tively. As can be seen in the spectrum, both the four-carbon unit and the ribityl function except C-4′ are significantly enriched, in agreement with these expectations. ^{13}C enrichments are in the range of 10–12% per site. The spectrum indicates extensive coupling between the 3* and 4* positions (approximate ratio of coupled to uncoupled signals 3:1),[7] whereas C-5′ of the side chain shows no one-bond coupling. Thus the terminal carbons of the glycerol become directly connected via an intramolecular process during conversion into the pyrazine ring of **2**, while they remain separated in the C-3′–to C-5′ portion of the ribityl side chain. The low degree of coupling observed between C-2′ and C-3′ is due to the statistical joining of two labeled trioses in the formation of a hexose. Analogous low-level couplings are observed between the 2* and 3* positions.

The present experiment gives no indication of whether the rearrangement occurs at the triose or pentose level or at some other stage. Further work is required to settle this issue and to unravel the mechanism of this intriguing rearrangement.

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Registry No. 2, 5118-16-1; **3**, 83-88-5; glycerol, 56-81-5.

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[7] This ratio is only approximate due to the effects on the relaxation characteristics of an observed ^{13}C by a neighboring ^{13}C. These effects have been found to be substantial for quaternary carbons, but relatively small for protonated carbons (ref 5b).

Novel Homo- and Heterometallic Coordination Macrocycles

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The bicyclic geometry of $P(OCH_2)_3P$[1] (**1**) permits complexation of each of the bridgehead phosphorus atoms to separate metal carbonyl moieties.[2] Although **1** is prone to forming insoluble polymers with most metal carbonyl substrates, the last step in the reactions shown in Scheme I provides 40–86% yields of the novel tetramers **5–9**, each of which are 20-membered rings.

Comparison of the ^{31}P NMR spectra of the mononuclear metal complexes **2–4** and the dinuclear compounds **10–12** in Tables I with those of **5–9** reveals as expected two equi-intensity peaks in all three sets of compounds.[3] Further, the ^{31}P δ values closely correspond for a given metal in the series **10–12** and **5–9**, and the same is true for **2–4** and **5–9** except for the uncoordinated PC_3 moiety in **2–4**. The single ^{1}H NMR resonance in this table for all three types of compounds also gives credence to the postulated cyclic nature of **5–9**, since the protons in such species are expected to be chemically equivalent in contrast to an acyclic oligomer. Moreover, the proton peaks of **5–9** are broad (~25 Hz) symmetrical multiplets stemming from the "virtual" coupling expected from these $AA'A''A'''MM'M''M'''X_6X_6'X_6''X_6'''$ spin systems. Efforts to obtain molecular weight data by osmometry failed owing to facile decomposition in pyridine, the only solvent found in which appropriate solubility could be achieved. In the case of **6**, however, the parent ion was clearly observed by FAB/MS.[4] Although the cyclic compounds **5–9** might be expected to show two sets of carbonyl bands in their IR spectra because of PC_3 and PO_3 coordination to the metals, this is not observed. Only **7** displays two A_1[2] peaks. This lack of band doubling is not unprecedented, however, since complete band superposition was observed in the IR spectra of **10–12**.[2]

The 1:1 stoichiometry of the reactants in the reactions in which **5–7** are formed (see Scheme I) coupled with the high yields in which these compounds are realized are consistent with cyclic tetramer formation. The unusually high yields of these compounds probably arise primarily from the opportunity for the unligated phosphorus in the final intermediate D shown in Scheme II to cyclize into a strainless macrocyclic ring structure by reacting with a nearby reactive metal center. Because of the 90° angle between

Scheme I[a]

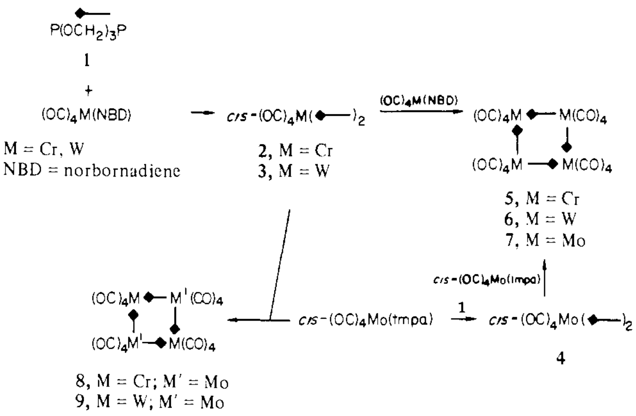

Table I. NMR Data[a]

compound	$^{31}PO_3$, δ	$^{31}PC_3$,[a] δ	^{1}H, δ
$P(OCH_2)_3P$ (1)	90.0	−67.0	4.45dd[b]
cis-$(OC)_4Cr(1)_2$ (2)	157.4	−68.1	4.91"dt"[c,d,e]
$(OC)_5Cr(1)Cr(CO)_5$ (10)	155.5[c]	8.2[c]	5.00dd[c]
cyclo-$[(OC)_4Cr(1)]_4$ (5)	160.5	11.9	4.80m
cis-$(OC)_4Mo(1)_2$ (4)	133.5	−68.4	4.77"dt"[e,f]
$(OC)_5Mo(1)Mo(CO)_5$ (11)	131.0[c]	−18.9[c]	4.98dd[c]
cyclo-$[(OC)_4Mo(1)]_4$ (7)	133.6	−14.6	4.85m
cis-$(OC)_4W(1)_2$ (3)	109.9	−68.6[g]	4.88"dt"[e,g]
$(OC)_5W(1)W(CO)_5$ (12)	108.4[c]	−36.4[c]	4.82dd[c]
cyclo-$[(OC)_4W(1)]_4$ (6)	112.6	−33.5	4.80m
cyclo-$[(OC)_4Cr(1)Mo(1)(CO)_4]_2$ (8)	159.8	−11.9	4.77m
cyclo-$[(OC)_4W(1)Mo(1)(CO)_4]_2$ (9)	111.2	−12.6	4.82m

[a] Positive chemical shifts are downfield from H_3PO_4 external standard. Measurements were made in $CDCl_3$ unless specified otherwise. [b] $(CD_3)_2CO$.[2] [c] CH_3CN.[2] [d] $^2J_{PH} = 8.4$, $^3J_{PH} = 5.3$ Hz.[2] [e] The outer lines of the apparent triplet are separated by $|^3J_{PH} + {}^5J_{PH}|$, but $^5J_{PH}$ is very small as is suggested by the spectrum of *cis*-$(OC)_4Mo[P(OCH_2)_3P][P(CH_2O)_3P]$, a ligand isomer of 4 in which all the P atoms are chemically different. No splitting due to $^5J_{PH}$ could be detected in the ^{1}H NMR spectrum (($(CH_3CN)PC_3$-bound 1, δ 4.84 dd, $^3J_{PH} = +5.3$, $^2J_{PH} = +8.5$ Hz; PC_3-bound 1, 4.46 t, $^3J_{PH} = {}^2J_{PH} = +2.6$ Hz). The ^{31}P NMR spectrum and the coupling signs were obtained by INDOR techniques described earlier.[2] Each of the 12 ^{31}P peaks is a septet owing to coupling to six equivalent protons (MoPO_3, 133.3 dd, $^3J_{PP} = -6.0$ Hz, $^2J_{PP} = |138.0|$; PO_3, 88.0 d, $^3J_{PP} = +20.0$ Hz; MoPC_3, −13.1 dd, $^3J_{PP} = +20.0$ Hz, $^2J_{PP} = |138.0|$; PC_3, −69.3, $^3J_{PP} = -6.0$ Hz). [f] $^2J_{PH} = 9.0$, $^3J_{PH} = 5.0$ Hz. [g] $^2J_{PH} = 8.5$, $^3J_{PH} = 5.5$ Hz. [g] $J_{WP} = 402.8$ Hz. This value is in the range reported for other $P(OR)_3$ ligands in $(OC)_5WL$ complexes (Verkade, J. G. *Coord. Chem. Rev.* 1972, *9*, 1).

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[3] The proton-decoupled ^{31}P peaks of **5–9** are about 200 Hz wide and are attributable to an $AA'A''A'''MM'M''M'''$ system, which could not be resolved.

[4] We thank Steve Vesey for these data obtained at the MCMS Regional NSF Facility, University of Nebraska, Lincoln, NE.

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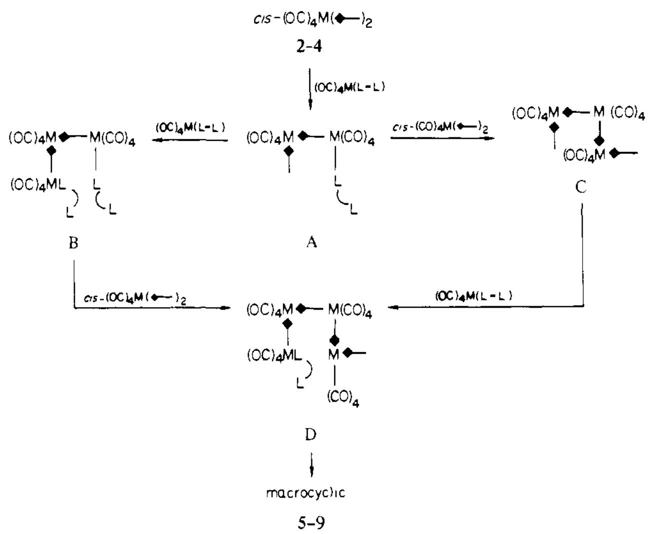
Scheme II



^{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}).

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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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