stabilities, the nucleobases close to the 3′-ends have to be taken into account. Biological phenomena that concern the accuracy of ribosomal translation should, particularly, be newly analysed in terms of their codon context. In this sense, we are extending the current studies towards a systematic comparison of coded and recoded codon–anticodon complexes encountered during ribosomal tRNA slippage, in order to reveal differences in the base-stacking patterns as a determinant for frameshift events.[15]

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[1] a) B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, J. D. Watson, *Molecular Biology of the Cell*, Garland, New York, **1995**; b) C. M. T. Spahn, K. H. Nierhaus, *Biol. Chem.* **1998**, *379*, 753–772.

[2] J. H. Cate, M. M. Yusupov, G. Z. Yusupova, T. N. Earnest, H. F. Noller, *Science* **1999**, *285*, 2095–2104.

[3] a) G. M. Clore, A. M. Gronenborn, L. W. McLaughlin, *J. Mol. Biol.* **1984**, *174*, 163–173; b) G. M. Clore, A. M. Gronenborn, E. A. Piper, L. W. McLaughlin, E. Graeser, J. H. van Boom, *Biochem. J.* **1985**, *221*, 737–751; for codon–anticodon interactions in general, see: c) S. Yoshizawa, D. Fourmy, J. D. Puglisi, *Science* **1999**, *285*, 1722–1725; d) R. C. Morris, K. G. Brown, M. S. Elliott, *J. Biomol. Struct. Dyn.* **1999**, *16*, 757–774; e) V. I. Lim, G. V. Aglyamova, *Biol. Chem.* **1998**, *379*, 773–781; f) D. Smith, M. Yarus, *Proc. Natl. Acad. Sci. USA* **1989**, *86*, 4397–4401.

[4] W. Saenger, *Principles of Nucleic Acid Structure*, Springer, Berlin, **1984**, pp. 141–149.

[5] a) E. Westhof, P. Dumas, D. Moras, *Acta Crystallogr. Sect. A* **1988**, *44*, 112–123; b) M. Sprinzl, C. Horn, M. Brown, A. Ioudovitch, S. Steinberg, *Nucleic Acids Res.* **1998**, *26*, 148–153.

[6] For examples of experimental references to interactions of this kind see: a) D. Ayer, M. Yarus, *Science* **1986**, *231*, 393–395; for theoretical concepts such as "The Hypercycle" see also: b) M. Eigen, P. Schuster, *Naturwissenschaften* **1978**, *65*, 341–369.

[7] For the natural occurrence and significance of m^1G see: a) G. R. Björk in *tRNA: Structure, Biosynthesis, and Function* (Eds.: D. Söll, U. RajBhandary), ASM Press, Washington DC, **1995**, pp. 165–205; b) S. Yokoyama, S. Nishimura in *tRNA: Structure, Biosynthesis, and Function* (Eds.: D. Söll, U. RajBhandary), ASM Press, Washington DC, **1995**, pp. 207–223; for the preparation of m^1G building blocks for automated solid-phase synthesis see: c) M. Sekine, T. Satoh, *J. Org. Chem.* **1991**, *56*, 1224–1227; d) P. F. Agris, A. Malkiewicz, A. Kraszewski, K. Everett, B. Nawrot, E. Sochacka, J. Jankowska, R. Guenther, *Biochimie* **1995**, *77*, 125–134.

[8] Linkers based on ethylene glycol, tri- and tetrakisethylene glycol phosphate, and 1-hydroxy-propan-3-phosphate were optimized at various length as loop replacements within the hairpin sequences rUGGA-UUUU-UCCAG, rUCCAG-UUUU-UGGA, and rUGGA-UUUU-GUCCA: W. Pils, R. Micura, unpublished results; see also: a) S. Rumney, E. T. Kool, *J. Am. Chem. Soc.* **1995**, *117*, 5635–5646; b) F. Benseler, D.-j. Fu, J. Ludwig, L. W. McLaughlin, *J. Am. Chem. Soc.* **1993**, *115*, 8483–8484; c) A. C. Moses, A. Schepartz, *J. Am. Chem. Soc.* **1997**, *119*, 11591–11597; d) J. P. Bartley, T. Brown, A. N. Lane, *Biochemistry* **1997**, *36*, 14502–14511; e) M. Durant, K. Chevrie, M. Chassignol, N. T. Thuong, J. C. Maurizot, *Nucleic Acid. Res.* **1990**, *18*, 6353–6359; f) M. Y.-X. Ma, K. McCallum, S. C. Climie, R. Kuperman, W. C. Lin, M. Sumner-Smith, R. W. Barnett, *Nucleic Acids Res.* **1993**, *21*, 2585–2589.

[9] $tRNA^{Phe}$ comprising m^1G (position 37) together with guanosine or 2′-*O*-methylguanosine (position 34) is found in several organisms see: ref. [5b].

[10] R. Micura, *Chem. Eur. J.* **1999**, *5*, 2077–2082.

[11] a) L. Marky, K. Breslauer, *Biopolymers* **1987**, *26*, 1601–1620; b) T. Xia, D. H. Mathews, D. H. Turner in *Comprehensive Natural Product Chemistry*, *Vol. 8* (Eds.: D. Söll, S. Nishimura, P. Moore), Elsevier, Oxford, UK, **1999**, pp. 21–47; c) M. Petersheim, D. H. Turner, *Biochemistry* **1983**, *22*, 256–263.

[12] P. Strazewski, *Helv. Chem. Acta* **1995**, *78*, 1112–1143.

[13] Effects of stabilization by tRNA-purine-37 are discussed, but have only been quantified with respect to tRNA/tRNA-dimerizations so far. See: C. Houssier, H. Grosjean, *J. Biomol. Struct. Dyn.* **1985**, *3*, 387–408.

[14] For the relevance of m^1G concerning frameshifting see: G. R. Björk, *EMBO J.* **1999**, *18*, 1427–1434.

[15] a) J. Atkins, R. Gesteland in *tRNA: Structure, Biosynthesis, and Function* (Eds.: D. Söll, U. RajBhandary), ASM Press, Washington DC, **1995**, pp. 471–490; b) R. Gesteland, J. Atkins, *Annu. Rev. Biochem.* **1996**, *65*, 741–768; c) P. Farabaugh, *Annu. Rev. Genet.* **1996**, *30*, 507–528.

A Convenient and General Tin-Free Procedure for Radical Conjugate Addition**

Cyril Ollivier and Philippe Renaud*

Radical reactions are becoming an extremely useful tool in organic synthesis, particularly for the formation of carbon–carbon bonds in intra- and intermolecular processes.[1] The very rapid development of these reactions could be attributed to the emergence of highly efficient ways to conduct them. Among these methods, the tin hydride mediated addition of radicals to activated alkenes has played a major role.[2] However, the application of this reaction for the synthesis of pharmaceuticals is severely limited by the toxicity of the tin reagents and by the difficulty in removing traces of organotin residues from the final products. Therefore, alternative ways of running radical reactions are under intensive investigation.[3] Recently, we have reported a modified version of the Brown–Negishi reaction[4] where efficient hydroborations with catecholborane and radical additions to enones and enals were performed in a one-pot procedure (Scheme 1).[5a] This oxygen-initiated reaction proved to be efficient with enones and enals. However, other classical radical traps such as unsaturated esters, amides, and sulfones failed to react. Herein, we present an efficient procedure to run one-pot hydroboration for radical addition to any kind of activated alkenes. The reaction is based on the use of a Barton carbonate as radical chain transfer reagent (RCTR).[6]

The failure of our modified version of the Brown–Negishi reaction with classical radical traps such as acrylate moieties was interpreted as a consequence of an inefficient propagation step resulting from the reaction between the radical adducts and *B*-alkylcatecholboranes. This inefficiency is caused by the lower density of unpaired electrons at the

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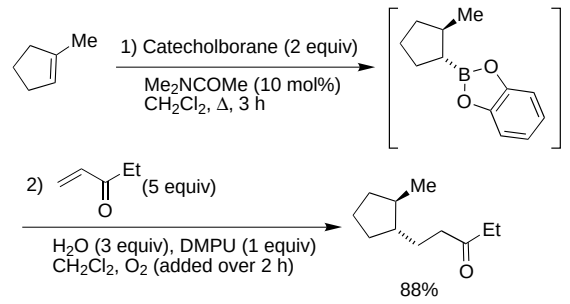
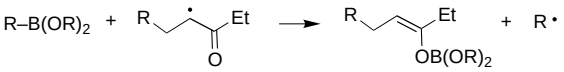
[**] Organoboranes in Radical Reactions. Part 4. This work was generously supported by the Fonds National Suisse de la Recherche Scientifique. We thank Valéry Weber for performing some preliminary experiments. Parts 1–3: see ref. [5].

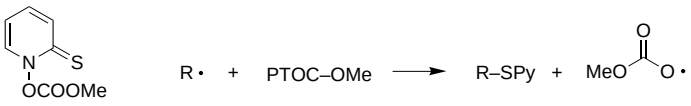


Propagation step:



Scheme 1. Modified Brown–Negishi reaction involving *B*-alkylcatecholboranes.[5a]

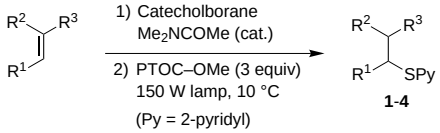
oxygenatom of these radicals relative to ketone–enolate and aldehyde–enolate radicals.[7, 8] Based on this assumption, we thought that, for radical traps other than enones and enals, the use of a chain transfer reagent able to convert the carbon-centered radical adduct into an oxygen-centered radical was necessary. The Barton carbonate PTOC-OMe (PTOC = pyridine-2-thione-*N*-oxycarbonyl),[9] easily prepared by reacting the commercially available sodium salt of *N*-hydroxypyridine-2-thione and methyl chloroformate, should possess the necessary reactivity to act as RCTR (Scheme 2). The yellow solution of the Barton carbonate PTOC-OMe is stable in the dark and is expected to furnish, upon irradiation with a standard lamp, the methoxycarbonyloxyl radical (MeO-COO•). Decarboxylation of this radical to afford the methoxyl radical cannot be excluded; however, this process is known to be slow.[10]



PTOC–OMe carbon-centered radical oxygen-centered radical

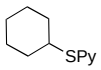
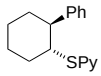
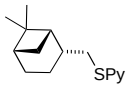
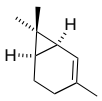
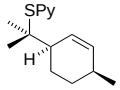
Scheme 2. The radical chain transfer reagent (RCTR) PTOC-OMe converts a carbon-centered into an oxygen-centered radical.

In a preliminary study, we have checked that the methoxycarbonyloxyl radical, generated by the simple irradiation of PTOC-OMe with a 150 W tungsten lamp, was able to react with *B*-alkylcatecholborane and to propagate efficiently the chain reaction. A one-pot procedure starting from the alkene was examined [Eq. (1)]. After hydroboration with catecholborane,[11] the in situ generated alkylborane was treated with three equivalents of PTOC-OMe and the solution was irradiated with a standard 150 W lamp for 12 h at 10 °C; the results are summarized in Table 1. Under these conditions,



1-4 (1)

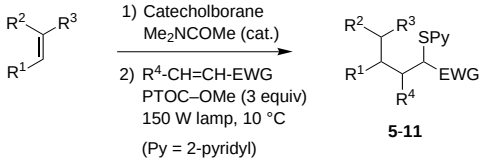
Table 1. Preparation of sulfur-containing derivatives by the hydroboration procedure shown by Equation 1.

Entry	Alkene	Product	Yield[a] [%]	Stereoselectivity
1		**1** 	74 (50[b])	
2		**2** 	62	d.r. = 82:18[c]
3		**3** 	75	d.r. = 90:10[c]
4		**4** 	52	

[a] All reactions used 3 mmol of the olefin. [b] Using 1 equiv of PTOC-OMe. [c] Only major isomer is shown.

sulfur-containing derivatives were easily prepared from primary and secondary alkyl radicals in 62% to 75% yield (Table 1, entries 1–3). Use of only one equivalent of PTOC-OMe led to a decrease of the yield (Table 1, entry 1); however, the cyclohexyl 2-pyridyl sulfide **1** was still isolated in 50% yield proving that the propagation step of the reaction is quite effective. The radical nature of the reaction was proved by the reaction with 2-carene, which gave the cyclohexene derivative **4** resulting from the ring opening of the intermediate cyclopropylmethyl radical (Table 1, entry 4).

Based on these encouraging results, a similar reaction procedure involving hydroboration with catecholborane, irradiation in the presence of five equivalents of an activated alkene as radical trap, and three equivalents of PTOC-OMe as mediator was examined [Eq. (2)]. Despite the greater complexity of this reaction sequence relative to the reaction depicted in Equation 1, we were pleased to notice that the yields were similar, and in several cases even higher, than in the absence of radical traps (Table 2).



5-11 (2)

In the first set of experiments, hydroboration of cyclohexene followed by reaction with different radical traps such as methyl acrylate, dimethyl fumarate, *N*-phenyl maleimide, or phenyl vinyl sulfone was examined (Table 2, entries 1–4). Yields between 70% (methyl acrylate) and 94% (dimethyl fumarate) were obtained. Interestingly, only small amounts of products from the direct reaction of the cyclohexyl radical with PTOC-OMe were observed when using a simple one-pot procedure. Indeed, all reagents are mixed together before irradiation and slow addition of the PTOC-OMe is not required. Similar results were obtained with phenylcyclopentene (Table 2, entry 5). In this case, the *trans* isomer of **9** is formed with a good diastereoselectivity (*trans*:*cis* 97:3). A

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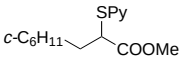
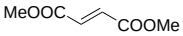
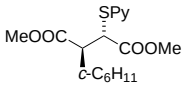
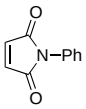
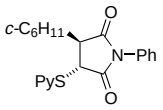
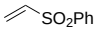
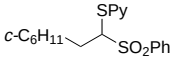
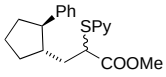
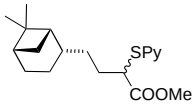
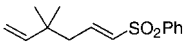
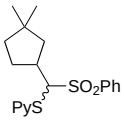
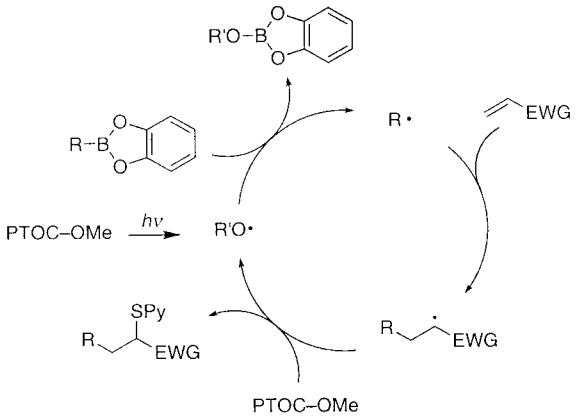
Table 2. Hydroboration and conjugate addition according to Equation 2.

Entry	Alkene	Radical trap	Product	Yield[a] [%] (direct addition)	Steroselectivity
1			**5** 	70 (14)	
2			**6** 	94 ($\leq$2)	d.r. 77:23[b]
3			**7** 	81 ($\leq$2)	d.r. > 98:2
4			**8** 	75 (15)	
5			**9** 	61 (21)	*trans*:*cis* 97:3[c]
6			**10** 	69 (15)	*cis*:*trans* 90:10[c]
7			**11** 	66 ($\leq$2)	d.r. 53:47

[a] All reactions were run on 3 mmol scale. [b] Relative configuration of the major isomer attributed by analogy to related reactions, see ref. [12]. [c] Mixture (1:1) of isomers relative to the center bearing the *S*-pyridyl group.

primary alkyl radical was also generated from β-pinene and added to methyl acrylate with similar efficiency (Table 2, entry 6). In this example, the *cis*/*trans* stereochemistry was controlled during the hydroboration step. In entry 7, the first example of cyclization reaction starting from a diene is presented. The interesting chemo- and regioselective hydroboration of the terminal double bond followed by an intramolecular radical addition furnished the cyclopentane **11** in 66% yield. This cyclization procedure starting from a diene is particularly attractive due to the extremely easy preparation of the starting material. Indeed, no reactive radical precursor such as a bromide or an iodide has to be prepared before running the cyclization reaction. As already mentioned, the yields observed in the conjugate additions compare favorably with the simpler processes described in Equation 1. This could be rationalized by taking into account the polar effects in the chain reaction. The general mechanism of the conjugate addition is depicted in Scheme 3.



Scheme 3. Radical chain mechanism for the conjugate addition of *B*-alkylcatecholboranes to activated olefins (R = alkyl group; EWG = electron withdrawing group; R′O• = MeOCOO•, MeO•).

Irradiation of the PTOC-OMe initiates the reaction by providing a methoxycarbonyloxyl or methoxyl radical (R′O•). This radical reacts with the borane to give the nucleophilic alkyl radical R• that adds to the radical trap. The radical adduct has some electrophilic character due to its substitution by an electron-withdrawing group (EWG) and therefore reacts rapidly with the electron-rich thiocarbonyl group of the PTOC-OMe. This mechanism parallels nicely the tin hydride mediated reaction: The abstraction of an halide atom by the tin radical is replaced by the reaction of an alkoxyl radical with a *B*-alkylcatecholborane. The three radicals involved in the chain reaction all possess a different reactivity to allow efficient fulfillment of the selectivity criteria formulated by Giese.[1a, 2d]

In conclusion, we believe that the present procedure represents a very valuable alternative to the tin hydride mediated reaction for the formation carbon–carbon bonds through a radical process. Good yields of the intermolecular reaction could be achieved in a simple one-pot procedure. Slow addition of the reagents is not necessary when activated radical traps are used. Moreover, the process is nonreductive and furnished products bearing a *S*-pyridyl group that can be

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removed or transformed into a variety of functional groups as amply demonstrated by Barton.[13] Since radical precursors are generated through a hydroboration step, this procedure could take advantage of the chemo- and regioselectivity of the hydroboration and offers a very simple and efficient method for the preparation of highly functionalized systems through inter- and intramolecular radical addition. Applications of this approach to cascade reactions starting from a polyene are currently under investigation. Finally, preparation of optically active materials through enantioselective hydroboration of prochiral alkenes should represent valuable entries into the synthesis of enantiomerically enriched compounds.

Experimental Section

Sulfur inclusion into *B*-Alkylcatecholboranes: Catecholborane (0.64 mL, 6.0 mmol) was added dropwise at 0 °C to a solution of the olefin (3.0 mmol) and *N*,*N*-dimethylacetamide (28.0 μL, 0.3 mmol) in CH_2Cl_2 (2.0 mL). The mixture was heated under reflux for 3 h. Methanol (0.15 mL, 3.6 mmol) was added at 0 °C and the mixture was stirred for 15 min at room temperature. The CH_2Cl_2 was evaporated under vacuum with strict exclusion of O_2.[14] A yellow solution of PTOC-OMe (9.0 mmol), freshly prepared by stirring for 1 h in the dark the sodium salt of *N*-hydroxypyridine-2-thione (1.41 g, 9.45 mmol) and methyl chloroformate (0.7 mL, 9.0 mmol) in benzene (15 mL), was added to the *B*-alkylcatecholborane followed by 1,3-dimethyl hexahydro-2-pyrimidone (DMPU; 0.36 mL, 3.0 mmol). The reaction mixture was irradiated at 10 °C with a 150 W tungsten lamp for about 14 h, and treated with 1N NaOH (20 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic phases were washed with a saturated NaCl solution (30 mL), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/EtOAc).

Conjugate addition: Catecholborane (0.64 mL, 6.0 mmol) was added dropwise at 0 °C to a solution of the olefin (3.0 mmol) and *N*,*N*-dimethylacetamide (28.0 μL, 0.3 mmol) in CH_2Cl_2 (2.0 mL). The reaction mixture was heated under reflux for 3 h. Methanol (0.15 mL, 3.6 mmol) was added at 0 °C and the mixture was stirred for 15 min at room temperature. A yellow solution of PTOC-OMe (9.0 mmol), freshly prepared as previously described, was added to the *B*-alkylcatecholborane followed by the activated alkene (15 mmol) in benzene (15 mL) and DMPU (0.36 mL, 3.0 mmol). In the case of dimethyl fumarate as the alkene, CH_2Cl_2 (15 mL) was used instead of benzene. The reaction mixture was irradiated at 10 °C with a 150 W tungsten lamp for about 14 h, and treated with 1N NaOH (20 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic phases were washed with a saturated NaCl solution (30 mL), dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/EtOAc).

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[1] a) B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon, Oxford, **1988**; b) D. P. Curran in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 715–777; c) W. B. Motherwell, D. Crich, *Free Radical Chain Reactions in Organic Synthesis*, Academic Press, London, **1992**; d) D. P. Curran, N. A. Porter, B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, **1996**; e) J. Fossey, D. Lefort, J. Sorba, *Free Radicals in Organic Synthesis*, Wiley, Chichester, **1995**; f) C. Chatgilialoglu, P. Renaud in *General Aspects of the Chemistry of Radicals* (Ed.: Z. B. Alfassi), Wiley, Chichester, **1999**, pp. 501–538.

[2] a) G. Stork, N. H. Baine, *J. Am. Chem. Soc.* **1982**, *104*, 2321–2323; b) S. D. Burke, W. F. Fobare, D. A. Armistead, *J. Org. Chem.* **1982**, *47*, 3348–3350; c) B. Giese, J. Dupuis, *Angew. Chem.* **1983**, *95*, 633–634; *Angew. Chem. Int. Ed. Engl.* **1983**, *23*, 622–623. For review articles, see ref. [1a] and d) B. Giese, *Angew. Chem.* **1983**, *95*, 771–782; *Angew. Chem. Int. Ed. Engl.* **1983**, *23*, 753–764.

[3] P. A. Baguley, J. C. Walton, *Angew. Chem.* **1998**, *110*, 3272–3283; *Angew. Chem. Int. Ed.* **1998**, *37*, 3072–3082.

[4] H. C. Brown, E. Negishi, *J. Am. Chem. Soc.* **1971**, *93*, 3777–3779.

[5] a) C. Ollivier, P. Renaud, *Chem. Eur. J.* **1999**, *5*, 1468–1473. For related radical reactions involving organoboranes, see b) C. Ollivier, R. Chuard, P. Renaud, *Synlett* **1999**, 807–809; c) N. Kihara, C. Ollivier, P. Renaud, *Org. Lett.* **1999**, *1*, 1419–1422.

[6] This work was presented at the 1999 meeting of the New Swiss, Chemical Society (Basel, October 12, 1999); abstract: C. Ollivier, P. Renaud, *Chimia* **1999**, *53*, 368.

[7] Recently, we have shown that the reaction of *B*-alkylcatecholboranes with stable aminoxyl radicals such as 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) produces cleanly alkyl radicals, see ref. [5b].

[8] It is well established that alkylboranes react efficiently with heteroatom-centered radicals such as alkoxyl radicals. For review articles, see H. C. Brown, M. M. Midland, *Angew. Chem.* **1972**, *84*, 702–710; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 692; A. Ghosez, B. Giese, H. Zipse in *Methoden der Organischen Chemie (Houben-Weyl) 4th ed. 1952–*, Vol. E19a, **1989**, pp. 753–765. Reaction with carbon radicals has not been observed except for a recently reported intramolecular reaction: R. A. Batey, D. V. Smil, *Angew. Chem.* **1999**, *111*, 1912–1915; *Angew. Chem. Int. Ed.* **1999**, *38*, 1798–1800.

[9] M. Newcomb, M. U. Kumar, J. Boivin, E. Crépon, S. Z. Zard, *Tetrahedron Lett.* **1991**, *32*, 45–48; A. L. J. Beckwith, I. G. E. Davison, *Tetrahedron Lett.* **1991**, *32*, 49–52.

[10] A. L. J. Beckwith, B. P. Hay, *J. Am. Chem. Soc.* **1988**, *110*, 4415–4416; A. L. J. Beckwith, B. P. Hay, *J. Am. Chem. Soc.* **1989**, *111*, 230–234.

[11] C. E. Garrett, G. C. Fu, *J. Org. Chem.* **1996**, *61*, 3224–3225.

[12] B. Giese, W. Damm, F. Wetterich, H.-G. Zeitz, *Tetrahedron Lett.* **1992**, *33*, 1863–1866.

[13] D. H. R. Barton, C. Y. Chern, J. C. Jaszberenyi, *Aust. J. Chem.* **1995**, *48*, 407–425, and references therein.

[14] Evaporation of CH_2Cl_2 afforded better results with tertiary radicals. With secondary and primary alkyl radicals, similar yields are obtained without evaporating the solvent. This evaporation step was not employed when running conjugate additions.

"Naked" Phosphorus as a Bent Bridging Ligand**

Peter Kramkowski and Manfred Scheer*

Dedicated to Professor Dirk Walther on the occasion of his 60th birthday

Only a small number of the complexes containing pnicogenido (E^{3-}) ligands of the heavier Group 15 elements (E = P, As, Sb, Bi)[1] are known in which the ligands display low coordination numbers 1 and 2. Only in 1995 were the first complexes of type **A**,[6] with terminal ligands and coordination number 1, synthesized and structurally characterized with the compounds $[(Ar'RN)_3Mo{\equiv}P]$ ($Ar' = 3,5\text{-}C_6H_3Me_2$, $R = C(CD_3)_2CH_3$)[2] and $[('N_3N')M{\equiv}E]$ ['N_3N' = $N(CH_2CH_2NSiMe_3)_3$; E = P, M = W, Mo;[3] E = As, M = W,[4] Mo[5]]. We recently found the asymmetric linear coordination mode **B** with coordination number 2 in the complexes $[('N_3N')M{\equiv}E \rightarrow ML_m]$ ($ML_m = GaCl_3$;[7] $M(CO)_4$, M = Cr, W[5]] and $[(RO)_3W{\equiv}P \rightarrow M(CO)_5]$ (M = Cr, W; R = *t*Bu[8], Ar (2,6-$Me_2C_6H_3$)[9]). Symmetrical linearly bridged complexes of

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