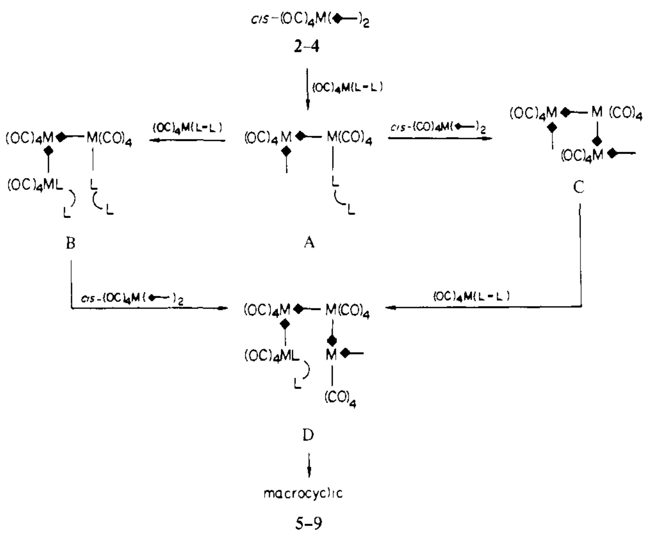
Scheme II



^{a} L-L = NBD or tmpa.

the 3-fold axes of the ligands at three metal corners of the polymer chain, cyclization beyond the tetramer stage is quite difficult.[5] If **5-9** were acylic oligomers, more than two ^{31}P NMR peaks would have been expected for even the simplest stable example (C in Scheme II) with the unligated PC_3 phosphorus atoms appearing at a chemical shift well separated from the coordinated PC_3 phosphorus atoms. Aside from the expectation that A, B, and D would be unstable, the proton NMR and IR spectra of **5-9** display insufficient peaks to be formulated as any one of these intermediates.

Experimental Section. *cis*-$(OC)_4M(NBD)$ (M = Cr,[6] Mo,[6] W[7]), $(OC)_4Mo(tmpa)$,[8] and **1**[9] were made as described previously. Infrared bands given are for the A_1^2, A_1^1, and B_1B_2 CO stretches in CH_2Cl_2. **2** (first prepared in 4% yield by Allison et al.[2]) was synthesized in 49% yield by adding a solution of 0.53 g (2.1 mmol) of *cis*-$(OC)_4Cr(NBD)$ in 25 mL of methylcyclohexane to a stirred solution of 0.69 g (4.6 mmol) of **1** in 25 mL of methylcyclohexane at room temperature over a period of 2 h. After the solution continued stirring for 4 h, the white solid that precipitated was filtered and chromatographed with acetone on a Florisil column to yield 0.48 g (49%) of **2**. The IR and ^{1}H and ^{31}P NMR parameters agree with those reported earlier.[2] **3** was similarly prepared and purified by dissolving it in $CHCl_3$ and precipitating with pentane (yield 36%; IR 2042, 1955, 1929 cm^{-1}). **4** and its ligand isomer *cis*-$(OC)_4Mo[P(CH_2O)_3P][P(OCH_2)_3P]$ were prepared analogously by using *cis*-$(OC)_4Mo(tmpa)$ and chromatographed on a Florisil column with 3:1 hexane:ethyl acetate (yield of isomer 6.6%; IR 2039, 1955, 1936 cm^{-1}; yield of **4** 31%; IR 2041, 1954, 1938 cm^{-1}).

5 was made by refluxing a solution of 0.14 g (0.30 mmol) of **2** and 0.08 g (0.30 mmol) of *cis*-$(OC)_4Cr(NBD)$ in 35 mL of CH_2Cl_2 for 1 day. After filtration, solvent removal left a light yellow solid, which was purified similarly to **3** (yield 85%; IR 2036, 1960, 1937 cm^{-1}). **6** and **7** were prepared analogously except that *cis*-$(OC)_4Mo(tmpa)$ was used for **7** (yield of **6** 86%; IR 2041, 1963, 1933 cm^{-1}; yield of **7** 86%; IR 2050, 2036 (both A_1^2), 1970, 1942 cm^{-1}). **8** and **9** were prepared analogously to **5** by reacting *cis*-$(OC)_4Mo(tmpa)$ with **2** and **3**, respectively (yield of **8** 40%; 2036, 1959, 1938; yield of **9** 70%; IR 2040, 1936, 1936 cm^{-1}).

Acknowledgment. We are grateful to the National Science Foundation for a grant in support of this work. We also thank P. D. Plummer for the preparation of **4** and *cis*-$(OC)_4Mo[P(CH_2O)_3P][P(OCH_2)_3P]$ and D. A. Allison for the ^{1}H and ^{31}P NMR spectral analysis of the latter compound.

Registry No. 1, 4579-03-7; **2**, 26062-35-1; **3**, 85202-47-7; **4** (isomer 1), 85202-48-8; **4** (isomer 2), 85202-54-6; **5**, 85202-49-9; **6**, 85202-50-2; **7**, 85202-51-3; **8**, 85202-52-4; **9**, 85202-53-5; $(OC)_4Cr(NBD)$, 12146-36-0; $(OC)_4W(NBD)$, 12129-25-8; $(OC)_4Mo(NBD)$, 12146-37-1; *cis*-$(OC)_4Mo(tmpa)$, 30003-65-7.

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(5) If intermediate D in Scheme II were to polymerize further, relatively strainless ring closure could occur to form a 60-membered ring macrocycle containing 8 metal atoms. Synthesis of such an enlarged macrocycle in the high yields realized for **5-9** is unexpected. Moreover, a model of such a macrocycle reveals that it would be conformationally rigid with half the metal atoms in a different chemical environment, thus engendering substantially more complicated NMR and IR spectra than are observed for **5-9**.

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Isolation of Some Sterically Protected Unsymmetrical Diphosphenes: Nature of the Phosphorus-Phosphorus Double Bond

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In recent years there has been much interest in compounds with a multiple bond containing third-row elements such as phosphorus(III)[1-4] and silicon,[5-9] because of their unusual chemical and physical properties. Numerous attempts to prepare such compounds have been made for their characterization.

By introducing a very bulky group into a molecule, we have been successful in the isolation and characterization of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1a**) as a stable compound containing a phosphorus-phosphorus double bond,[10] which has been of current attraction.[11-13] It is of interest to prepare unsymmetrical diphosphenes, which cannot be prepared from a dechlorination reaction with magnesium, in order to investigate the nature of the P-P double bond.

We now report an alternative way to prepare sterically stabilized diphosphenes, which is particularly suitable for the preparation of unsymmetrical diphosphenes (**1b-d**). The method, one of the

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Table I. Some Spectral Data of Diphosphenes (1)

diphosphene	^{31}P NMR (C_6D_6)^a δ_P, ppm P^2	P^1	$^1J_{PP}$, Hz	MS, *m/e* found (calcd)	UV (CH_2Cl_2), λ_{max} (ϵ), nm
1a^b	492.4			552.4012 (552.4012)	284 (15660), 340 (7690), 460 (1360)
1b	517.0	480.1	583.5	510.3521 (510.3542)	279 (13800), 330 (5080), 461 (468)
1c	540.4	467.6	573.7	426.2614 (426.2604)	273 (9830), 326 (2500), 456 (220)
1d	525.5	455.5	548.7		

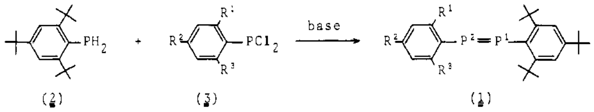
^{a} 1d was measured in THF. ^{b} Taken from ref 10.

Table II. Ab Initio Calculation of the Geometries of P_2H_2, PH, P_2, and P_2H_4

molecule	point group	geometrical parameter and energy^a	44-31G*	44-31G	STO-3G	exptl
trans-P_2H_2	C_{2h}	*r*(PP)	1.996	2.121	1.961	
		r(PH)	1.419	1.444	1.387	
		∠PPH	95.1	95.4	95.9	
		energy	−681.8527	−681.7414	−674.9227	
cis-P_2H_2	C_{2v}	*r*(PP)	2.000	2.122	1.964	
		r(PH)	1.414	1.445	1.387	
		∠PPH	100.4	100.4	99.7	
		energy	−681.8469	−681.7372	−674.9166	
PH, singlet	$C_{\infty v}$	*r*(PH)	1.422	1.470	1.397	
		energy	−340.8227	−340.7930	−337.3486	
PH, triplet	$C_{\infty v}$	*r*(PH)	1.422			1.422^c
		energy	−340.9037			
P_2	$D_{\infty v}$	*r*(PP)	1.847	1.914^b		1.893^c
		energy	−680.7081	−680.6073^b		
P_2H_4	C_{2h}	*r*(PP)	2.250	2.354^b		2.219^d
		r(PH)	1.411	1.432^b		1.417^d
		∠(HPH)	93.2			
		∠(PPH)	94.7			
		energy	−683.0397	−682.9215^b		

^{a} Units are shown in angstroms, degrees, and atomic units. ^{b} Taken from ref 24. ^{c} Experimental data from ref 25. ^{d} Experimental data from ref 26.

Scheme I^a



^{a} Key: a, $R^1 = R^2 = R^3 = t$-Bu; b, $R^1 = R^2 = t$-Bu, R^3 = Me; c, $R^1 = R^2 = R^3$ = Me; d, $R^1 = R^2 = R^3$ = H.

standard preparative methods of cyclopolyphosphines,[14] involves dehydrochlorination reaction of 2,4,6-tri-*tert*-butylphenylphosphine (**2**) and the corresponding phosphonous dichlorides (**3**)[15] in the presence of organic bases as shown in Scheme I.

2,4,6-Tri-*tert*-butylphenylphosphonous dichloride (**3a**) was reduced by lithium aluminum hydride in ether at 0 °C to give **2** almost quantitatively. **2** was recrystallized from ethanol; mp 150–152 °C; ^{31}P NMR ($CDCl_3$) −129.9 ppm (from external 85% H_3PO_4),[13] $^1J_{PH}$ = 210.6 Hz. The phosphine **2** is quite stable in air and odorless. **2** and the dichloride **3** were dissolved in THF, and a slight excess of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added at 0 °C to give a yellow-orange solution with insoluble salts. The unsymmetrical diphenyldiphosphenes (**1b,c**) thus obtained were purified by column chromatography (silica gel) to give a stable orange solid (**1b**, 31% yield based on **2**, mp 122 °C; **1c**, 76%, mp 104 °C). The structure was confirmed by high-resolution mass spectral analysis as well as ^{1}H, ^{13}C, and ^{31}P NMR spectral analyses. ^{31}P{^{1}H} NMR of **1b–d** appeared as an AB pattern at lower field than 450 ppm with large coupling constants.[16] The $^1J_{PP}$ values in **1b–d** appear to be one of the largest values (Table I) yet reported for directly bonded P–P coupling constants.[17,18] The extremely low chemical shifts seem to be characteristic for diphosphenes. In ^{31}P NMR spectra of **1c** with and without proton decoupling, P^1 and P^2 were thus assigned: the lower doublet centered at 540.4 ppm became short (line width at half-height, 9.7 Hz) where the upper doublet at 467.6 ppm remained fairly sharp (6.3 Hz) on non noise decoupling, indicating the existence of coupling between ortho-methyl protons and mesitylphosphorus, $^4J_{PH}$ = 1.95 Hz, observed in the ^{1}H NMR spectrum.

It is of interest to note that in ^{13}C{^{1}H} NMR spectra (at 22.6 MHz) of **1a–c** in CD_2Cl_2 methyls of ortho-*tert*-butyl groups, ortho-methyls, and ortho- and ipso-carbons of aromatic rings appeared as triplets (**1a**) or double doublets (**1b,c**), indicating that there exists a strong interaction between the two phosphorus atoms through the double bond. UV spectra of **1b** and **1c** were almost the same as that of **1a**. The preparation of **1a** by this method was successful only when triethylamine was used as base with low yield. The diphosphene **1d** was not stable enough to permit isolation in the pure state by means of column chromatography; however, the ^{31}P{^{1}H} NMR spectral data were consistent with the structure proposed for **1d**, indicating that the phenyl group is not large enough to protect the P=P bond. The resonance Raman spectrum of **1a** was recorded with 363.8-nm excitation, and a band at 610 (±2) cm^{-1} was tentatively assigned to the P=P stretching vibration, whereas the IR spectra of **1b** and **1c** showed weak bands at 620 and 622 cm^{-1}, respectively.

The short distance observed in the X-ray crystallographic analysis of **1a**[10] for the P–P bond, 2.034 (2) Å, indicates that the bond has a double-bond character to some extent. Therefore, we have been much interested in the bonding nature of P=P, and ab initio calculations were carried out[19] on *trans*-HP=PH

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(15) 2,4-Di-*tert*-butyl-6-methylphenylphosphonous dichloride (**3b**) was prepared by a similar method for **3a** from the corresponding bromobenzene: ^{31}P NMR ($CDCl_3$) 167.5 ppm. Mesitylphosphonous dichloride (**3c**) was prepared by the reported method: Davies, W. C. *J. Chem. Soc.* **1935**, 562.

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molecule as a model of the diphosphene (**1**) for the computation. The geometry optimizations were carried out with STO-3G,[20] 44-31G,[21] and 44-31G + polarization function on the phosphorus atom (44-31G*).[22] Table II shows the calculated results of phosphinidenes ($\mathrm{H{-}\ddot{P}{:}}$), diphosphenes (*trans*- and *cis*-H—P=P—H),[23] diphosphyne (P≡P), and diphosphane ($H_2P\text{-}PH_2$). The 44-31G bond lengths are considerably larger than the corresponding experimental values. The basis set, therefore, is not adequate for the prediction of the geometries of the molecules. On the other hand, the geometries calculated at the 44-31G* level are in good accord with the experimental values. By comparison with theoretical values (P≡P, 1.85; P=P, 2.00; P-P 2.25) and the observed distance for **1a**, it is suggested that the phosphorus-phosphorus bond in **1a** has normal double-bond character. The observed larger bond angle (∠PPC, 102.8°) in **1a** than the optimized angle in *trans*-P_2H_2 might be attributed to the steric hindrance due to ortho-*tert*-butyl groups. The computation was carried out on a HITAC M-200H computer at the Institute for Molecular Science, Okazaki, Japan.

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Registry No. **1a**, 79073-99-7; **1b**, 85028-85-9; **1c**, 85028-86-0; **1d**, 85028-87-1; **2**, 83115-12-2; **3a**, 79074-00-3; **3b**, 85028-88-2; **3c**, 6781-96-0; **3d**, 644-97-3.

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Nucleophile Addition/Carbonylation with η^4-Dienetricarbonyliron(0) Complexes

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We recently reported that reactive carbanions will add to η^4-(1,3-diene)Fe(CO)$_3$ complexes and that the stable intermediate can be protonated with trifluoroacetic acid to give substituted alkenes.[3,4] The results were interpreted in terms of intermediates **1** (from the 1,3-cyclohexadiene complex **2**; see Scheme I) and implied attack of the anion at C-1 of the diene ligand, although a minor product arising from CO incorporation (**3**) suggested some tendency toward attack at C-2. We now report studies undertaken to determine if CO insertion can be the major process in the presence of external CO.

Scheme I

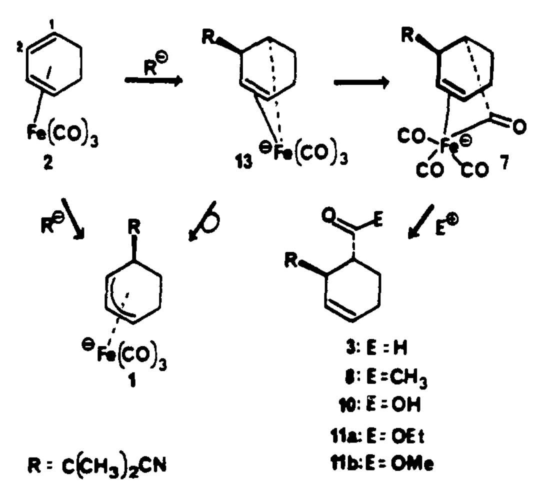
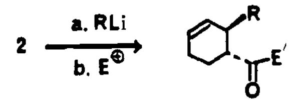


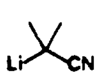
Table I. Reactions of **2** with Carbanions in the Presence of CO



en-try	RLi	E⁺	E′	yield, %[b]
1	$LiC(CH_3)_2CN$	CF_3CO_2H	H	93[c]
2	$LiC(CH_3)_2CN$	CH_3I	CH_3	87[c]
3	$LiC(CH_3)_2CN$	O_2	OH	96[c]
4	$LiC(CH_3)_2CN$	$CH_3CH_2OSO_2F$	OCH_2CH_3	100[c]
5	$LiC(CH_3)_2CN$	CH_3OSO_2F	OCH_3	100[c]
6	$Li{*}CH(CH_3)CN$	CF_3CO_2H	H	77[c-e]
7	$Li{*}CH(CH_3)CN$	CH_3I	CH_3	83[d]
8	$LiCH_2CN$	CF_3CO_2H	H	81[e]
9	$LiCH_2CN$	CH_3I	CH_3	72[c]
10	$LiC(CH_3)_2CO_2Et$	$CH_3CH_2OSO_2F$	OCH_2CH_3	96[c]
11	$LiC(CH_3)_2CO_2Et$	CH_3I	CH_3	98[c]
12	$Li{*}CH(CH_3)CO_2\text{-}t\text{-}Bu$	$CH_3CH_2OSO_2F$	OCH_2CH_3	100[d]
13	$LiCH_2CO_2\text{-}t\text{-}Bu$	$CH_3CH_2OSO_2F$	OCH_2CH_3	42[c]
14	$LiC(CH_3)_2CO_2Li$	CF_3CO_2H	18[f]	
15	2-lithio-1,3-dithiane	CF_3CO_2H	H	58[e]

[a] For the general procedure, see ref 14. [b] The yields are based on distilled samples, homogeneous by GLPC and ^{13}C NMR data. [c] The structures are assigned as trans on the basis of selective proton-decoupling experiments in comparison with data for 9. [d] This product was obtained as a mixture of epimers about the chiral carbon (denoted by the asterisks) in the carbanion unit. [e] This product was obtained as a mixture of cis and trans isomers. [f] This product was established to be the pure cis-anhydride 18 isomer based on proton-decoupling experiments, IR, and ^{13}C NMR spectral data (see ref 9).

When anion **4** is combined with complex **2**[5] under argon (−78 to +25 °C) and then exposed to CO at about 1.5 atm, protonation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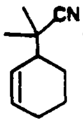
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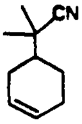
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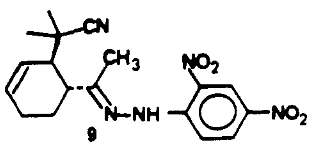

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(1) (a) Princeton University. (b) Merck Institute for Therapeutic Research.

(2) Trainee of the National Institutes of Health, 1980–1981. Exxon Fellow, Princeton University, 1982–1983.

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