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P(*i*-PrNCH$_2$CH$_2$)$_3$N: An efficient nonionic catalyst for the regioselective Michael addition of a β,γ-unsaturated ester and a nitrile

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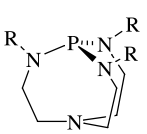
Abstract—Michael additions of a β,γ-unsaturated ester and a nitrile to a variety of α,β-unsaturated ketones can be effected with high regioselectivity and in good yields using P(*i*-PrNCH$_2$CH$_2$)$_3$N as a catalyst.

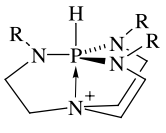
1. Introduction

Carbon–carbon bond formation is a fundamental transformation in organic chemistry. Addition of enolate anions to the β carbon of substrates such as α,β-unsaturated ketones and esters (Michael reaction) constitutes one of the most important approaches to effecting such transformations.[1,2] Initially, strong ionic bases were used for these reactions. However, a significant number of functional groups do not withstand basic conditions of this type thereby limiting the utilization of Michael addition in the synthesis of complex organic molecules. In modern synthetic methodologies, especially in those directed towards asymmetric Michael reactions, various metal complexes have been used. The long list of recent examples includes applications of copper,[3–11] iron,[12–16] nickel,[17–20] rhodium,[21–23] ruthenium,[14,24,25] palladium,[26,27] samarium ,[28,29] lithium,[30,31] gold,[32] lanthanum,[33] scandium,[34] and iridium[35] compounds complexed with various homochiral ligands. Furthermore, basic catalysts, among them, chiral azacrown ethers,[36,37] chiral quaternary ammonium salts[38–40] and hydroxides,[41] modified guanidine bases[42–45] and silica-supported imines,[46] have also been successfully employed for this purpose. Examples of self-catalytic Michael additions are also known.[47,48]

Proazaphosphatranes[49–52] **1a** and/or **1b** have been used as strong nonionic bases for the synthesis of α,β-unsaturated nitriles,[53] β-hydroxynitriles,[54] homoallylic alcohols,[55] β-nitroalkanols,[56] α,α-dicyano-α,β-olefins,[57] glutaronitriles,[58] benzofurans,[59] oxazolines,[60] *C*-alkyl esters,[61] pyrrols,[62] alkenes[63] and *trans*-epoxides from aryl aldehydes.[64] Other applications of proazaphosphatranes include trimerization of isocyanates,[65] the dehydrohalogenation of alkyl[66] and allylic[67] halides, the transesterification of esters,[68] deprotection of silylated[69] and acylated[68] esters and the silylation of hindered alcohols.[70]



1a R = *i*-Pr
1b R = Me



1aH$^+$ R = *i*-Pr
1bH$^+$ R = Me

In our continuing exploration of the synthetic utility of **1a**, we discovered its usefulness as a catalyst for the regioselective Michael reaction of a β,γ-unsaturated ester and a nitrile. Herein, we report on the synthesis of 1,4-Michael adducts by connection of the α carbon of a β,γ-unsaturated ester or a nitrile with the β carbon of α,β-unsaturated ketones while preserving the *trans*-configuration of the 1-propenyl group giving 1,4-α-*trans* adducts. No literature precedents for an analogous transformation were found. The reaction of dianions obtained from sorbic acid with Michael acceptors[71] is the only example that relates to the transformation described in this paper. However, mixtures of 1,4-α-and 1,4-γ-adducts were obtained.[71]

It has been pointed out by others that the symmetry of the carbanion produced from a β,γ-unsaturated donor precludes differentiation of 1,4-α- and 1,4-γ-adducts.[72]

Keywords: Michael addition; regioselective; pro-azaphosphatrane, catalyst.
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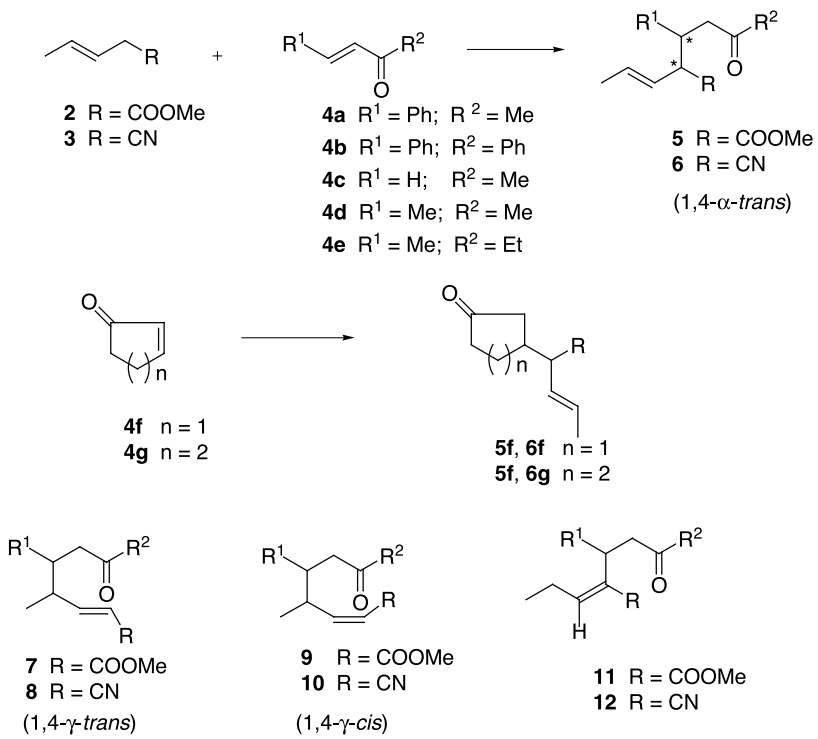
2. Results and discussion

At −60°C in the presence of 0.2–0.4 equiv. of **1a**, addition of the ester **2** in Scheme 1 to α,β-unsaturated ketones **4a**–**4g** in this scheme leads to mixtures of the corresponding diastereoisomeric ester **5** in good yields (Table 1) which were not optimized. Careful examination of ^{1}H NMR spectra of the crude reaction mixtures revealed (Table 1) the presence of small amounts of co-products in a few cases (for **4a** and **4b**) namely, diastereoisomeric 1,4-γ-*trans* adducts **7** and **8**, a single diastereoisomer of 1,4-γ-*cis* adducts **9** and **10** and *E*-isomers **11** and **12**.

No 1,2-adducts were detected. Isobutyronitrile was a substantially superior solvent to THF in this study, since in the latter solvent much more undesired co-products **7/8**, **9/10**, or **11/12** were formed, and under comparable conditions (−60°C, 2 h) significant amounts of starting materials were found unreacted. We also found it important to maintain the reaction mixture at −60°C (*vide infra*) and to quench the catalyst with an acid at this temperature. Purification of the crude products was effected by chromatography on a silica gel column and the following order of increasing polarity was observed in all cases: **11**, diastereoisomers of **5**, **7**.



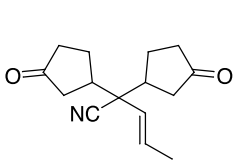
Scheme 1.

Table 1. Addition of β,γ-unsaturated ester **2** and nitrile **3** to α,β-unsaturated ketones effected by **1a**

Donor	Acceptor	**1a** (equiv.)	Time (h)	Adduct	Diastereomeric ratio[a]	Yield[b]
2	**4a**	0.2	2	**5a**	53:47	80[c]
	4b	0.2	3	**5b**	52:48	84[d]
	4c	0.2	3	**5c**		71[e,f]
	4d	0.2	3	**5d**	59:41	69[g]
	4e	0.3	3	**5e**	68:32	78[g,h]
	4f	0.4	3	**5f**	91:9	83[g]
	4g	0.4	3	**5g**	81:19	77[g]
3	**4d**	0.4	3	**6d**	52:48	68[i]
	4e	0.4	3	**6e**	52:48	72[j]

At −60°C in *i*-PrCN, a 1:1 molar donor/acceptor ratio was employed.
[a] Calculated from integration of ^{1}H NMR spectra.
[b] Chromatographic yields.
[c] **7a** (2.5%) and **11a** (1.5%) detected in the crude product.
[d] **7b** (6%) and **11b** (2%) detected in the crude product.
[e] **7c** (1.0%) and **15** (10%) detected in the crude product.
[f] Chromatographed product still contained **13** (7%).
[g] No co-products were detected in the crude product.
[h] 60% yield with 0.2 equiv. of **1a**.
[i] **8d** (2%) and **12d** (1%) were detected in the crude product.
[j] **8e** (1%) and **12e** (2%) were detected in the crude product.

Surprisingly, the cyanide **3** was found to be quite capricious as a donor for the Michael reaction in the presence of proazaphosphatrane **1a**. Thus, good yields of 1,4-α-*trans* adducts were obtained only for ketones **4d** and **4e** while cyclic unsaturated ketones **4f** and **4g** reacted too slowly with **3** under our standard conditions (*i*-PrCN solvent, −60°C, 3 h) to afford the 1,4-α-*trans* adducts in acceptable yields. Furthermore, significant amounts of co-products accompanied **6f** and **6g**, one of which was separated in a fairly pure state and was identified by ^{1}H and ^{13}C NMR spectroscopy as the double Michael adduct **13** (*meso* and *dl* mixture). Reactions of **3** with **4a** and **4b** gave (in both THF and *i*-PrCN) complex reaction mixtures containing in addition to **6a** (59%) and **6b** (14%) both diastereoisomers of **8a** (R^1=Ph, R^2=Me) (8%) and **8b** (R^1=R^2=Ph) (28%) 1,4-γ-*cis* adducts **10a** (R^1=Ph, R^2=Me) (14%) and **10b** (R^1=R^2=Ph) (46%), traces of **12a** (R^1=Ph, R^2=Me) and **12b** (R^1=R^2=Ph) and isomeric **14a** (R^1=Ph, R^2=Me) (19%) and **14b** (R^1=R^2=Ph) (13%). From these crude products, **10b**, (4*R**,5*R**)-**8a**, and one isomer of **14a** were separated by repeated column chromatographic runs in sufficient purity to allow unambiguous structural assignments after careful analysis of the ^{1}H and ^{13}C NMR spectra.



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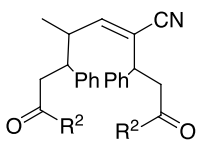

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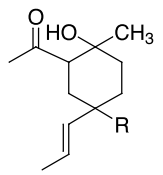
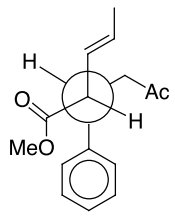


15 R = $COOCH_3$
16 R = CN

The reactivity of 3-buten-2-one (**4c**) with **2** or **3** requires special comment. Under standard conditions (Table 1) **4c** reacted with ester **2** to form the expected 1,4-α-*trans* adduct **5c** which was contaminated with **15** (10%) as a single diastereomer. When 3 equiv. of **4c** were used and the amount of catalyst **1a** was doubled, the yield of **15** increased to 18%. The reaction of **4c** with nitrile **3** led to a much more complex mixture containing a higher percentage (ca. 35%) of **16**. As could be expected, mesityl oxide formed no adducts with **2** or **3**.

2.1. Structural and stereochemical considerations

The structural assignments in the 1,4-α-*trans*, 1,4-γ-*trans* and 1,4-γ-*cis* adducts, **5/6**, **7/8** and **9/10**, respectively, are based on ^{1}H NMR data associated with the CH_3–CH=CH–CHR– and –CHMeCH=CHR moieties. Although in each case (Table 1) a pair of diastereoisomeric 1,4-α-*trans* adducts was formed, their partial separation was achieved only for **5a**. The less polar isomer was assigned the 2*R**,3*R** and the more polar the 2*R**,3*S** relative configuration. The vicinal H–C2–C3–H couplings in the less and more polar isomers were found to be 9.6 and 8.4 Hz, respectively. Thus, the conformations shown on the Newman projections **17** [for (2*R**,3*R**)-**5a**] and **18** [for 2*R**,3*S**)-**5a**] are considered to be predominant, if not exclusive for (2*R**,3*R**)-**5a**. Due to the proximity of the phenyl ring, the methyl substituent in the MeO_2C group in conformation **17** is expected to be shielded in comparison to that in conformation **18**. For the same reason, the ^{1}H resonances of the CH_3CH=CH fragment will be shifted upfield in conformation **18**. Both shieldings are actually observed with $\Delta\delta$~0.2 ppm. The same arguments allowed for the configurational assignments of **5b** with 2*R**,1′*R** for the major, and 2*R**,1′*S** for the minor diastereoisomer. The relative stereochemistry of the other diastereoisomeric 1,4-α-*trans* adducts could not be assigned because of a lack of stereochemically useful differences in their ^{1}H NMR spectra.



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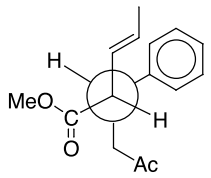

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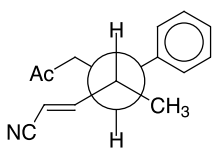
A similar approach was employed for the structural elucidation of the 1,4-γ-*trans* adducts **8a** (**19** and **20**) leading to the assignment of 4*R**,5*R** relative configuration for the major, and 4*R**,5*S** for the minor diastereoisomer. Although the more polar minor diastereoisomer of **8a** was not separated, the stereochemically relevant ^{1}H NMR data (δ H_3CCH=, 1.03 ppm; δ HC=CH, 6.48 and 5.17 ppm) were unequivocally extracted from the spectra of fractions containing increasing amounts of this isomer along with decreasing amounts of the less polar isomer. In a similar manner, the relative configurations of the major (4*R**,5*R**)-**7a** and (4*R**,5*R**)-**7b**, and minor (4*R**,5*S**)-**7a** and (4*R**,5*S**)-**7b** diastereoisomers were established.



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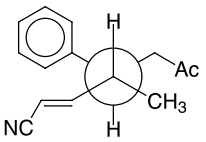

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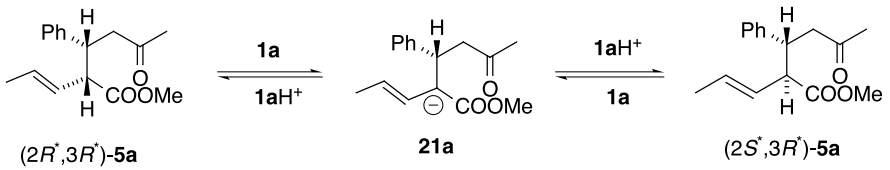
The formation of single diastereoisomers of the 1,4-γ-*cis* adducts **10** precluded the unequivocal stereochemical assignments for the isolated isomer of **10b** (R^1=Ph, R^2=Ph). We were unable to isolate any pure isomeric **11a** (R^1=Ph, R^2=Me), **11b** (R^1=R^2=Ph), **12d** (R^1=R^2=Me) or **12e** (R^1=Me, R^2=Et), because of the trace quantities of these compounds present in the crude products. However, their identity comes from the appearance of triplets at δ 1.00–1.10 (J=7.5 Hz) for H_3CCH_2CH= and at δ ~6.8 ppm (J=7.2 Hz) for H_3CCH_2CH= in the ^{1}H NMR spectra of the respective reaction mixtures. The *E* configuration in **11a** (R^1=Ph, R^2=Me) and **11b** (R^1=R^2=Ph) is assigned on the basis of deshielding of *H*C=CCOOMe by the C=O bond of the carbomethoxy group.[73]

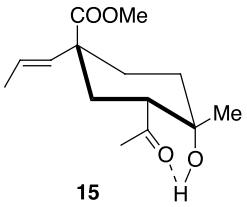
The stereochemistry of **15** stems in part from the literature precedence[74] and from confirmation by our ^{1}H–^{1}H and ^{1}H–^{13}C COSY experiments, except for the configuration at C-1. However, based on the comparison of the conformational energies of the COOMe and CH_3CH=CH



(2R*,3R*)-**5a** **21a** (2S*,3R*)-**5a**

Scheme 2.

(approximated by the vinyl group) substituents,[75] it is expected that the 1-propenyl group has a stronger equatorial preference.



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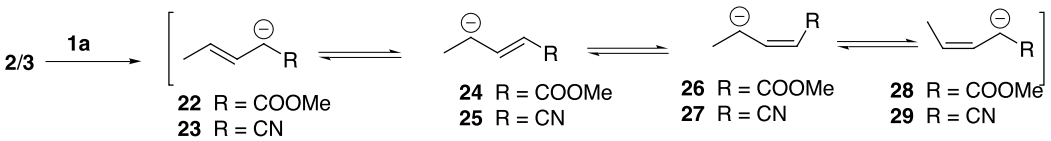
2.2. Mechanistic considerations

In order to determine whether the ratios of 1,4-α-*trans* addition products are under kinetic or thermodynamic control, equilibration studies were undertaken. When pure (2*R**,3*R**)-**5a** was exposed to **1a** (0.2 equiv.) at −60°C for 3 h, an 89:11 mixture of (2*R**,3*R**)-**5a** and (2*R**,3*S**)-**5a** was obtained, while from pure (2*R**,3*S**)-**5a** a different ratio (37:63) of 2*R**,3*R** and 2*R**,3*S** diastereoisomers was obtained. The equilibration presumably involves the formation of carbanion **21a** (Scheme 2) since no cross-Michael products derived from a retro Michael/Michael sequence were obtained when **5a** and **4e**, and **5e** and **4a** were treated under our standard reaction conditions (−60°C, 3 h), and starting adducts were recovered quantitatively. However the ratios of (2*R**,2*R**)- and (2*R**,3*S**)-**5a** obtained in the equilibration studies from pure diastereoisomers do not match the composition (47:53) of the adducts we synthesized. When the equilibration was performed on a 28:72 mixture at −40°C, (2*R**,3*R**)- and (2*R**,3*S**)-**5a** were obtained in a 62:38 ratio, but **11a** (R^1=Ph, R^2=Me) was also formed (3%). At −20°C the same starting mixture of diastereoisomers was transformed into a complex reaction mixture consisting of *ca*. 60% diastereoisomeric **5a**, **11a** (17%) and several other unidentified products. Thus, the final diastereoisomeric ratios of 1,4-α-*trans* adducts reflect neither kinetic nor thermodynamic preferences of the reaction under investigation, at least in the case of **5a**. Under these circumstances a discussion of the facial reactivity of 'naked' (*Z*)-and (*E*)-enolates **22** and **23** (Scheme 3) obtained from **2** and **3**, respectively, is not fruitful.

Full regioselectivity of the addition of **2** to Michael acceptors **4d**–**4g** renders this application of **1a** rather startling, and it reflects the extremely high reactivity of **22** in comparison with other possible carbanions (**24**, **26**, **28**) including **21a**. Only for the more reactive **4c** does carbanion **30** compete with **22**, leading to the double Michael adduct **31** which undergoes further aldol condensation to produce **15** (Scheme 4). From the less reactive α,β-unsaturated ketones **4a** and **4b**, small amounts of 1,4-γ-*trans* adducts **7a** (R^1=Ph, R^2=Me) and **7b** (R^1=R^2=Ph) were obtained through the intermediacy of carbanion **24**. Carbanion **23** is less reactive than **22**, since addition of the cyanide **3** to **4d** and **4e** leads to the formation of small amounts of 1,4-γ-*trans* products **8d** and **8e**. The reactivity of **23** is comparable to that of **32** (Scheme 5), because the crude product contained almost identical amounts of **6f** and **13**. Double Michael addition (followed by aldol condensation) was also observed for **6c**. With less reactive ketones **4a** and **4b**, carbanion **33** (Scheme 6) apparently also competes with **23**, **25**, and **29** for the acceptors, thus leading to **14a** (R^1=Ph, R^2=Me) or **14b** (R^1=R^2=Ph) as co-products.

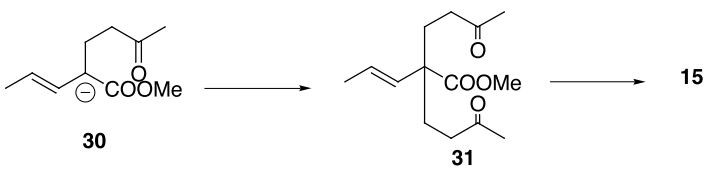
3. Summary

Synthetically valuable Michael addition of β,γ-unsaturated ester **2** to α,β-unsaturated ketones can be achieved in the presence of proazaphosphatrane **1a** at −60°C. For β,γ-unsaturated cyanide **3** this transformation is limited to aliphatic acyclic α,β-unsaturated ketones. Through equilibration and competition studies it was shown that the addition is under kinetic control, but the final composition of



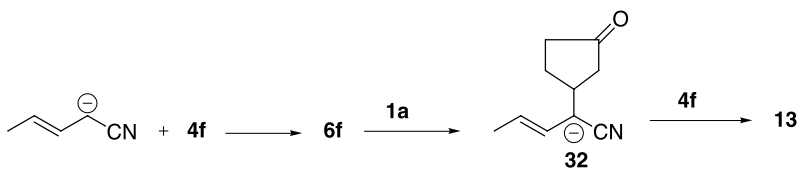
22 R = COOMe
23 R = CN
24 R = COOMe
25 R = CN
26 R = COOMe
27 R = CN
28 R = COOMe
29 R = CN

Scheme 3.

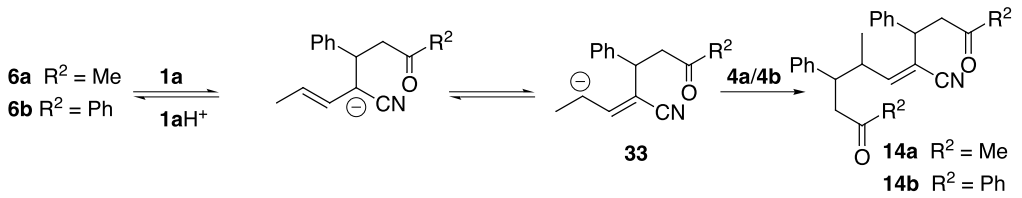


30 **31**

Scheme 4.



Scheme 5.



Scheme 6.

diastereoisomeric 1,4-α-*trans* products is influenced by deprotonation–reprotonation at C-2 in **5** and **6**.

4. Experimental

Isobutyronitrile was stored over 4 Å molecular sieves. All substrates were purchased from Aldrich Chemical Co. and were used as received. The proazaphosphatrane **1a** was prepared according to our previously published method.[50]

4.1. General procedure

To a solution of the β,γ-unsaturated ester or nitrile (1.0 mmol) in 1 mL of isobutyronitrile was added a solution of **1a** (0.2–0.4 mmol) in isobutyronitrile (0.5 mL) at −60°C under argon. After 5 min a solution of α,β-unsaturated ketones (1.0 mmol) in isobutyronitrile (0.5 mL) was added via cannula. The reaction mixture was kept at −60°C for 3 h. The catalyst was quenched at −60°C by injecting CF_3COOH (23–46 μL). The reaction mixture was warmed to room temperature and filtered through a pad (3 g) of silica gel using ether as an eluent. The crude product obtained after removal of solvents was evaporated on a Rotovap apparatus with a AcOEt/hexane mixture and with hexanes, and was analyzed by ^1H NMR spectroscopy. Purification was effected by chromatography on silica gel using hexanes/ethyl acetate mixtures (20:1–5:1, v/v). The products were characterized by ^1H and ^{13}C NMR spectroscopy and by MS (Supporting information).

5. Supporting information

^1H and ^{13}C NMR and mass spectral data.

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References

1. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, UK, 1991; Vol. 4.
2. Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon: Oxford, UK, 1992.
3. Evans, D. A.; Scheidt, K. A.; Johnston, J. N.; Willis, M. C. *J. Am. Chem. Soc.* **2001**, *123*, 4480–4491.
4. Christoffers, J.; Mann, A. *Chem.-Eur. J.* **2001**, *7*, 1014–1027.
5. Woodward, S. *Chem. Soc. Rev.* **2000**, *29*, 393–401.
6. Evans, D. A.; Rovis, T.; Kozlowski, M. C.; Downey, C. W.; Tedrow, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 9134–9442.
7. Christoffers, J.; Mann, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2752–2754.
8. Bulbule, V. J.; Deshpande, V. H.; Bedekar, A. V. *J. Chem. Res. Synop.* **2000**, 220–221.
9. Sato, K.; Tamura, M.; Tamoto, K.; Omote, M.; Ando, A.; Kamadaki, I. *Chem. Pharm. Bull.* **2000**, *48*, 1023–1025.
10. Chataigner, I.; Gennari, C.; Piarulli, U.; Ceccarelli, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 916–918.
11. Evans, D. A.; Rovis, T.; Johnson, J. S. *Pure Appl. Chem.* **1999**, *71*, 1407–1415.
12. Christoffers, J. *Synlett* **2001**, 723–732.
13. Chibiryaev, A. M.; De Kimpe, N.; Tkachev, A. V. *Tetrahedron Lett.* **2000**, *41*, 8011–8013.
14. Hirano, M.; Kiyota, S.; Imoto, M.; Komiya, S. *Chem. Commun.* **2000**, 1679–1680.
15. Christoffers, J.; Oertling, H.; Omal, N. *J. Prakt. Chem.* **2000**, *342*, 546–553.
16. Christoffers, J.; Oertling, H. *Tetrahedron* **2000**, *56*, 1339–1344.
17. Cai, C.; Soloshonok, V. A.; Hruby, V. J. *J. Org. Chem.* **2001**, *66*, 1339–1350.
18. Soloshonok, V. A.; Cai, C.; Hruby, V. J. *Tetrahedron Lett.* **2000**, *41*, 9645–9649.
19. Soloshonok, V. A.; Cai, C.; Hruby, V. J.; Meervelt, L. V.; Yamazaki, T. *J. Org. Chem.* **2000**, *65*, 6688–6696.
20. Christoffers, J.; Rossler, U.; Werner, T. *Eur. J. Org. Chem.* **2000**, 701–705.
21. Suzuki, T.; Torii, T. *Tetrahedron: Asymmetry* **2001**, *12*, 1077–1081.
22. Krause, N.; Hoffmann-Rooder, A. *Synthesis* **2001**, 171–196.
23. Sawamura, M.; Hamashima, H.; Ito, Y. *Bull. Chem. Soc. Jpn* **2000**, *73*, 2559–2562.

24. Naota, T.; Tanna, A.; Murahashi, S.-I. *Chem. Commun.* **2001**, 63–64.
25. Murahashi, S.-I.; Take, K.; Naota, T.; Takaya, H. *Synlett* **2000**, 1016–1018.
26. Ohe, T.; Wakita, T.; Motofusa, S.; Cho, C. S.; Ohe, K.; Uemura, S. *Bull. Chem. Soc. Jpn* **2000**, *73*, 2149–2155.
27. Stark, M. A.; Jones, G.; Richards, C. J. *Organometallics* **2000**, *19*, 1282–1291.
28. Nishiura, M.; Kameoka, M.; Imamoto, T. *Kidorui* **2000**, *36*, 294–295, *Chem. Abstr*. **2000**, *134*, 102–495.
29. Chen, X. Y.; Bao, W. L.; Zhang, Y. M. *Chin. Chem. Lett.* **2000**, *11*, 483–484, *Chem. Abstr*. **2000**, *133*, 252035.
30. Sundararajan, G.; Prabagaran, N. *Org. Lett*. **2001**, *3*, 389–392.
31. Irurre, J.; Riera, M.; Amela-Cortes, C. *Enantiomer* **2000**, *5*, 255–261.
32. Hashmi, A. S. K.; Schwartz, L.; Choi, J.-H.; Frost, T. M. *Angew Chem., Int. Ed.* **2000**, *39*, 2285–2288.
33. Kim, Y. S.; Matsunaga, S.; Das, J.; Sekine, A.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 6506–6507.
34. Mori, Y.; Kakumoto, K.; Manabe, K.; Kobayashi, S. *Tetrahedron Lett.* **2000**, *41*, 3107–3111.
35. Matsuda, I.; Makino, T.; Hasegawa, Y.; Itoh, K. *Tetrahedron Lett.* **2000**, *41*, 1409–1412.
36. Novak, T.; Tatai, J.; Bako, P.; Czugler, M.; Keglevich, G.; Toke, L. *Synlett* **2001**, 424–426.
37. Itoh, T.; Shirakami, S. *Heterocycles* **2001**, *55*, 37–43.
38. Zhang, F.-Y.; Corey, E. J. *Org. Lett.* **2001**, *3*, 639–641.
39. Corey, E. J.; Zhang, F.-Y. *Org. Lett.* **2000**, *2*, 4257–4259.
40. Zhang, F.-Y.; Corey, E. J. *Org. Lett.* **2000**, *2*, 1097–1100.
41. Shibatomi, K.; Nakahaski, T.; Uozumi, Y. *Synlett* **2000**, 1643–1645.
42. Ishikawa, T.; Araki, Y.; Kumamoto, T.; Isobe, T.; Seki, H.; Fukuda, K. *Chem. Commun.* **2001**, 245–246.
43. Kotsuki, H.; Sugino, A.; Sakai, H.; Yasuoka, H. *Heterocycles* **2000**, *53*, 2561–2567.
44. Peng, B.; Cheng, K.-J.; Ma, D.-W. *Chin. J. Chem.* **2000**, *18*, 411–413, *Chem. Abstr*. **2000**, *133*, 150431.
45. Ostendorf, M.; Van der Neut, S.; Rutjes, F. P. J. T.; Hiemstra, H. *Eur. J. Org. Chem.* **2000**, 105–113.
46. Utting, K. A.; Macquarrie, D. J. *New J. Chem.* **2000**, *24*, 591–595.
47. Krawczyk, H. *Synth. Commun.* **2000**, *30*, 1787–1797.
48. Krawczyk, H. *Synth. Commun.* **2000**, *30*, 657–664.
49. Schmidt, H.; Lensink, C.; Xi, S. K.; Verkade, J. G. L. *Anorg. Allg. Chem.* **1989**, *578*, 75–80.
50. Wroblewski, A. E.; Pinkas, J.; Verkade, J. G. *Main Group Chem.* **1995**, *1*, 69–79.
51. Kisanga, P. B.; Verkade, J. G. *Tetrahedron* **2001**, *57*, 467–475.
52. Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483–489.
53. D'Sa, B.; Kisanga, P.; Verkade, J. G. *J. Org. Chem.* **1998**, *63*, 3961–3967.
54. Kisanga, P. B.; McLeod, D.; D'Sa, B.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 3090–3094.
55. Wang, L.; Kisanga, P.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 6459–6461.
56. Kisanga, P.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 4298–4303.
57. McLaughlin, P.; Verkade J. G. manuscript in preparation.
58. Kisanga, P.; D'Sa, B.; Verkade, J. G. *J. Org. Chem.* **1998**, *63*, 10057–10059.
59. D'Sa, B.; Kisanga, P.; Verkade, J. G. *Synlett* **2001**, 670–672.
60. Kisanga, P.; Verkade, J. G. *Synth. Commun.* **2002**, *42*, 6263–6266.
61. Arumugam, S.; McLeod, D.; Verkade, J. G. *J. Org. Chem.* **1998**, *63*, 3677–3679.
62. Tang, J. S.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 7793–7802.
63. Arumugam, S.; Verkade, J. G. *J. Org. Chem.* **1997**, *62*, 4827–4828.
64. Liu, X.; Verkade, J. G. *J. Org. Chem.* **2000**, *65*, 4560–4564.
65. Tang, J. S.; Mohan, T.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 4931–4938.
66. Liu, X.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 4840–4843.
67. Wroblewski, A. E.; Verkade, J. G. *J. Org. Chem.* **2002**, *67*, 420–425.
68. Ilankumaran, P.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 3086–3089.
69. Yu, L.; Verkade, J. G. *J. Org. Chem.* **2000**, *65*, 2065–2068.
70. D'Sa, B.; Verkade, J. G. *J. Org. Chem.* **1996**, *61*, 2963–2966.
71. Ballester, P.; Costa, A.; Garcia-Raso, A.; Mestres, R. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2797–2803.
72. Schwerdtfeger, A. E.; Chan, T. H. *J. Org. Chem.* **1993**, *58*, 6513–6516.
73. Saegusa, T.; Ito, Y.; Tomita, S.; Kinshita, H. *J. Org. Chem.* **1970**, *35*, 670–675.
74. Gomez-Bengoa, E.; Cuerva, J. M.; Mateo, C.; Echavarren, A. M. *J. Am. Chem. Soc.* **1996**, *18*, 8553–8565.
75. Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 697.