dissolved in toluene (5 mL) and ethyl acrylate (2.5 mL, inhibitor-free), followed by three freeze–pump–thaw cycles, prior to further chain-extension polymerization.

RAFT: RAFT polymerization was carried out in glass bottles. Hexakis-(thiobenzoylthiomethyl)benzene (50 mg) and styrene (10 mL) were mixed together and degassed by purging with nitrogen. The bottles were sealed and placed in an oil bath at 100 °C. In typical reaction conditions a conversion of 50% was attained after 75 h. The polymer was isolated by evaporation of the styrene.

Analyses: The stars were characterized by size exclusion chromatography and NMR spectroscopy. The porous films were analyzed by SEM. The molecular weights quoted in the paper were determined against linear polystyrene standards and are provided as an approximate guide to the true molecular weight.

Film casting: The films were prepared[4] from carbon disulfide solutions with a polymer concentration of 10 g L^{-1} (unless specified differently in Table 1). The solution was cast on a glass support and dried with a humid air (or nitrogen) flow at 22 °C. The casting process was carried out in a box at a humidity of 85%. The saturation of the air flow was achieved by bubbling the gas through a water reservoir. The air flow was measured with a flow meter to ensure reproducibility.

Received: March 14, 2001
Revised: June 27, 2001 [Z16719]

[1] V. P. Shastri, I. Martin, R. Langer, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 1970.
[2] O. Karthaus, X. Cieren, N. Maruyama, M. Shimomura, *Mater. Sci. Eng. C* **1999**, *10*, 103.
[3] O. Karthaus, N. Maruyama, X. Cieren, M. Shimomura, H. Hasegawa, T. Hashimoto, *Langmuir* **2000**, *16*, 6071.
[4] G. Widawski, M. Rawiso, B. Francois, *Nature* **1994**, *369*, 387.
[5] T. Nishikawa, J. Nishida, R. Ookura, S.-I. Nishimura, S. Wada, T. Karino, M. Shimomura, *Mater. Sci. Eng. C* **1999**, *8–9*, 495.
[6] K. Inoue, *Prog. Polym. Sci.* **2000**, *25*, 453.
[7] O. Pitois, O. Francois, *Eur. Phys. J. B* **1999**, *8*, 225.
[8] O. Pitois, B. Francois, *Colloid Polym. Sci.* **1999**, *277*, 574.
[9] Y. K. Chong, T. P. T. Le, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1999**, *32*, 2071.
[10] M. Stenzel-Rosenbaum, T. P. Davis, V. Chen, A. G. Fane, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2777.
[11] D. M. Haddleton, R. Edmonds, A. M. Heming, E. J. Kelly, D. Kukulj, *New J. Chem.* **1999**, *23*, 477.
[12] Y. Kotani, M. Kamigaito, M. Sawamoto, *Macromolecules* **1999**, *32*, 6877.
[13] Y. Kotani, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 3543.
[14] Y. Kotani, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 6746.
[15] M. H. Stenzel-Rosenbaum, T. P. Davis, V. Chen, A. G. Fane, *Macromolecules* **2001**, *34*, 5433.

Rapid Access to Diverse Arrays of Chiral 3,4-Diazaphospholanes**

Clark R. Landis,* Wiechang Jin, Jonathan S. Owen, and Thomas P. Clark

Chiral phosphine ligands are central to many developments in transition metal catalyzed enantioselective transformations.[1] Recent demonstrations of high enantioselectivity for a wide range of hydrogenation reactions with Rh complexes of DuPHOS,[2] PennPHOS,[3] RoPHOS,[4] BASPHOS,[5] CnrPHOS,[6] and related ligands highlight the unusual efficacy of rigid phosphacycles.[7] Other emerging trends in ligand design include the use of heterofunctional bidentate ligands,[8] implementation of attractive "secondary interactions" between complementary functional groups of the substrate and the catalyst periphery,[9] and the construction of large libraries of chiral phosphines for high-throughput catalyst screening.[10] All these strategies for the discovery of enantioselective catalysts can be accelerated by new synthetic methods for constructing cyclic phosphanes. We report a versatile synthetic route to a large number of new chiral diazaphospholanes that uses aldehydes, hydrazines, and primary phosphines as starting materials.

By analogy with P–C bond formation by means of the classic Mannich condensation[11] reaction, we reasoned that the condensation of primary phosphines with azines (R–CH=N–N=CH–R), prepared by the treatment of hydrazine with two equivalents of the corresponding aldehyde, would yield diazaphospholanes such as **1** (Scheme 1). This procedure yields a variety of 3,4-diazaphospholanes in good yields (25–95%) with *rac* selectivity under mild reaction conditions. All compounds were thoroughly characterized by using ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and in most cases, X-ray crystallography (Figure 1). To the best of our knowledge, the only previous report of 3,4-diazaphospholanes involved the stepwise condensation of formaldehyde and phenylphosphane, followed by ring closure with *N*,*N*′-dialkylhydrazines.[12]

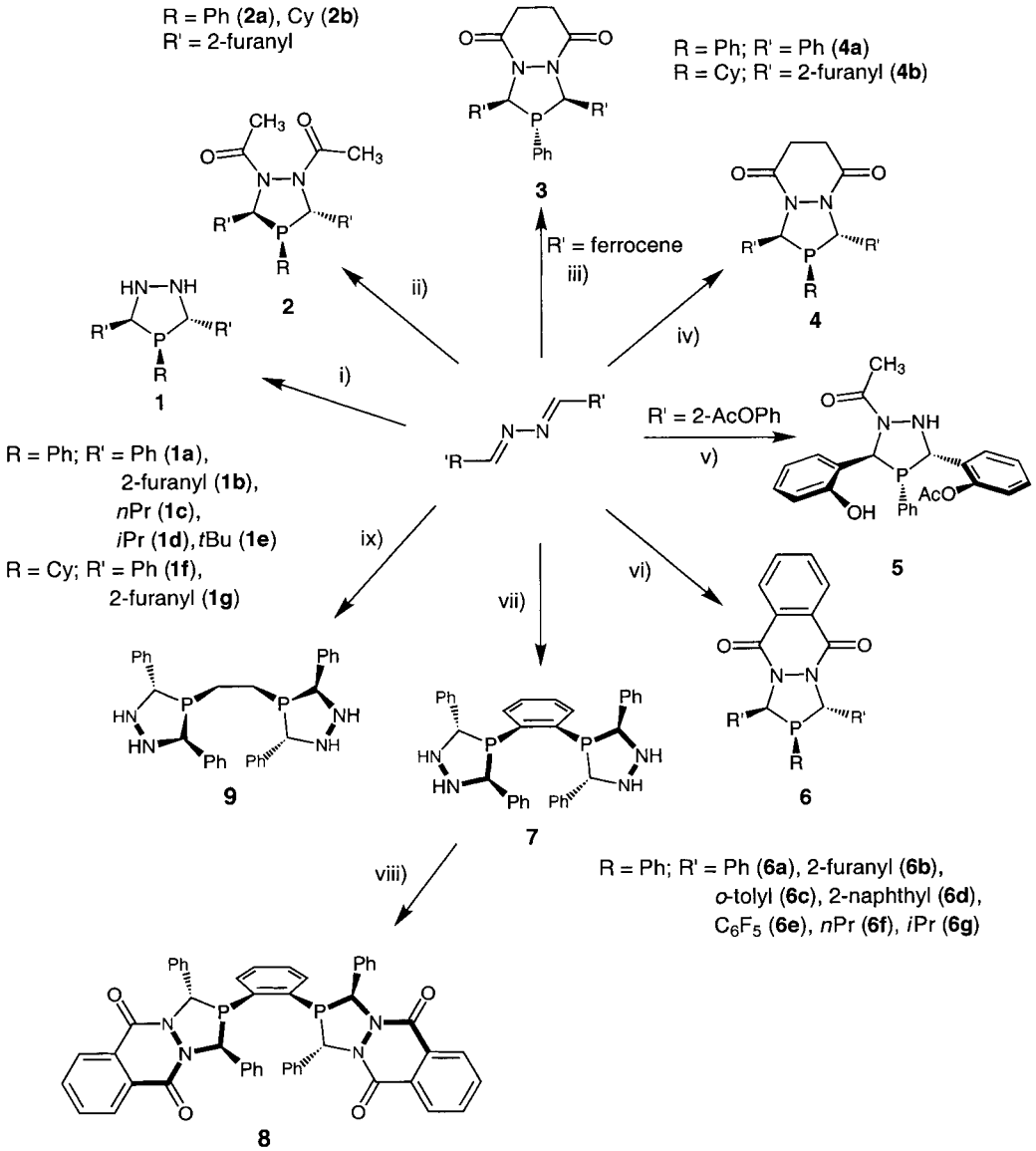
The condensation of azines and primary phosphines with one equivalent of dry HCl as acid promoter renders simple 3,4-diazaphospholanes (**1**, **7**, **9**) upon workup. Acid chlorides function as both promoters and N-functionalization reagents to yield *N*,*N*′-dicarboxy-3,4-diazaphospholanes (**2**, **3**, **4**, **6**) directly in a one-step synthesis. The reaction of phenylphosphane with the azine derived from acetyl salicylaldehyde yields **5**, in which one of the salicyl acetyl groups is transferred to the hydrazine moiety. As exemplified by the transforma-

[*] Prof. Dr. C. R. Landis, W. Jin, J. S. Owen, T. P. Clark
Department of Chemistry, University of Wisconsin-Madison
1101 University Ave, Madison, WI 53706 (USA)
Fax: (+1) 608-262-6143
E-mail: landis@chem.wisc.edu

[**] We thank the Department of Energy, Office of Basic Energy Sciences for financial support of this work. All crystal-structure determinations were performed by Dr. Doug Powell or Dr. Ilyea Guzei. The cone-angle measurements were made with the gracious assistance of Dr. David White of the UNC-Wilmington.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

  1433-7851/01/4018-3432 $ 17.50+.50/0



Scheme 1. i) HCl, RPH_2; ii) CH_3COCl, RPH_2; iii) succinyl chloride, $PhPH_2$; iv) succinyl chloride, RPH_2; v) HCl, $PhPH_2$; vi) phthaloyl chloride, $PhPH_2$; vii) HCl, 1,2-$(PH_2)_2C_6H_4$; viii) phthaloyl chloride in THF; ix) HCl, $PH_2CH_2CH_2PH_2$. All the reactions were worked up with aqueous K_2CO_3 (10%).

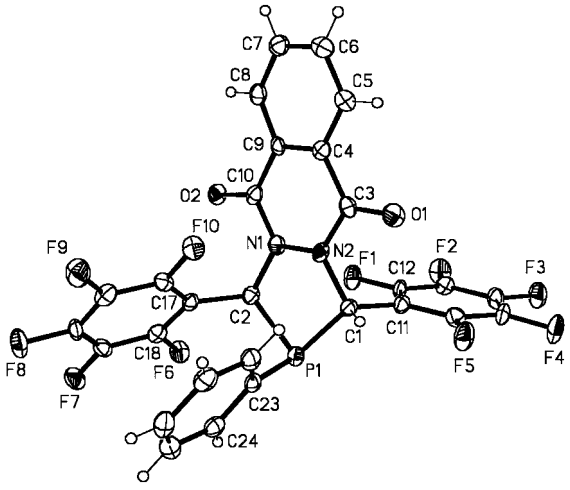


Figure 1. The X-ray crystal structure of *rac*-**6e**. The displacement ellipsoids are drawn at the 50% probability level.

tion of **7** into **8**, 3,4-diazaphospholanes and acid chlorides cleanly react to give *N*,*N*′-dicarboxy-3,4-diazaphospholanes. The *N*,*N*′-dicarboxy-3,4-diazaphospholanes exhibit substantially higher thermal and chemical stability than the simple 3,4-diazaphospholanes. For example, **3** persists for hours in refluxing toluene, whereas the ferrocenyl derivative of **1** decomposes upon warming at 80° for three hours; presumably functionalization at N inhibits the retroaddition of the phosphine to the azine.

Acid-promoted additions of primary phosphines to azines are generally *rac* selective, but sensitive to the substituents at the phosphorus center or at the 2- and 5-positions of the heterocyclic ring. For example, whereas phenylphosphane affords *rac*/*meso* ratios (0.6–30:1) that are dependent on the substituents at the 2- and 5-positions, only the *rac* isomers are observed for cyclohexylphosphane. Azines derived from bulky, electron-withdrawing substituents such as pentafluorophenyl and ferrocenyl result in low *rac*/*meso* ratios (**6e** 2:1; **3** 0.6:1). For most diazaphospholanes, a simple recrystallization at room temperature effects the separation of diastereomers (e.g. *rac*/*meso* 30:1 for **1a**).

The racemic diazaphospholanes **1a**, **1e**, and **9** are resolved by N-functionalization with di-*O*-methyl-L-tartaric acid dichloride to form bicyclic diastereomers, followed by chromatographic separation on silica gel. The exploration of other resolution protocols is an active line of our research.

Crystallographic analysis reveals interesting structural details of the 3,4-diazaphospholanes. The X-ray crystal structure determination of *rac*-**8** (Figure 2) exemplifies the approximate C_2 symmetry of bis(diazaphospholanes) (**7**–**9**). Clearly there is a remarkable communication of stereochemical information between the two phospholane rings during the condensation. 3,4-Diazaphospholanes are bulky ligands; for example, the cone angle[13] of **1a** (172°) is comparable to that of $P(Cy)_3$ (170°) (Cy = cyclohexyl).

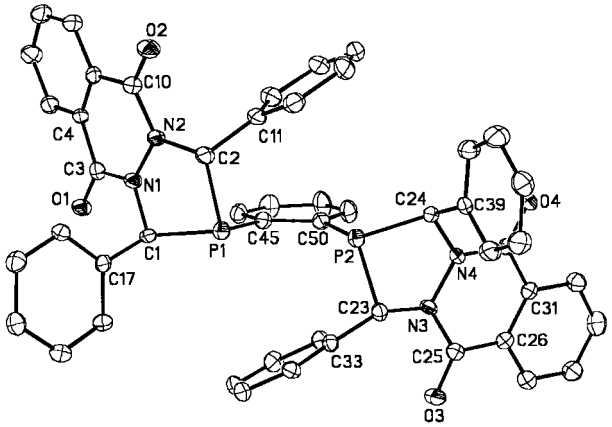


Figure 2. The X-ray crystal structure of *rac*-**8**. The ORTEP diagram is drawn at the 30% probability level. Solvent molecules and hydrogen atoms have been omitted for clarity.

Preliminary data indicate that *N*,*N*′-dicarboxy-3,4-diazaphospholanes ligate to transition metals in a manner similar to other phospholanes. For example, excess **6a** and **6b** react with 1/2 [{Rh(nbd)Cl}$_2$] (nbd = norbornadiene) to afford adducts with the formula [(**6**)Rh(nbd)Cl] in quantitative yield. Similarly, the reaction of the *N*,*N*′-phthaloyl derivative of **9** with [(cod)Pt(CH$_3$)$_2$] (cod = cyclooctadiene) in solution yields [(**9**-phthaloyl)Pt(CH$_3$)$_2$] in quantitative yield, as determined by NMR spectroscopic and X-ray crystallographic analysis. Preliminary studies revealed that Rh complexes of 3,4-diazaphospholanes are active hydrogenation catalysts.

In summary, we have report herein an unprecedented, simple synthesis of a wide variety of 3,4-diazaphospholanes based on the acid-promoted addition of primary phosphines to azines. Functionalization of the diazaphospholanes at N stabilizes and rigidifies the 3,4-diazaphospholanes. Future work concerns the application of these functionalized, bulky phosphines to reactions catalyzed by transition metal complexes.

Experimental Section

Full experimental details can be found in the Supporting Information. The crystal structures of the following compounds are available[14]: *rac*-**1a**, *rac*-**1c**, *rac*-**1d**, *rac*-**2a**, *meso*-**3**, *rac*-**4a**, *rac*-**4b**, *rac*-**5**, *rac*-**6a**, *rac*-**6b**, *rac*-**6c**, *rac*-**6e**, *rac*-**7**, *rac*-**8**.

General Procedure: A solution of the azine derivative (4.55 mmol) in diethyl ether (20 mL) was treated with HCl (ca. 4.75 mL, 4.75 mmol, 1.0 M in Et$_2$O solution) at 0 °C. A white solid precipitated immediately. Phenyl- or cyclohexylphosphane (4.55 mmol) was added to this suspension at 0 °C and the reaction mixture was stirred for 4 h (or overnight) at room temperature. A degassed aqueous solution of K$_2$CO$_3$ (≈30 mL, 10%) was added to the resultant white slurry at 0 °C. The ether layer was separated by means of a cannula, dried over MgSO$_4$, and filtered through a cannula to obtain a colorless solution. The diethyl ether was evaporated under vacuum to yield the corresponding diazaphospholanes.

Received: March 5, 2001 [Z16720]

[1] R. Noyori, *Asymmetric Catalysis*, Wiley, New York, **1994**.
[2] a) M. J. Burk, *J. Am. Chem. Soc.* **1991**, *113*, 8518–8519; b) M. J. Burk, *Chemtracts: Org. Chem.* **1998**, *11*, 787–802; c) M. J. Burk, A. Pizzano, J. A. Martin, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **2000**, *19*, 250–260; d) M. J. Burk, F. Bienewald, S. Challenger, A. Derrick, J. A. Ramsden, *J. Org. Chem.* **1999**, *64*, 3290–3298.
[3] a) Z. Zhang, G. Zhu, Q. Jiang, D. Xiao, X. Zhang, *J. Org. Chem.* **1999**, *64*, 1774–1775; b) Q. Jiang, Y. Jiang, D. Xiao, P. Cao, X. Zhang, *Angew. Chem.* **1998**, *110*, 1203–1207; *Angew. Chem. Int. Ed.* **1998**, *37*, 1100–1103; c) G. Zhu, P. Cao, Q. Jiang, X. Zhang, *J. Am. Chem. Soc.* **1997**, *119*, 1799–1800; d) Z. Chen, Q. Jiang, G. Zhu, D. Xiao, P. Cao, C. Guo, X. Zhang, *J. Org. Chem.* **1997**, *62*, 4521–4523.
[4] a) J. Holz, M. Quirmbach, U. Schmidt, D. Heller, R. Stürmer, A. Börner, *J. Org. Chem.* **1998**, *63*, 8031–8034; b) W. Li, Z. Zhang, D. Xiao, X. Zhang, *J. Org. Chem.* **2000**, *65*, 3489–3496; c) W. Li, Z. Zhang, D. Xiao, X. Zhang, *Tetrahedron Lett.* **1999**, *40*, 6701–6704; d) Y.-Y. Yan, T. V. Rajan Babu, *J. Org. Chem.* **2000**, *65*, 900–906.
[5] J. Holz, D. Heller, R. Stürmer, A. Börner, *Tetrahedron Lett.* **1999**, *40*, 7059–7062.
[6] a) A. Marinetti, S. Jus, J.-P. Genêt, *Tetrahedron Lett.* **1999**, *40*, 8365–8368; b) A. Marinetti, S. Jus, J. P. Genêt, L. Ricard, *Tetrahedron* **2000**, *56*, 95–100.
[7] F. Guillen, J.-C. Fiaud, *Tetrahedron Lett.* **1999**, *40*, 2939–2942.
[8] a) G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336–345; b) preparation of novel ligands for chiral catalysis: K. Burgess (Texas A & M University System, USA), WP 0061589, **2000**; c) D.-R. Hou, K. Burgess, *Org. Lett.* **1999**, *1*, 1745–1747; d) D. G. Blackmond, A. Lightfoot, A. Pfaltz, T. Rosner, P. Schnider, N. Zimmerman, *Chirality* **2000**, *12*, 442–449; e) S. R. Gilbertson, D. Xie, *Angew. Chem.* **1999**, *111*, 2915–2918; *Angew. Chem. Int. Ed.* **1999**, *38*, 2750–2752.
[9] a) M. Sawamura, Y. Ito, *Chem. Rev.* **1992**, *92*, 857–871; b) C. R. Landis, R. Sawyer, E. Somsook, *Organometallics* **2000**, *19*, 994–1002; c) B. Kimmich, C. R. Landis, *Organometallics* **1996**, *15*, 4141–4146.
[10] a) S. R. Gilbertson, X. Wang, *Tetrahedron* **1999**, *55*, 11609–11618; b) S. R. Gilbertson, S. E. Collibee, A. Agarkov, *J. Am. Chem. Soc.* **2000**, *122*, 6522–6523; c) K. Burgess, D. Moye-Sherman, A. M. Porte, *Mol. Diversity Comb. Chem.: Libr. Drug Discovery Conf.* **1996**, 128–136; d) K. Burgess, A. M. Porte, *Adv. Catal. Processes* **1997**, *2*, 69–82.
[11] a) B. B.-A. Bar-Nir, M. Portnoy, *Tetrahedron Lett.* **2000**, *41*, 6143–6147; b) K. Kellner, B. Seidel, A. Tzschach, *J. Organomet. Chem.* **1978**, *149*, 167–176.
[12] G. Märkl, G. Y. Jin, *Tetrahedron Lett.* **1981**, *22*, 229–232.
[13] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-158926–158939. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

  1433-7851/01/4018-3434 $ 17.50+.50/0