino)propanal) (**1**) and the minor products are *n*-aldehyde (4-(acetylamino)butanal) (**2**), 1-acetylpyrrolidine (**3**), and/or 1-acetyl-2-formylpyrrolidine (**4**), which is the product of novel sequential double carbonylation (eq 1).

Scheme I. Proposed Mechanism for Double Carbonylation





(1)

It is well known that the hydroformylation of 1-alkenes catalyzed by rhodium complexes gives *n*-aldehyde as the predominant product, and the *n*-aldehyde selectivity is increased when phosphine ligands are introduced, i.e., the *n*/iso ratio is in the range of 5–10 for phosphine–rhodium complexes and 1.1–2 for rhodium carbonyls.[5] Accordingly, good isoselectivities observed in the present system are *opposite* to those for usual 1-alkenes. It is noteworthy that the Co–Rh mixed metal catalyst, $Co_2Rh_2(CO)_{12}$,[6] brings

(1) E.g., (a) Halpern, J. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, pp 41–69 and references cited therein. (b) Halpern, J. *Science (Washington, D.C.)* **1982**, *217*, 401 and references cited therein. (c) Brown, J. M.; Chaloner, P. A. *J. Am. Chem. Soc.* **1980**, *102*, 3040. (d) Ojima, I.; Kogure, T.; Yoda, N. *J. Org. Chem.* **1980**, *45*, 4728. For peptides, (e) Ojima, I.; Yoda, N.; Yatabe, M.; Tanaka, M.; Kogure, T. *Tetrahedron* **1984**, *40*, 1255 and references cited therein. (f) Meyer, D.; Poulin, J.-P.; Kagan, H. B.; Levine-Pinto, H.; Morgat, J. L. *J. Org. Chem.* **1980**, *45*, 4680. (g) Onuma, K.; Ito, T.; Nakamura, A. *Chem. Lett.* **1980**, 481. (h) Kleeman, A.; Martens, J.; Samson, M.; Bergstein, W. *Synthesis* **1981**, 740. For hydroxyl-directed stereoselective hydrogenation, see: (i) Evans, D. A.; Morrissey, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3866. (j) Brown, J. M.; Hall, S. A. *Tetrahedron Lett.* **1984**, *25*, 1393.

(2) E.g., (a) Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, pp 247–308 and references cited therein. (b) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.

(3) E.g., (a) Otsuka, S.; Tani, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, pp 171–191 and references therein. (b) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208. (c) Tani, K.; Yamagata, T.; Otsuka, S.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T. Takaya, H.; Miyashita, A.; Noyori, R. *J. Chem. Soc., Chem. Commun.* **1982**, 600. (d) Tani, K.; Yamagata, T.; Tatsuno, Y.; Yamagata, Y.; Tomita, K.; Akutagawa, S.; Kumobayashi, H; Otsuka, S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 217.

(4) Becker, Eisenstadt, and Stille reported the hydroformylation of *N*-allylacetamide catalyzed by $HRh(CO)(PPh_3)_3$ at 40 °C and 500 psi (CO/H_2 = 1), which gave the isoaldehyde (**1**) and *N*-acetyl-2-pyrroline with a 54:46 ratio. See: Becker, Y.; Eisenstadt, A.; Stille, J. K. *J. Org. Chem.* **1980**, *45*, 2145. As Table I shows, we observed different selectivities and products under our reaction conditions, viz., the formation of *N*-acetyl-2-pyrroline was not observed at all. Although triphenylphosphine–rhodium complexes did not give good selectivities in our cases either, it is suggested that the chelation-controlled hydroformylation includes rather complicated kinetic as well as thermodynamic factors, which should be clarified in further studies.

(5) Cornils, B. In *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; pp 1–225 and references cited therein.

(6) It has been shown that $Co_2Rh_2(CO)_{12}$ is a precursor of $CoRh(CO)_7$, which may well be the active catalyst under hydroformylation conditions.[8] The rhodium moiety of $CoRh(CO)_7$ is considered to be the active site in its catalysis.[8a]

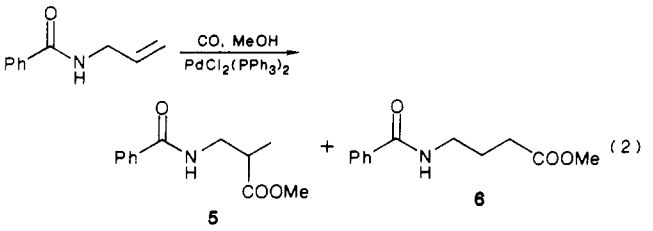
Table II. Hydrocarbonylation of *N*-(2-Methyl-2-propenyl)benzamide[a]

entry	catalyst (mol %)	CO (psi)	H_2 (psi)	yield,[b] %	products ratio[b] 10	11	12
1	[Rh(dppb)(NBD)]ClO_4[c] (1.0)	600	600	94	62	27	11
2		1500	300	90	87		13
3[d]		1700	150	87	>99.5		
4	$RhCl(PPh_3)_3$ (1.0)	600	600	85	54	46	
5		1500	300	91	82	7	11
6	$HRh(CO)(PPh_3)_3$ (1.0)	600	600	93	48	13	39[e]
7	$Rh_4(CO)_{12}$ (0.25)	600	600	95	46	20	34[f]
8		600	200	87			100[g]
9	$Co_2Rh_2(CO)_{12}$ (0.5)	600	600	83	2	98	
10		300	900	85	0	100	

[a] All reactions were run with use of a Pyrex reaction vessel (50 mL) in a stainless steel autoclave (300 mL) with 1.50 mmol of *N*-(2-methyl-2-propenyl)benzamide in THF (3.6 mL) at 100 °C for 18 h unless otherwise noted. The products were isolated by a column chromatography on silica gel and identified by ^1H and ^{13}C NMR and mass spectroscopies. [b] Determined by ^1H NMR and GLC analyses. [c] For the abbreviations for dppb and NBD, see the footnote *c* of Table I. [d] The reaction was run with 2.0 mol % of the catalyst for 71 h. [e] Containing 15% of *n*-aldehyde. [f] Containing 18% of *n*-aldehyde. [g] Containing 13% of *n*-aldehyde.

about substantially better product selectivity than other rhodium complexes (entries 6 and 7, Table I), which implies the synergistic effects of the mixed metal system.[7] The observed unique isoselectivity is best interpreted by taking into account the amide-directed chelation control of regioselectivity.[4]

Next, the hydroesterification of N-allylbenzamide with methanol catalyzed by $PdCl_2(PPh_3)_2$ was carried out at 80 °C and 1350 psi of carbon monoxide in benzene. The reaction gave isoester (*N*-benzoyl-α-methyl-β-alanine methyl ester; **5**) and *n*-ester (**6**) in 71% and 18% yields, respectively, i.e., iso/*n* = 4 (eq 2).

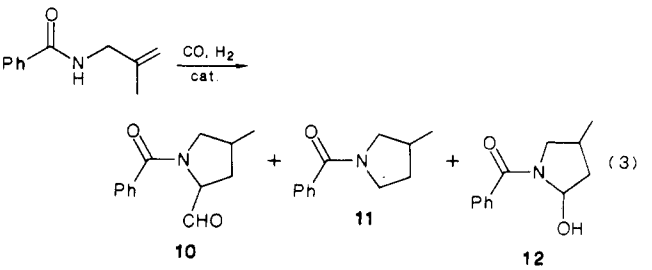


(2)

The result clearly indicates that an amide-directed chelation control is operative in the palladium complex catalyzed reaction as well.[10]

N-acetyl-2-formylpyrrolidine (**4**) obtained as a minor product in the rhodium-catalyzed reactions is formed through a new type of amidocarbonylation via a hemiamidal (**7**) arising from *n*-aldehyde (**2**) followed by the sequential formation of an alkyl–Rh complex (**8**) and an acyl–Rh complex (**9**) as shown in Scheme I. In the final reductive elimination step, the acyl–Rh bond is selectively cleaved by hydrogen, giving the aldehyde (**4**), which forms a sharp contrast to the cobalt-catalyzed amidocarbonylation, which gives the corresponding carboxylic acid exclusively.[9,12] This new type of amidocarbonylation reaction provides the first example of rhodium-catalyzed sequential double carbonylation. Since this novel reaction has a high potential as a synthetic method, we further studied the reaction to make it more selective.

We employed *N*-(2-methyl-2-propenyl)benzamide as a substrate. Results are summarized in Table II. Because of the 2-methyl group, initial hydroformylation became highly regioselective, and thus the reaction gave an expected 2-formylpyrrolidine (**10**) (1:1 diastereomer mixture) as the predominant product (almost exclusive in entry 3) together with a pyrrolidine (**11**) and a hemiamidal (**12**) in rhodium-catalyzed reactions (entries 1–8, Table II). In contrast to the rhodium-catalyzed reactions, the $Co_2Rh_2(CO)_{12}$-catalyzed reaction gave **11** with ≥98% selectivity (entry 9, 10, Table II), which clearly demonstrates the synergistic effects of the mixed metal system.[7] A control experiment clearly showed that the hemiamidal (**12**) was the precursor of **10** and **11**.[13]



(3)

The formation of **10** and **11** is rationalized by the formylation and the hydrogenolysis, respectively, of an al-

(7) The $Co_2(CO)_8$-catalyzed hydrocarbonylation was reported to give a mixture of three amino acids instead of amino aldehydes,[9] i.e., 2-(benzoylamino)butanoic acid (45%), 2-methyl-3-(benzoylamino)propanoic acid (8%), and *N*-benzoylproline (21%).[9a] The results of the rhodium complex catalyzed reactions are shown in Table I, which are not as selective as the $Co_2Rh_2(CO)_{12}$-catalyzed reaction. Thus, it is apparent there is a substantial synergistic effect when the two metals are combined.

(8) (a) Ojima, I.; Okabe, M.; Kato, K.; Kwon, H. B.; Horváth, I. T. *J. Am. Chem. Soc.* **1988**, *110*, 150. (b) Spindler, F.; Bor, G.; Pino, P. *J. Organomet. Chem.* **1981**, *213*, 303. For the isolation and characterization of $CoRh(CO)_7$, see: (c) Horváth, I. T.; Bor, G.; Garland, M.; Pino, P. *Organometallics* **1986**, *5*, 1441.

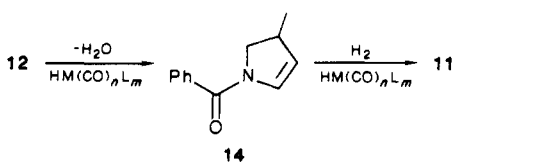
(9) (a) Sato, S. *Nippon Kagaku Zasshi* **1969**, *90*, 404. (b) Nishi, S.; Asada, S.; Izawa, K. *31st Symposium on Organometallic Chemistry*; Japan; Tsukuba, Oct 30–31, 1984; Abstracts B202.

(10) Since it has been shown that the hydroesterification of 1-alkenes gives *n*-ester as major products,[11] the observed isoselectivity forms a sharp contrast to the usual 1-alkene case.

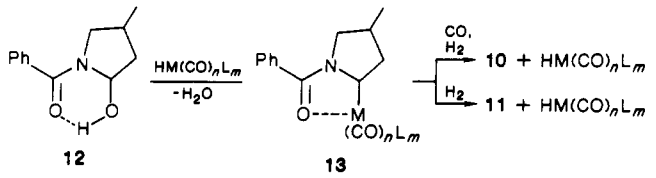
(11) (a) Mullen, A. In *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; pp 280–284. (b) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; pp 233–250.

(12) (a) Wakamatsu, H; Uda, J.; Yamakami, N. *Chem. Commun.* **1971**, 1540. (b) H. Wakamatsu, *Sekiyu Gakkai Shi* **1974**, *17*, 105.

(13) Controlled experiments using the isolated **12** (obtained almost exclusively in entry 8, Table II) revealed that **12** was actually converted to **10** quantitatively in the presence of CO (1500 psi), H_2 (300 psi), and $RhCl(PPh_3)_3$ (1 mol %) at 100 °C for 18 h and also found that **12** was completely transformed to **11** in the presence of CO (600 psi), H_2 (600 psi), and $Co_2Rh_2(CO)_{12}$ (1 mol %) at 100 °C for 18 h. An alternative route to **11** is through a hydridometal-promoted dehydration of **12** to 4-methyl-2-pyrroline (**14**) followed by the hydrogenation. This possibility cannot be excluded at this stage. A detailed mechanistic study is currently under way.



kyl–metal complex (13), which is generated from 12 (eq 4). Namely, the two reactions are competing processes: The carbon monoxide insertion is the predominant process for rhodium catalysts while the hydrogenolysis is almost exclusive for $Co_2Rh_2(CO)_{12}$.



12 13

M = Rh or CoRh (4)

Further studies on the mechanisms and applications of chelation-controlled hydrocarbonylations and novel double carbonylation (a new intramolecular amidocarbonylation) including asymmetric synthesis are in progress.

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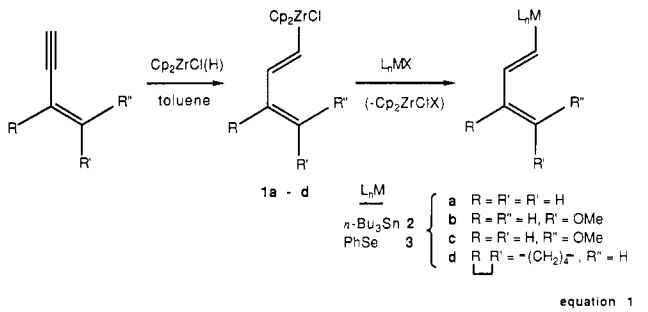
Transition Metal Dienyls in Organic Synthesis. Dienyl Transfer Reactions from Zirconium to Phosphorus and to Boron

Summary: The stereoselective preparation of 1,3-dienylphosphines and boranes, via a transfer process from zirconium, proceeds smoothly in excellent yields. The analogous reaction does not occur for silicon.

Sir: The preparation of heterosubstituted 1,3-dienes with oxygen-, nitrogen-, and sulfur-bonded functional groups has greatly enhanced the scope of the Diels–Alder reaction.[1] Not only do these substituents activate the diene, thereby extending the range of usable dienophiles, but they can also serve as focal points for subsequent synthetic elaboration.

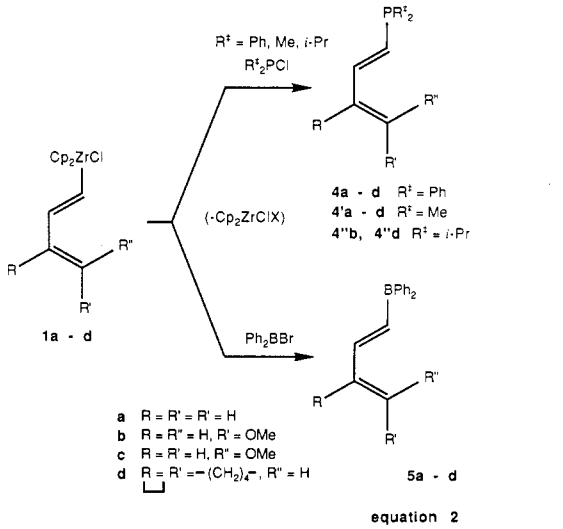
Our continuing interest in the preparation of transition metal and metalloid substituted 1,3-dienes has already provided examples of zirconium dienyls **1a–d prepared** by hydrozirconation of conjugated **enynes, which can be** subsequently used to generate tin[2] **(2a–d) and selenium**[3] **(3a–d)** dienes via transmetalation **(eq 1). In this paper,** we further establish the synthetic utility of **these zirconium** dienyl reagents in the general preparation of functionalized 1,3-dienes substituted in the 1-position with organophosphorus[4] and boron[5] derivatives. A similar strategy to



equation 1

generate main group heterocycles has been reported recently.[6]

Reaction of the zirconium dienyls **1a–d** with 1 equiv of either Ph_2PCl or Me_2PCl in toluene proceeds rapidly at room temperature to generate the corresponding stereoisomerically pure dienylphosphines **4a–d** and **4′a–d** (eq 2), respectively, in quantitative yields (by ^1H NMR spectroscopy). Isolated yields of 80–90% are easily obtained



equation 2

by extraction with hexanes and filtration through alumina (to remove Cp_2ZrCl_2). The analogous reaction with the more sterically crowded diisopropylchlorophosphine (i-Pr_2PCl) requires heating to 80 °C for several hours to generate the expected products (**4″b** and **4″d**) as mixtures of rotamers. A more detailed description of the latter reaction will appear in a future publication. The coordination chemistry of these new tertiary phosphines is now under investigation.[7]

The dienyl unit can also be transferred from zirconium to boron. The addition of diphenylbromoborane (Ph_2BBr) **to the zirconium reagents (in the dark**[8]**), in the same way as described for phosphorus, generates the corresponding diphenylboron-substituted dienes 5a–d stereoisomerically pure (by ^1H NMR spectroscopy) and in excellent isolated yields. While this two-step method may not be as convenient or as tolerant of other functional groups as the hydroboration of enynes,[5] there is the advantage that less hindered boranes can be used since the regiochemistry is**

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(2) Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537.
(3) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1987**, *52*, 2334.
(4) For the preparation of some 1,3-dienylphosphines (via a five-step process), see: Mathey, F.; Mercier, F.; Santini, C. *Inorg. Chem.* **1980**, *19*, 1813.
(5) For reports on the preparation of other 1,3-dienylboranes, see: (a) Clark, G. M.; Hancock, K. G.; Zweifel, G. *J. Am. Chem. Soc.* **1971**, *93*, 1308. (b) Vaultier, M.; Truchet, F.; Carboni, B.; Hoffmann, R. W.; Denne, I. *Tetrahedron Lett.* **1987**, *28*, 4169.
(6) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.
(7) Reference 4 contains examples of 1,3-dienylphosphines bound to Ni, Mn, and Fe.
(8) Compounds 5 appear to be photochemically labile, for photolysis of 1,3-dienylboranes see: Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1977**, *99*, 5192.

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