cation (No. 143022, 203518, 265253) and the Kurata Research Grant of the Kurata Foundation, for partial financial support of this work, and Shin-etsu Chemical Co., Ltd., for a gift of trichlorosilane.

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(1) Part I: K. Tamao, J. Yoshida, M. Takahashi, H. Yamamoto, T. Kakui, H. Matsumoto, A. Kurita, and M. Kumada, *J. Am. Chem. Soc.*, **100**, 290 (1978).
(2) Cited from C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements", Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, p 357.
(3) For a pertinent compilation of references, see ref 1.
(4) Indirect oxidative cleavage of the carbon–silicon bond via rearrangement of triorganosilyl peroxybenzoate[5] or α,β-epoxysilanes[6] has been reported.
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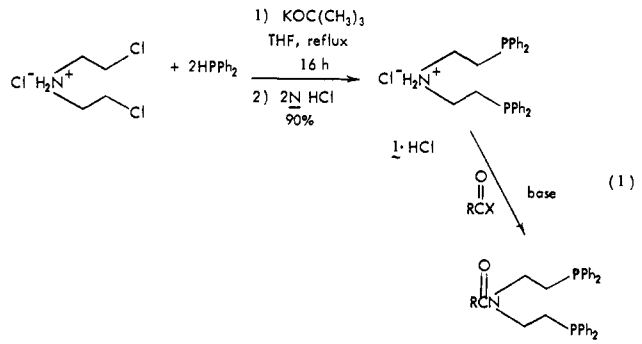
Bis(2-diphenylphosphinoethyl)amine. A Flexible Synthesis of Functionalized Chelating Diphosphines[1]

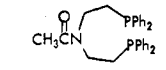
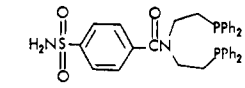
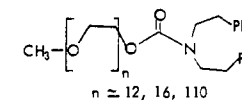
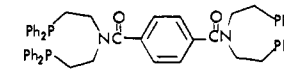
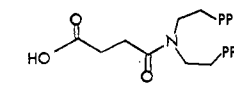
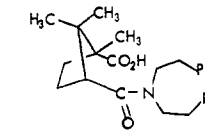
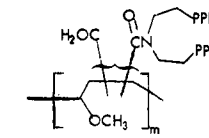
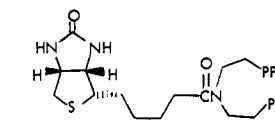
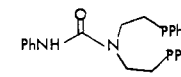
Sir:

Chelating diphosphines are an important class of ligand in inorganic and organometallic chemistry. Applications of these materials in areas such as asymmetric synthesis and catalysis by polymer-bound metals increasingly require incorporation of diphosphine units into complicated organic structures. The most commonly used methods for synthesis of polydentate phosphines involve the introduction of multiple individual phosphine units into a precursor, ordinarily by displacement of halides or tosylates by diphenylphosphide ion or by addition of diphenylphosphine to activated olefins.[2] These syntheses suffer from unpredictable yields and incompatibility with many functional groups. Here we outline an alternative and widely applicable synthetic method in which the chelating diphosphine moiety is introduced as a unit, taking advantage of the highly reliable coupling of amines with carbonyl halides, anhydrides, active esters, and isocyanates (eq 1).



(1)

Table I. Functionalized Diphosphines Derived from **1**[a]

Compd	Structure	Reacting group	Yield, %
2		RCOCl or $(RCO)_2O$, CH_2Cl_2, Et_3N	> 95
3		RCOCl, Pyr, THF	50[b]
4		ROCOCl, THF (n = 12, 16) CH_2Cl_2 (n = 110), Et_3N	(high)[c]
5		$R(COCl)_2$, CH_2Cl_2, Et_3N	70
6		Anhydride, THF, Et_3N	96
7		Anhydride, BuLi, THF[d]	85[d]
8		Anhydride, CH_3CN, Et_3N	95[e]
9		, DMF, Et_3N	84
10		PhN=C=O, CH_2Cl_2, Et_3N	93

[a] Except where indicated, **1** was allowed to react with 1 equiv of the derivatizing agent for 15 h at room temperature. Yields are based on **1** unless noted otherwise. Satisfactory elemental analyses were obtained for compounds **2**, **3**, **7**, **9**, and **10**. Compounds **4** and **8** were intrinsically heterogeneous, and were amenable only to spectroscopic characterization, although elemental analysis afforded the approximate degree of substitution in **8**. Compounds **5** and **6** were characterized spectroscopically. [b] The **1** involved in this reaction was generated directly by reaction of $LiPPh_2$[3] and $HN(CH_2CH_2Cl)_2$ and was acylated in situ. The yield is based on $HPPh_2$. [c] The starting materials for these preparations were commercial monomethyl polyethylene glycols. The average degree of polymerization of these materials is indicated by *n*. Reactions were carried out at room temperature for these durations: $n = 12$, 16 h; $n = 16$ and 110, 1 h. The product yield was difficult to estimate accurately, but essentially all of the **1** was converted to a water-soluble derivative. [d] Compound **1** was converted to $LiN(CH_2CH_2PPh_2)_2$ by reaction with butyllithium, before addition of camphoric anhydride. [e] Prepared by reaction of poly(methyl vinyl ether-*co*-maleic anhydride) with quantities of **1** sufficient to consume between 10 and 50% of the anhydride moieties. The initial product was a pink gum, insoluble in acetonitrile, which contained the major part of the **1** added. This gum was suspended in a 1:1 mixture of ~0.1 N aqueous HCl and acetonitrile and refluxed for 30 min to hydrolyze remaining anhydrides. The resulting white solid was dried at ~0.5 Torr.

The central intermediate in this scheme, bis(2-diphenylphosphinoethyl)amine (**1**) was prepared and isolated as a

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crystalline, air-stable, hydrochloride salt by the following procedure. Diphenylphosphine[3] (28.0 mL, 29.6 g, 160 mmol) was added by syringe to a suspension of potassium *tert*-butoxide (28 g, 250 mmol) in 500 mL of dry THF under argon. The resulting deep red solution was stirred for 5 min and bis(2-chloroethyl)amine hydrochloride (14.3 g, 80 mmol) added as a coarse powder.[4] The mixture was refluxed for 16 h, poured into 800 mL of hexane, and washed in succession with 300-mL portions of 10% aqueous NaOH and saturated aqueous NaCl solutions. The hexane layer was separated, filtered, and stirred vigorously with 800 mL of 2 N aqueous HCl solution giving a dense white precipitate of **1** HCl. Recrystallization from 300 mL of boiling acetonitrile gave a 90% yield (34.4 g) of fine white needles, mp 174.5–175.5 °C.[5,6]

Acylation of **1** was accomplished by a number of the procedures commonly used for the formation of amides (Table I). Isocyanates and carboxylic acid chlorides, anhydrides, and active esters appear to react cleanly with the nitrogen atom of **1**. Sulfonyl chlorides and cyanogen bromide give complex product mixtures: no N-functionalized derivatives of **1** have been isolated from these reactions. D-Gluconic acid δ-lactone, *O*-alkylisouronium bromides, and *S*-alkylisothiouronium bromides were unreactive toward **1**. A representative procedure is that for *N,N*-bis(2-diphenylphosphinoethyl)biotinamide (**9**). The *N*-hydroxysuccinimide active ester of *d*-biotin[7] (67 mg, 0.20 mmol), **1** HCl (95 mg, 0.20 mmol), and triethylamine (80 mg, 0.80 mmol) were added to 3 mL of degassed DMF. The reaction mixture was stirred at room temperature for 60 h under argon, slowly diluted with 8 mL of water, and cooled to 4 °C. The resulting white precipitate was collected, washed with water, and dried (0.3 Torr), yielding 112 mg of **9** as a waxy solid.[8] Other compounds in Table I were also prepared using unexceptional procedures.

The range of structural types represented in Table I attests to the generality of this method of preparing phosphines appropriately functionalized for specific uses. Compounds **3** and **9** introduce diphosphine ligands into proteins (carbonic anhydrase[9] and avidin[10]) by noncovalent binding; **4** is a water-soluble diphosphine which serves as the basis for water-soluble rhodium-based homogeneous hydrogenation catalysts;[11] the rhodium(I) complex of **7** is an asymmetric hydrogenation catalyst showing modest enantioselectivity (30% enantiomeric excess for hydrogenation of α-acetamidoacrylic acid); **5** is a potential tetradentate phosphine; **8** is a chelating polyphosphine showing interesting surfactant properties in aqueous solutions.

The usefulness of this procedure for diphosphine synthesis rests on four features. First, the formation of amides by acylation of amines is one of the best understood and most general coupling methods in organic chemistry. The fact that it is possible to acylate the secondary amine of **1** without interference by the diphenylphosphine groups makes it possible to utilize this reaction for the preparation of a wide variety of diphosphines. Second, since the preformed diphosphine moiety is introduced as a unit, yields are relatively high. Third, the coupling reaction is compatible with a range of functionalities. Fourth, carboxylic acids and their derived acylating agents are readily available in great variety. We will describe details of the procedures reported here, extensions to other aminopolyphosphines and acylating agents, and applications of the resulting functionalized phosphines in subsequent publications.

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(3) R. E. Ireland and D. M. Wells, *Org. Syn.*, **56**, 44 (1977).
(4) *CAUTION:* Bis(2-chloroethyl)amine is a severe irritant and a potential carcinogen.
(5) NMR ($CDCl_3$): δ 2.3–3.3 (m, 8 H), 7.0–7.6 (m, 20 H), 9.9 (s, 2 H). Anal. Calcd for $C_{28}H_{30}ClNP_2$: C, 70.42; H, 6.33; N, 2.93. Found: C, 70.30; H, 6.27; N, 2.90.
(6) Recrystallization is unnecessary for some further uses, but high purity for **1** HCl makes it easier to crystallize difficulty purified derivatives such as **5** and **9**.
(7) This compound was prepared by the method of E. Bayer and M. Wilchek, *Methods Enzymol.*, **34**, 265 (1974); it was recrystallized from acetonitrile with charcoal to mp 213–214 °C.
(8) This substance was typical of those in Table I in being poorly crystalline. Its IR spectrum (Nujol, cm^{-1}) had peaks at 1705 and 1630, and its NMR spectrum showed aryl and biotinyl absorptions. Anal. Calcd for $C_{38}H_{43}N_3O_2P_2S$: C, 68.35; H, 6.49; N, 6.29. Found: C, 68.34; H, 6.40; N, 5.99.
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(11) R. Nuzzo, M. Wilson, and G. M. Whitesides, unpublished work; D. Feitler, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1977.
(12) Predoctoral trainee: NIH 5 T32 CA 09112 CT.

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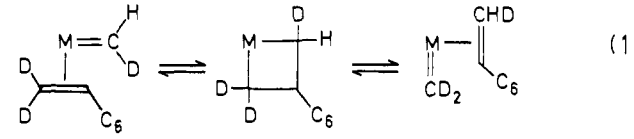
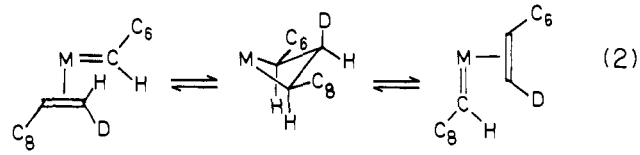
Stereochemistry of the Degenerate Metathesis of Terminal Alkenes—the Nature of the Chain-Carrying Metal–Carbene Complex

Sir:

The recent demonstration that the transition metal catalyzed metathesis of alkenes proceeds by a nonpairwise process[1] is most readily explained by a mechanism involving the equilibration of a metal-carbene-alkene complex with a metallacyclobutane.[2] The degenerate metathesis of terminal alkenes has been demonstrated with deuterium labeled alkenes[3] and was found to be much more rapid than productive metathesis which yields ethylene and an internal alkene. A priori, there are two explanations which can account for the degenerate metathesis of terminal alkenes. (1) The reaction may proceed



(1)



(2)

via a M=CH_2-carbene complex which reacts selectively with a terminal alkene to transfer the most substituted alkylidene unit and to regenerate a M=CH_2-carbene complex. Such a selectivity could be attributed either to steric preferences or to electronic stabilization of a negatively polarized carbene ligand, $M^+—C^-H_2$. (2) Alternatively, the reaction may proceed via a M=CHR complex which reacts selectively with a terminal alkene to transfer the least substituted alkylidene unit and to regenerate a M=CHR-carbene complex. Such a selectivity could be attributed to electronic stabilization of a positively polarized carbene ligand, $M^-—C^+HR$.

Model studies with isolated carbene complexes have led to

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