Experimental Section

Diazocyclopentadiene (1.78 M in pentane) was prepared by a literature method.[6b] Polymer-supported triphenylphosphane **3** and all other chemicals were obtained from commercial sources unless otherwise specified. Boronic acid (**7d**) was prepared from 1-nonyne by a literature method.[12] Characterization data and purification details of complexes **6a**,[2] **6b–e**,[3a] and **8a–d**[3b] have already been reported.

2: A 1.78 M pentane solution of diazocyclopentadiene (4 mL, 1.2 equiv) was added to a well stirred suspension of the heterogeneous phosphane **3** (2.0 g, ≈5.6 mmol of P) in CH_2Cl_2 (15 mL) at room temperature. The mixture was stirred for a further 2 h, after which time Et_2O (30 mL) was added and the orange insoluble polymer was collected by filtration, washed with Et_2O (3×10 mL), and dried under vacuum to yield **2** (2.4 g) as an orange powder. Elemental analysis revealed 5.39 % N, which corresponded to a 85 % functionalization of the phosphane groups. IR (CH_2Cl_2 film): $\tilde{\nu} = 1517$ (C=N), 1102 (P=N), 974 cm^{-1} (N–N); ^{31}P MAS NMR (121 MHz, neat solid, external reference: H_3PO_4, see Figure 1): $\delta = 21.10$ (phosphazine), -7.03 (phosphane) .

8e (Table 2, entry 5): m.p. 86 °C; R_f (silica gel, hexane) 0.14; IR (KBr): $\tilde{\nu} =$ 2018 (CO_{asym}), 1910 cm^{-1} ($CO_{sym.}$); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.32$ (dd, $J = 5.0$, 2.9 Hz, 1H, H5 thienyl), 7.28 (dd, $J = 2.9$, 1.5 Hz, 1H, H2 thienyl), 7.07 (dd, $J = 5.0$, 1.5 Hz, 1H, H4 thienyl), 5.67 (pseudo t, $J =$ 2.2 Hz, 2H, Hα C_5H_4Ar), 5.37 (pseudo t, $J = 2.2$ Hz, 2H, Hβ C_5H_4Ar); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 194.04$ (CO), 132.72 (C4 thienyl), 126.64, 126.20, 121.59 (C3 thienyl), 103.91 (C4 C_5H_4Ar), 84.01, 81.63 (C3 C_5H_4Ar); MS (70 eV): *m/z* (%): 418 (100) [M^+, ^{187}Re], 416 (62) [M^+, ^{185}Re], 390 (36) [$M^+ - CO$, ^{187}Re], 388 (23) [$M^+ - CO$, ^{185}Re], 362 (60) [$M^+ - 2CO$, ^{187}Re], 360 (37) [$M^+ - 2CO$, ^{185}Re].

Received: November 24, 1998 [Z 12710 IE]
German version: *Angew. Chem.* **1999**, *111*, 1730–1732

Keywords: cyclopentadienes · diazo compounds · heterogeneous reactions · multicomponent reactions · rhenium.

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Memory of Chirality in Electron Transfer Mediated Benzylic Umpolung Reactions of Arene–$Cr(CO)_3$ Complexes**

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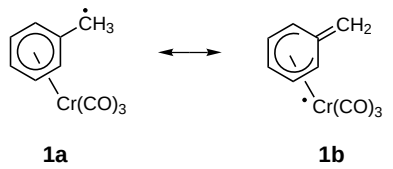
Since the discovery of arene–tricarbonylchromium complexes in 1958[1] this class of compounds has been studied extensively. It has been shown that the $Cr(CO)_3$ group activates the arene ligand in different ways to facilitate transformations that cannot be achieved with the free arenes.[2] Furthermore, it has been demonstrated that novel and competitive strategies for the enantioselective synthesis of complex organic molecules are possible if both the chemical and stereochemical properties of such complexes are exploited.[3, 4] While the vast majority of applications of arene–$Cr(CO)_3$ complexes are based on polar reactions involving coordinatively saturated (18 valence electron (VE)) anionic or cationic intermediates,[2] it has only recently been realized that transformations involving $Cr(CO)_3$-complexed benzylic radicals are also useful for organic synthesis.[5]

A theoretical investigation carried out in this laboratory suggests that the parent benzyl radical complex **1a** is better described as the 17 VE resonance structure **1b**. This structure clearly indicates the presence of an exocyclic C–C double bond and shows delocalization of a significant portion of the spin density onto the chromium atom (Scheme 1).[6]



1a **1b**

Scheme 1. Resonance structures for the $Cr(CO)_3$-complexed benzyl radical.

As a consequence, derivatives of **1** that carry an additional substituent in the benzylic position (for example, **2**) are planar chiral radical species and should exhibit a significant degree of configurational stability. Indeed, the barrier for the racemization of **2** was calculated to be 13.2 kcal mol^{-1} (Scheme 2),[7] which corresponds to a half-life of about one minute at -78 °C.[8]

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[**] This work was supported by the Volkswagenstiftung and the Fonds der Chemischen Industrie. C.B.deK. thanks the Foundation for Research Development (FRD) and the University of the Witwatersrand, South Africa for financial support. We thank Prof. Dr. W. Koch, Technical University Berlin, for support and helpful discussions concerning the quantum chemical calculations. We also thank Chemetall GmbH for the generous gifts of chemicals.

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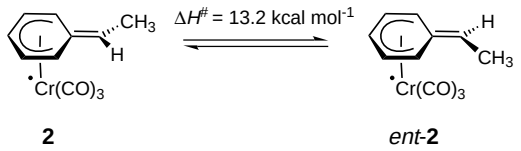
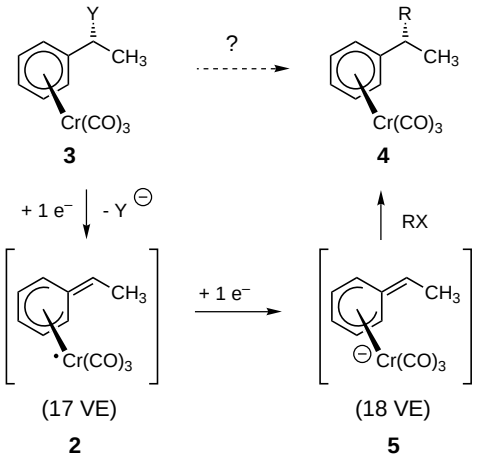


2 *ent*-**2**

Scheme 2. Racemization of the planar chiral radical intermediate **2**.

Based on these predictions we envisaged that, provided one could generate the radical intermediate **2** in a stereocontrolled fashion, for example, from a chiral precursor of type **3**, it would be possible to convert **2** into chiral products, such as **4**, without much loss of stereochemical information (Scheme 3). This transformation (**3**→**4**) would represent a novel reaction where "memory of chirality" would apply, even though a (normally notoriously labile) radical intermediate is involved.[9]



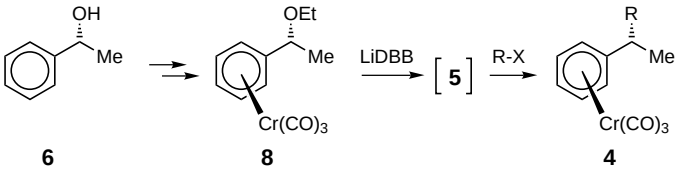
3 **4** **2** **5**

Scheme 3. Concept for the formation of **4** from **3**.

In accordance with our program on electron transfer driven transformations of transition metal π complexes,[10] the plan was to generate **2** from **3** by a single electron reduction and to immediately convert this 17 VE intermediate into the anionic 18 VE species **5** by a second electron transfer. The latter species represents a configurationally stable benzylic anion[11] that should react with electrophiles to give products of type **4** with overall retention of configuration (Scheme 3). Herein we disclose the first experimental evidence for the validity of this concept by describing an efficient method for the stereospecific umpolung[12] of 1-arylalkanol–$Cr(CO)_3$ derivatives.

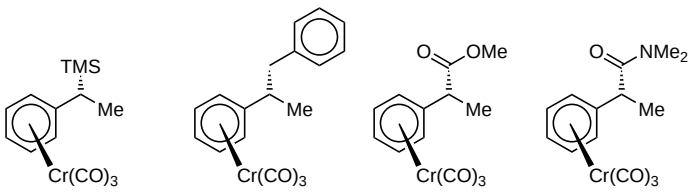
Starting from readily available (*R*)-1-phenylethanol (**6**; 91 % *ee*)[13] the complex **8** (91 % *ee* (HPLC); $[\alpha]_D^{20} = +30$; $c =$ 0.10 in $CHCl_3$; Table 2) was obtained by formation of the ethyl ether (EtBr, NaH, THF, sealed tube, 7 h, 88 %) followed by complexation ($Cr(CO)_6$, Bu_2O, THF, 65 h, 72 %). Treatment of **8** with 2.1 equivalents of lithium 4,4′-di-*tert*-butylbiphenyl (LiDBB)[14, 15] in THF at −78 °C afforded a solution of the anion **5**, which was treated with a variety of electrophiles to give rise to the desired products **4** (Scheme 4).

In all instances, the reactions were first carried out with racemic mixtures in order to obtain reference material for analysis of the *ee* by means of HPLC on a chiral column.[16] The results of the various experiments conducted in the optically active series, summarized in Table 1, show that the products **9**–**12** (Table 2) were obtained in fair yields and, as anticipated, with a high degree of retention of the absolute stereochemical information.



6 **8** **4**

Scheme 4. Synthesis of **4**.



9 **10** **11** **12**

Table 1. Results of the experiments with **8** (91 % *ee*)[16] according to Scheme 4.

Entry	RX	Product	Yield[a] [%]	*ee*[b] [%]	*ee*[c] [%]	$[\alpha]_D^{20}$ (concn)
1	TMSCl	**9**	72 %	87 %	98 %	+25 ($c = 0.08$)[d]
2	$PhCH_2Br$	**10**	37 %	87 %	87 %	+34 ($c = 0.09$)
3	MeOC(O)Cl	**11**	67 %	86 %	98 %	−52 ($c = 0.05$)[d]
4	$Me_2NC(O)Cl$	**12**	57 %	84 %	>99 %	−15 ($c = 0.04$)[d]

[a] Yields after chromatographic purification. [b] *ee* value of the chromatographically pure products. [c] *ee* value after one recrystallization from heptane or hexane. [d] Values refer to the recrystallized samples, concentration is given in g per 100 ml $CHCl_3$.

From the fact that all products were obtained almost without racemization, it is concluded that all three parts of the process, namely, 1) the reductive generation of the radical intermediate **2**, 2) its reduction to the anion **5**, and 3) the final alkylation, occur with a high degree of stereochemical control (Scheme 3). As no external chiral environment is involved in these reactions, the origin of the stereoselectivity can only be ascribed to the preservation of the chiral information in both the radical and the anionic intermediates. Hence during the process, the chirality of the molecule is temporarily transferred from a stereogenic center to a chiral plane and finally back to a center.[17] This represents an example of self-regeneration of a stereo center.[18]

To demonstrate the value of this new methodology we have completed a five step enantioselective synthesis of the sesquiterpene (+)-α-curcumene (Scheme 5).[19] The alcohol **13** ($[\alpha]_D^{20} = +53$; $c = 0.9$ in $CHCl_3$) was obtained in 93 % *ee* by enantioselective reduction of cheap, commercially available *p*-methylacetophenone.[13] Formation of the ethyl ether and attachment of the chromium unit as described previously afforded **14**. Treatment of **14** with LiDBB and then 5-iodo-2-methyl-2-pentene gave the desired product, which on oxidative removal of the $Cr(CO)_3$ unit afforded (+)-α-curcumene (**15**) with an enantiomeric purity of approximately 90 %

Table 2. Characteristic data for compounds **8**, **9**, **10**, **11**, **12**, and **14**. IR (ATR); ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (67.7 MHz, $CDCl_3$ with DEPT).

8: M.p. 44 °C (heptane); IR: $\tilde{\nu}$ = 1961, 1874 cm^{-1}; ^{1}H NMR: δ = 1.26 (t, J = 7.0 Hz, 3H), 1.46 (d, J = 7.0 Hz, 3H), 3.64 (dq, J = 9.5, 7.0 Hz, 2H), 4.16 (q, J = 7.0 Hz, CH), 5.26–5.40 (m, 4H), 5.54–5.63 (m, 1H); ^{13}C NMR: δ = 15.4 (CH_3), 22.9 (CH_3), 65.1 (CH_2), 75.1 (CH), 91.2 (CH), 91.5 (CH), 91.6 (CH), 91.9 (CH), 92.8 (CH), 114.0 (C), 232.9 (CO); HR-MS calcd for $C_{13}H_{14}O_4Cr$: 286.0297, found: 286.0297.

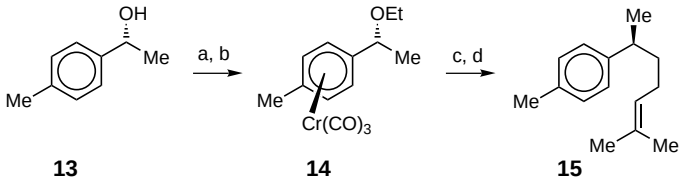
9: M.p. 105 °C (hexane); IR: $\tilde{\nu}$ = 1959, 1865 cm^{-1}; ^{1}H NMR: δ = 0.80 (s, 9H), 2.85 (d, J = 7.0 Hz, 3H), 2.46 (q, J = 7.0 Hz, 1H), 5.58–5.70 (m, 2H), 5.74–5.84 (m, 1H), 5.86–5.99 (m, 2H); ^{13}C NMR: δ = −3.4 (CH_3), 13.9 (CH), 28.3 (CH_3), 88.9 (CH), 90.5 (CH), 92.9 (CH), 93.3 (CH), 93.6 (CH), 120.7 (C), 233.7 (CO); HR-MS calcd for $C_{14}H_{18}O_3SiCr$: 314.0430, found: 314.0429.

10: M.p. 50–51 °C (heptane); IR: $\tilde{\nu}$ = 1960, 1870 cm^{-1}; ^{1}H NMR: δ = 1.22 (d, J = 6.0 Hz, 3H), 2.66–2.75 (m, 2H), 2.82–3.90 (m, 1H), 5.04–5.08 (m, 1H), 5.18–5.40 (m, 4H), 7.06–7.10 (m, 2H), 7.19–7.33 (m, 3H); ^{13}C NMR: δ = 19.7 (CH_3), 40.2 (CH), 45.1 (CH_2), 91.3 (CH), 91.9 (CH), 92.2 (CH), 92.5 (CH), 93.5 (CH), 118.0 (C), 126.4 (CH), 128.3 (2 × CH), 129.4 (2 × CH), 139.0 (C), 233.2 (CO); HR-MS calcd for $C_{18}H_{16}O_3Cr$: 332.0505, found: 332.0505.

11: M.p. 44 °C (hexane); IR: $\tilde{\nu}$ = 1957, 1863, 1730 cm^{-1}; ^{1}H NMR: δ = 1.50 (d, J = 7.0 Hz, 3H), 3.40 (q, J = 7.0 Hz, 1H), 3.72 (s, 3H), 5.24–5.42 (m, 4H), 5.49–5.54 (m, 1H); ^{13}C NMR: δ = 17.7 (CH_3), 43.8 (CH), 52.4 (CH_3), 91.3 (2 × CH), 92.4 (CH), 94.3 (CH), 109.7 (C), 173.3 (CO), 232.5 (CO); HR-MS calcd for $C_{13}H_{12}O_5Cr$: 300.0090, found: 300.0091.

12: M.p. 117–118 °C (heptane); IR: $\tilde{\nu}$ = 1957, 1868, 1640 cm^{-1}; ^{1}H NMR: δ = 1.45 (d, J = 8.0 Hz, 3H), 2.99 (s, 3H), 3.18 (s, 3H), 3.66 (q, J = 8.0 Hz, 1H), 5.20–5.24 (m, 1H), 5.25–5.30 (m, 1H), 5.38–5.42 (m, 1H), 5.56–5.62 (m, 1H); ^{13}C NMR: δ = 19.8 (CH_3), 35.9 (CH_3), 37.8 (CH_3), 40.0 (CH), 91.0 (2 × CH), 93.8 (CH), 94.2 (CH), 94.8 (CH), 111.3 (C), 172.4 (CO), 232.9 (CO); HR-MS calcd for $C_{14}H_{15}O_4NCr$: 313.0406, found: 313.0411.

14: M.p. 36 °C (hexane); IR: $\tilde{\nu}$ = 1957, 1870 cm^{-1}; ^{1}H NMR: δ = 1.23 (t, J = 7.0 Hz, 3H), 1.42 (d, J = 6.5 Hz, 3H), 2.18 (s, 3H), 3.57 (dq, J = 9.5, 7.0 Hz, 1H), 3.64 (dq, J = 9.5, 7.0 Hz, 1H), 4.08 (q, J = 6.5 Hz, 1H), 5.12 (d, J = 7.0 Hz, 1H), 5.14 (d, J = 7.0 Hz, 1H), 5.44 (d, J = 7.0 Hz, 1H), 5.61 (d, J = 7.0 Hz, 1H); ^{13}C NMR: δ = 15.4 (CH_3), 20.4 (CH_3), 23.2 (CH_3), 65.0 (CH_2), 75.0 (CH), 91.5 (CH), 91.8 (CH), 92.7 (CH), 93.5 (CH), 109.7 (C), 111.0 (C), 233.3 (CO); HR-MS calcd for $C_{14}H_{16}O_4Cr$: 300.0454, found: 300.0451.



13 **14** **15**

Scheme 5. a) EtBr, NaH, THF, sealed tube, 50 °C, 7 h, 70%; b) $Cr(CO)_6$, Bu_2O, THF, 145 °C, 30 h, 76%; c) LiDBB, THF, −78 °C, then 5-iodo-2-methyl-2-pentene, 27%; d) air, sunlight, 99%.

(HPLC). The analytical and spectroscopic data of **15** were in agreement with those reported in the literature.[19] In this example the overall stereochemical retention was unequivocally established by determining the absolute configuration of the product **15** from its molecular rotation ($[\alpha]_D^{20} = +31$; c = 0.95 in $CHCl_3$).[20]

In conclusion, we have developed a new, convenient method for the stereospecific umpolung of readily available chiral 1-arylalkanol–$Cr(CO)_3$ derivatives. This was accomplished by exploiting the configurative stability of the $Cr(CO)_3$-complexed benzylic radical and anion intermediates. Having demonstrated the usefulness of this novel concept, we are now investigating the scope of the methodology by using different substrates and electrophiles. This investigation will include the use of other transition metal π complexes.[21]

Experimental Section

Lithium (ca. 40 mg, excess) was added under an argon atmosphere to a solution of 4,4′-di-*tert*-butylbiphenyl (188 mg, 0.71 mmol) in dry THF (7 mL) in a Schlenk tube equipped with a glass stirring bar. The mixture was stirred rapidly at 0 °C for 3 h. The blue/green solution was then transferred by cannula to a second Schlenk tube cooled to −78 °C leaving the excess lithium metal behind. A solution of **8** (100 mg, 0.35 mmol) in dry THF (2 mL) was injected into the solution of LiDBB and the resulting dirty red solution was stirred at −78 °C for 30 min before the appropriate electrophile (2 equiv) was added under argon with a syringe. After stirring the reaction mixture for 1 h at −78 °C it was quenched by careful addition of wet *tert*-butyl methyl ether (20 mL) and water (5 mL). The mixture was allowed to warm to room temperature before more water (30 mL) was added. The organic phase was separated and the aqueous layer washed with more *tert*-butyl methyl ether (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent removed in vacuo to give a brown-yellow residue. Chromatography of the residue (SiO_2, EtOAc/hexane (5/95), then to more polar mixtures of EtOAc/hexane) afforded the desired products.

Received: December 29, 1998 [Z12849IE]
German version: *Angew. Chem.* **1999**, *111*, 1721–1724

Keywords: arene complexes · chirality transfer · chromium · electron transfer · umpolung

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[12] For the origins of the term "umpolung", see a) D. Seebach, *Angew. Chem.* **1969**, *81*, 690; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 639; b) D. Seebach, *Angew. Chem.* **1979**, *91*, 259; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239.
[13] (*R*)-**6** was prepared from acetophenone by enantioselective, oxazaborolidine-catalyzed borane reduction; for a recent review, see E. J. Corey, C. Helal, *Angew. Chem.* **1998**, *110*, 2093; *Angew. Chem. Int. Ed.* **1998**, *37*, 1986.
[14] P. K. Freeman, L. L. Hutchinson, *J. Org. Chem*. **1980**, *45*, 1924.
[15] The use of LiDBB for the reductive lithiation of acetals derived from benzaldehyde–$Cr(CO)_3$ derivatives has been reported, see M. J. Siwek, J. R. Green, *Synlett* **1996**, 560.
[16] The enantiomeric excess was determined on a *Daicel Chiralcel OJ* column with hexane/isopropanol mixtures as eluant.
[17] A similar type of chirality transfer is involved in S_N1 transformations in the benzylic position of arene–$Cr(CO)_3$ complexes;[2e] for a recent report, see U. Englert, A. Salzer, D. Vasen, *Tetrahedron Asymmetry* **1998**, *9*, 1867.
[18] D. Seebach, A. R. Sting, M. Hoffmann, *Angew. Chem.* **1996**, *108*, 2880; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2708.
[19] For previous syntheses of nonracemic α-curcumene, see a) M. C. Pirrung, A. T. Morehead, Jr. in *The Total Synthesis of Natural Products*, *Vol. 10* (Ed.: D. Goldsmith), Wiley, New York **1997**, p. 29, and references therein; for a more recent synthesis of (+)-α-curcumene (**15**), see b) A. I. Meyers, D. Stoianova, *J. Org. Chem.* **1997**, *62*, 5219.
[20] It has been established unequivocally that (+)-α-curcumene has the *S* configuration.[19]
[21] Density functional calculations predict, for instance, the barrier of racemization for the pseudo-benzylic radical formally derived from ethylferrocene to be 11.4 kcal mol^{-1}.

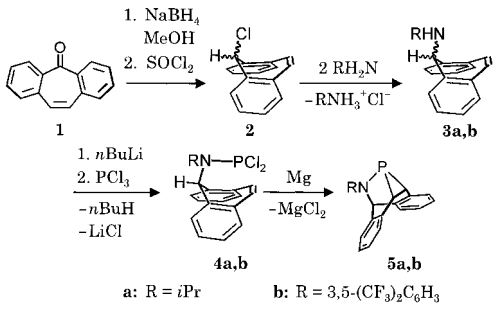
Very Stable Phosphiranes**

Jürgen Liedtke, Sandra Loss, Gilles Alcaraz, Volker Gramlich, and Hansjörg Grützmacher*

Dedicated to Professor Edgar Niecke on occasion of his 60th birthday

Phosphiranes are strained three-membered PC_2-heterocycles[1] which are potentially interesting ligands for homogeneous transition metal catalyst complexes. Their small sum of bond angles at the phosphorus center ($\Sigma\sphericalangle$(P): 240–275) should make them good π acceptors; however, these heterocycles are usually labile towards [2+1] cycloreversions into phosphinidines, RP, and olefins.[2] Although in recent years some rather stable phosphiranes bearing bulky substituents at the phosphorus center (i.e. *t*Bu, adamantyl, mesityl, supermesityl, $N(SiMe_3)_2$) have been prepared,[3] their use in catalysis was found to be limited because of ligand decomposition.[4] In order to suppress this undesired cycloreversion reaction, we searched for a simple high-yield synthesis of phosphiranes, in which the PC_2 ring is embedded in a polycyclic framework.[5]

Starting from the dibenzoannelated tropolone **1**, amines **3a** and **3b** are obtained following known literature procedures.[6] After lithiation and subsequent reaction with PCl_3 the dichloroaminophosphanes **4a** and **4b** are isolated as colorless crystals in more than 90% yield. Using commercially available magnesium turnings and thf as solvent, dehalogenation of **4a** and **4b** led to gram quantities of the amino-substituted[7] phosphiranes **5a** and **5b** in excellent yields (>90%; Scheme 1).



Scheme 1. Synthesis of **5a** and **5b**.

Formally these compounds are formed by an intramolecular [2+1] cycloaddition of an R_2NP phosphinidene unit to the C–C double bond of the central seven-membered ring of

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[**] We thank the ETH-Zürich for financial support and especially Prof. P. S. Pregosin for fruitful discussions. S.L. thanks the DAAD for a grant.

  1433-7851/99/3811-1623 $ 17.50+.50/0