cluster, B_4Cl_4. Both the speed and the selectivity of the first reaction (that with Me_3SnH) are remarkable. The halogen ligands are exchanged, two hydrogen atoms are positioned along one of the B–B vectors, and the four newly exposed edges of the former tetrahedron are hydrogenated, all within seconds and in 95% yield overall. The only product isolated, B_4H_{10}, clearly arises from a 6 electron reduction of the 4 vertex–8 electron B_4Cl_4 core, generating a 14 electron cluster with the appropriate butterfly geometry.

The second reaction (that with $LiBH_4$) indicates the ease with which electron-rich fragments can be incorporated into the B_4Cl_4 framework. Here, the insertion of one or two two-electron-donating BH vertices is accompanied by the formation of four BHB bridges to again form reduced (nido) species, B_5H_9 and B_6H_{10}, in 82% combined yield.

Perhaps the most interesting reaction is that between B_4Cl_4 and diborane, the latter at least potentially a 2 vertex–8 framework electron donor. The first product observed, after 6 h, is the 6 framework atom–16 electron cluster $B_6H_6Cl_4$. The final products, the chlorinated decaboranes, arise from the fusion of a second molecule of B_4Cl_4 with $B_4H_6Cl_4$, generating a 10 vertex–24 framework electron cluster in the process. The cluster fusion reaction is followed by ligand-exchange reactions with the excess B_2H_6 present. Under the conditions examined, the overall stoichiometry of the reaction corresponds very closely to $2B_4Cl_4 + 2B_2H_6 \rightarrow B_{10}Cl_xH_{14-x} + 2BCl_3$, $x \approx 2$.[5]

Collectively, as shown in Figure 1, the reactions of B_4Cl_4 demonstrate in a most concise fashion four different modes of cluster reactivity: ligand exchange, core reduction, framework atom incorporation, and cluster fusion. While these types of reactions have been previously observed in other chemical systems, it is very rare to find all four modes of reactivity demonstrated in the same substrate. These results suggest that B_4Cl_4 may prove to be a very suitable model compound for both experimental and theoretical studies of cluster reactivity. They also suggest that cluster fusion reactions of B_4Cl_4 with larger boranes or their halogenated derivatives might result in the formation of very large cluster compounds, boranes whose structures are based upon transicosahedral geometries.[6]

Acknowledgment. The financial assistance of the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. B_4Cl_4, 17156-85-3; Me_3SnH, 1631-73-8; B_4H_{10}, 18283-93-7; $LiBH_4$, 16949-15-8; B_5H_9, 19624-22-7; B_6H_{10}, 23777-80-2; B_2H_6, 19287-45-7; $B_6H_6Cl_4$, 95979-59-2; $B_{10}Cl_3H_{11}$, 95979-60-5; $B_{10}Cl_6H_8$, 95979-61-6; $B_{10}Cl_5H_9$, 95979-62-7; $B_{10}Cl_4H_{10}$, 95979-63-8; $B_{10}Cl_2H_{12}$, 93385-83-2; BCl_3, 10294-34-5; $BHCl_2$, 10325-39-0; B_2H_5Cl, 17927-57-0; $B_6H_7Cl_3$, 95979-64-9; $B_6H_8Cl_2$, 95979-65-0.

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Articles

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Synthesis of Unusual Phosphine Ligands. Use of the 1-Naphthylmethyl Moiety as a P–H Protecting Group in the Synthesis of a Phosphino Macrocycle That Contains a Secondary-Phosphino Ligating Site[1]

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Received August 14, 1984

A protecting group for a P–H group in a secondary phosphine has been developed, which is a (1-naphthylmethyl)phosphine sulfide. This has been used to convert (1-naphthylmethyl)phosphine into bis(3-chloropropyl)(1-naphthylmethyl)phosphine sulfide, which upon reaction with bis(lithiophenylphosphino)benzene, was transformed into the 11-P_3 macrocycle *cis*-2,10-diphenyl-6-(1-naphthylmethyl)-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene 6-sulfide. The 1-naphthylmethyl moiety was removed quantitatively with potassium naphthalenide to give the 11-P_3 molecule with a secondary phosphine sulfide at the 6-position. This was reduced with a reagent derived from lithium aluminum hydride and trimethylsilyl chloride to give the 11-P_3 macrocycle containing a secondary phosphine, *cis*-2,10-diphenyl-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene (**2a**), which exists as two isomers (H cis and trans to the phenyl groups). Ligand **2a** forms complexes with Rh(I) and Mo(0) in which all three ligating sites are involved in the metal coordination.

Introduction

As part of our longstanding interest in phosphino macrocycles, we have wished to synthesize such species that contain secondary-phosphino sites. Such ligands could be converted into bicyclic species and linked to other cycles to give clam-like ligands. In metal complexes, the PH could be deprotonated, thereby easily changing (fine-tuning) the properties of the coordinated metal. In addition, the secondary phosphine could serve as a precursor to a bridging phosphide in bi- and polynuclear complexes.[2] We have described three macrocycles that contain PH sites, but these were of the arylalkylphosphine types (**1**),[3] and we sought to have a more general approach that would allow us to incorporate dialkylphosphines into macrocyclic ligands, as exemplified by **2**.

Results and Discussion

In order to synthesize **2**, it would be necessary to prepare **6** (eq 1) or a functional-group equivalent. We had established that commercially available **3** could be transformed into **4** and then

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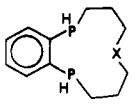
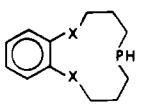
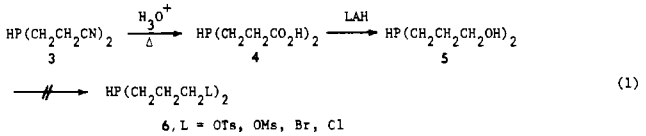


1
X = S, NMe, PPh

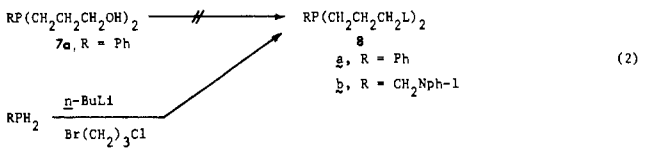


2
a, X = PPh
b, X = S
c, X = AsMe

into **5** in good yield.[4] Many attempts to obtain **6** from **5** led inevitably to either oxidation or alkylation of the secondary phosphine.[4] We had observed similar results even earlier with **7a**, obtained from the free-radical addition of phenylphosphine to allyl alcohol,[5] in which all attempts at tosylate, mesylate, or bromide formation led to destruction of the tertiary phosphine (eq 2).[6]

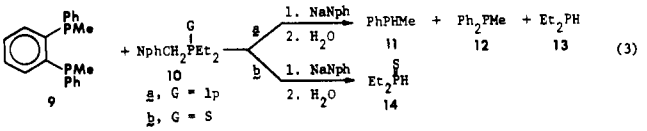


(1)



(2)

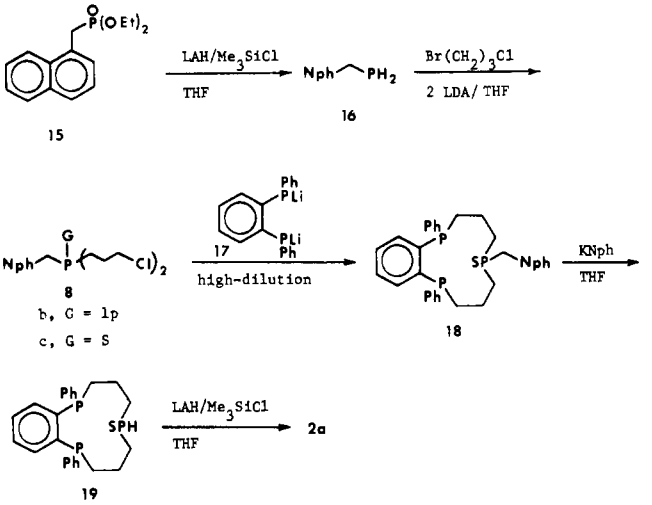
Since we had been successful in our macrocycle syntheses using tertiary phosphine **8a** (L = Cl)[3,7] obtained from 1-bromo-3-chloropropane as shown (eq 2), we felt that **8b** would be an excellent candidate for incorporation of the bis(trimethylene)(1-naphthylmethyl)phosphino moiety into a macrocycle, e.g., a precursor of **2**. The notion was that reductive cleavage of the 1-naphthylmethyl-P bond would be facile and would reveal the dialkyl-P–H group in **2**. This strategy was soon changed on the basis of a study of a model system. When an equimolar mixture of **9** and **10a** in THF was treated with 2 equiv of sodium naphthalenide followed by a water quench, a mixture of products was obtained, including **11** and **12** (major, P–C cleavage in **9**) and **13** (P–C cleavage in **10a**) (eq 3). In contrast, the same treatment of a solution of **9** and **10b** gave exclusively **14** and recovered **9**.



(3)

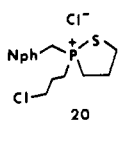
On the basis of these observations, we planned and executed the synthesis of **2a** shown in Scheme I, in which we illustrate the use of the 1-naphthylmethyl and =S groups in combination as a synthon for a hydrogen atom in a secondary phosphine. Reduction of **15**[8] with a mixture of LAH and trimethylsilyl chloride (1:1 Si:Al)[9] gave **16** in 76% distilled yield. This combination of reagents, which we believe to generate $LiCl{\cdot}AlH_3$,[10] is necessary,

Scheme I

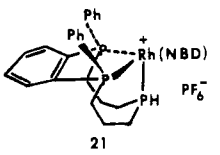


since reduction with LAH in THF alone at temperatures ranging from −78 °C to ambient gives 1-methylnaphthalene in 85–90% yields and only about 3% of the primary phosphine **16**. Alkylation of **16** to give **8b** with 1-bromo-3-chloropropane proceeded in high yield and was best promoted by lithium diisopropylamide (LDA), since *n*-BuLi led to substantial amounts of C-alkylation α to the naphthyl group. As the functionalized tertiary phosphine **8b** was quite sensitive to decomposition via intermolecular alkylation, it was generally stored at −20 °C and used soon after it was prepared.

Phosphine **8b** was transformed into the sulfide **8c** quantitatively by reaction with excess S_8 in benzene. This species was also quite sensitive to decomposition and upon dissolution in THF precipitated a high yield of a white crystalline material, which we did not characterize fully but which we belive to be **20**. This reaction was very much slower in benzene, and as a consequence, we carried out the high-dilution macrocyclization[11] to **18** in 36% yield with **17**[7] in THF and **8c** in benzene so that only a small amount of **8c** was transformed into **20** during the 24-h addition period. The 1-naphthylmethyl[12] protecting group was removed by treatment with excess potassium naphthalenide[13] at −78 °C, followed by addition of the resulting solution to aqueous THF, to give **19** in quantitative yield. Reduction of **19** with the LAH/Me_3SiCl reagent[9] gave **2a** in 78% yield. Here also, LAH in THF alone gave very poor yields of **2a**.[10] Ligand **2a** was obtained as a viscous oil, which was a mixture of two isomers as evidenced by its ^{31}P NMR spectrum; isomer A, δ −27.0, −64.9 ($^1J_{P-H}$ = 203 Hz); isomer B, δ −30.0, −73.3 ($^1J_{P-H}$ = 210 Hz); isomer ratio A:B = 2:3.



20



21

This new ligand readily coordinates transition metals as illustrated by the following two examples. When **2a** was mixed

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(9) Kyba, E. P.; Liu, S.-T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877.
(10) To our knowledge $LiCl{\cdot}AlH_3$ has not been described in the literature. We have made no attempt to isolate this material, but we have observed that if the solvent and other volatile materials are removed under vacuum and trapped, the ^{13}C NMR signal for Me_3SiH (δ −2.8) can be observed. In addition, the solid residue, upon disolution in THF, exhibits the same reduction behavior as a THF solution not treated in this way.
(11) Kyba, E. P.; Chou, S.-S. P. *J. Org. Chem.* **1981**, *46*, 860.
(12) A reviewer questioned whether or not a benzyl group would work as well as the naphthylmethyl system. We chose the latter because of the well-known naphthalenide radical anion,[13a] anticipating that "electron injection" would occur into the naphthyl portion of the desulfurized analog of **18** in preference to the *o*-$P_2C_6H_4$ portion. We had already developed the synthetic methodology for the naphthylmethyl system when it became clear that we would have to use the sulfur species. It is possible that the $PhCH_2P(S)$ moiety would work as well as the naphthyl system that we described, but we did not test it. One disadvantage that can be envisaged is the higher volatility (and thus greater stench) of the requisite synthetic intermediate $PhCH_2PH_2$.
(13) (a) The KNph was found to be superior to NaNph in this operation. For a pertinent review, see: Holy, N. L. *Chem. Rev.* **1974**, *74*, 243. (b) Ager, D. J. *J. Organomet. Chem.* **1983**, *241*, 139.

with 1 equiv of $(NBD)_2RhPF_6$ in dichloromethane, a dark red complex was formed. $^{31}P\{^1H\}$ NMR: δ 53.3 (dd, J_{Rh-P} = 120, J_{P-P} = 24 Hz), −51.3 (dt, J_{Rh-P} = 113, J_{P-P} = 24 Hz); coordination chemical shift Δ(tertiary phosphine) $\simeq$ 80 ppm, Δ(secondary phosphine) $\simeq$ 20 ppm. These data are consistent with structure **21**. A zerovalent complex of molybdenum was prepared by heating **2a** with $Mo(CO)_6$ in toluene under reflux for 3 h.[14] *fac*-(**2a**)-$Mo(CO)_3$ (**22**) was obtained in 29% yield.[15] The $^{31}P\{^1H\}$ NMR spectrum exhibited absorptions at δ 50.7 (d, J = 30 Hz) and −35.2 (t, J = 30 Hz); Δ(tertiary phosphine) $\simeq$ 80 ppm and Δ(secondary phosphine) $\simeq$ 35 ppm. Interestingly, in the proton-coupled ^{31}P NMR spectrum, $^1J_{P-H}$ = 347 Hz and $^3J_{P-H}$ = 330 Hz. We were unable to observe either a $^1H_{P-H}$ or $^3J_{P-H}$ in the case of **21**. We will present a full report on the coordination chemistry of **2a** in a future publication.

Experimental Section

General Information. Proton magnetic resonance spectra were recorded on either a Varian EM-390 or a Varian FT-80 spectrometer. Carbon-13 and proton-decoupled phosphorus-31 NMR spectra were determined on a Varian FT-80 spectrometer at 20.1 and 32.4 MHz, respectively. Chemical shifts are given in parts per million relative to Me_4Si for ^{13}C and relative to 85% H_3PO_4 for ^{31}P NMR spectra in $CDCl_3$, unless otherwise noted. Chemical shifts upfield of the standard are defined as negative.

Mass spectra (MS or HRMS) were determined on a CEC 21-100 high-resolution instrument or a Du Pont 21-491 instrument at 70 eV.

Infrared spetra were obtained on a Perkin-Elmer 298 infrared spectrophotometer.

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected.

All of the reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen or argon atmosphere. Air-sensitive liquids were transferred by Teflon flexneedles by using nitrogen pressure or by syringe. All concentrations of solutions were carried out on a rotary evaporator with water aspirator pressure. Solutions were dried with anhydrous, degassed magnesium sulfate.

Diethyl (1-naphthylmethyl)phosphonate (**15**),[8] 1,2-bis(phenylphosphino)benzene,[7] and **9**[16] were prepared as described previously. Tetrahydrofuran and diethyl ether were distilled under nitrogen from benzophenone ketyl radical. Benzene was purified by distillation over sodium metal under nitrogen. Dichloromethane was distilled from phosphorus pentoxide under nitrogen. Other solvents and chemicals from commercial sources were used without further purification, except as noted. The concentration of potassium naphthalenide was determined by titration according to a literature method.[12b]

(1-Naphthylmethyl)phosphine (16). Trimethylsilyl chloride (83.0 g, 0.764 mol) was added to a stirred solution of lithium aluminum hydride (28.0 g, 0.738 mol) in THF (450 mL) at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for 2 h. A solution of phosphonate **15** (68.5 g, 0.246 mol) in THF (200 mL) was then slowly added to the reducing mixture at −78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred overnight. Water (150 mL) followed by 2.0 N aqueous sodium hydroxide was added, and the two layers were separated. The aqueous layer was extracted with diethyl ether (2 × 200 mL), and the combined organic extracts were dried and concentrated. Distillation of the residue gave two fractions of colorless, very air-sensitive liquids. The first fraction (8.33 g), bp 85–90 °C (80 μm), contained 20% 1-methylnaphthalene (by ^1H NMR). The second fraction was pure **16** (37.5 g, 76%): bp 90–103 °C (100 μm); ^1H NMR δ 7.1–8.0 (m, 7 H), 3.18 (dt, J = 7.0, 5.0 Hz), 3.04 (dt, J = 196, 7.0 Hz); ^{13}C NMR δ 138.8 (s), 134.1 (d, J = 0.9 Hz), 130.6 (d, J = 1.8 Hz), 128.9 (s), 126.6 (d, J = 1.7 Hz), 125.8 (s), 125.7 (s), 125.6 (s), 125.3 (s), 123.6 (s), 17.9 (d, J = 11.0 Hz); ^{31}P NMR δ −124.8 (s); IR ($C_2H_2Cl_2$) 2293 cm^{-1} (P–H stretch).

Anal. Calcd for $C_{11}H_{11}P_2$: C, 75.85; H, 6.36. Found: C, 75.94; H, 6.27.

The reduction of **15** by using lithium aluminum hydride at low temperature gave 1-methylnaphthelene as the major product, accompanied by less than 5% of phosphine **3**.

Bis(3-chloropropyl)(1-naphthylmethyl)phosphine (8b). To a mixture of **16** (2.0 g, 11.48 mmol) in 1-bromo-3-chloropropane (3.67 g, 23.31 mmol) in THF (70 mL) was added a 1.54 M THF solution of lithium diisopropylamide (16.2 mL, 25.0 mmol) at −78 °C. The reaction mixture was allowed to stir for 1 h and then quenched with degassed water at −78 °C. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic extracts were dried and concentrated, and the residue was evacuated for several hours to give a clear, colorless oil $C_{17}H_{21}P^{35}Cl_2$). g, 83%): ^1H NMR δ 7.10–8.17 (m, 7 H), 3.38 (t, J = 7.0 Hz, 4 H), 3.13 (s, 2 H), 1.16–2.02 (m, 8 H); ^{13}C NMR δ 133.8, 133.8 (d, J = 4.4 Hz), 131.6 (d, J = 2.2 Hz), 128.6, 126.7, 126.6 (d, J = 7.6 Hz), 125.6, 125.2 (d, J = 1.2 Hz), 124.2 (d, J = 5.4 Hz), 45.6 (d, J = 13.3 Hz), 32.6 (d, J = 16.2 Hz), 29.0 (d, J = 16.0 Hz), 24.9 (d, J = 15.6 Hz); ^{13}P NMR δ −26.5; HRMS m/e 326.076 55 (calcd m/e 326.075 79 for $C_{17}H_{21}P^{35}Cl_2$).

Bis(3-chloropropyl)(1-naphthylmethyl)phosphine Sulfide (8c). A. From 8b. A solution of **8b** (2.20 g, 6.72 mmol) was treated with sulfur (0.23 g, 0.90 mmol) at room temperature. The reaction was stirred until all the solids disappeared. After removal of the solvent under vacuum, **8c** was obtained as a light yellow oil (2.40 g,99%): ^1H NMR 7.35–8.10 (m, 7 H), 3.74 (d, J = 15 Hz, 2 H), 3.30–3.60 (m, 4 H), 1.55–2.30 (m, 8 H); ^{13}C NMR (partial) δ 45.1 (d, J = 17.9 Hz), 37.4 (d, J = 46.3 Hz), 28.3 (d, J = 51.7 Hz), 25.8 (d, J = 2.1 Hz); ^{31}P NMR δ 49.2; HRMS m/e 358.0491 (calcd m/e 358.0479 for $C_{17}H_{21}SP^{35}Cl_2$).

This phosphine sulfide can also be prepared on a large scale from **16** in a one-pot reaction without isolation of **8b**, as described below.

B. From 16. A stirred solution of phosphine **16** (6.86 g, 39.38 mmol) and 1-bromo-3-chloropropane (15.4 g, 97.8 mmol) in THF (300 mL) was cooled to −78 °C and then treated with a 0.76 M THF solution of lithium diisopropylamide (130 mL, 98.8 mmol). The resulting mixture was kept stirred at −78 °C for 30 min followed by a quench with water (5 mL). This mixture was allowed to warm to room temperature and transferred into a degassed flask containing sulfur (1.20 g, 4.68 mmol). The reaction mixture was stirred at room temperature until the solid disappeared. It was washed with H_2O (2 × 100 mL), and the combined aqueous portions were extracted with diethyl ether (100 mL). The combined organic extracts were dried and concentrated, and the residue was passed through silica (50 g) with hexane/ethyl acetate (1:2 v/v) to give 15.9 g of crude product. This material was chromatographed on a Waters Prep-500 instrument with 10% ethyl acetate in hexane. The major fraction gave **8c** as a yellow clear oil (10.3 g, 77%), having physical properties identical with those described in part A. This compound reacts rapidly (<1 h) in THF solution to give **20** as a white solid: ^1H NMR δ 8.63–8.82 (m, 1 H), 7.40–8.10 (m, 6 H), 5.32 (d, J = 15 Hz, 2 H), 2.90–3.80 (m, 8 H), 1.70–2.40 (m, 4 H); ^{13}C NMR (partial) 43.9 (d, J = 20 Hz), 38.4 (d, J = 3.9 Hz), 31.5, 29.2 (t, J = 8 Hz), 26.8, 25.7 (t, J = 4 Hz), 23.4; ^{31}P NMR δ 90.0.

***cis*-2,10-Diphenyl-6-(1-naphthylmethyl)-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene 6-Sulfide (18).** The dianion **17** solution was prepared by the reaction of a 3.01 M hexane solution of *n*-BuLi (19.0 mL, 57.19 mmol) with a solution of 1,2-bis(phenylphosphino)benzene (8.56 g, 29.08 mmol) in THF (150 mL) at 0 °C. It was reacted with a solution of **8c** (10.3 g, 28.67 mmol) in benzene (170 mL) under high-dilution conditions[11] with benzene as the solvent. The reaction mixture was concentrated, and the residue was partitioned between water (100 mL) and dichloromethane (2 × 100 mL). The organic extracts were dried and concentrated to give viscous oil, which was passed through silica gel (ca. 30 g) with dichloromethane/ethyl acetate (1:1 v/v). The filtrate was concentrated and dissolved in acetone/dichloromethane (1:1 v/v), which upon cooling to −20 °C gave **18** (4.7 g, 28%) as a white crystalline solid. The mother liquor was concentrated and chromatographed on silica gel (100 g) with dichloromethane/hexane/ethyl acetate (25:73:2 v/v/v) followed by ethyl acetate/dichloromethane (1:1 v/v). The eluate gave more **18** (1.4 g, 8%, total yield 36%) upon crystallization from acetone/dichloromethane (1:1 v/v): mp 202.5–204 °C; ^1H NMR δ 7.25–8.38 (m, 21 H), 3.86 (d, J = 14 Hz, 2 H), 1.5–2.9 (7, 12 H); ^{13}C NMR δ 146.6 (t, J = 11.1 Hz), 139.9 (t, J = 3.5 Hz), 133.9 (d, J = 2.5 Hz), 133.0 (t, J = 1.5 Hz), 132.1 (d, J = 4.2 Hz), 131.2 (t, J = 8.5 Hz), 129.8, 129.1, 128.7, 128.3 (t, J = 2.5 Hz), 127.6, 125.8 (d, J = 8.4 Hz), 125.2 (d, J = 3.7 Hz), 124.2 (d, J = 1.5 Hz), 38.1 (d, J = 47.5 Hz), 32.5 (t, J = 6.3 Hz), 30.0 (m), 19.3 (m); ^{31}P NMR δ 48.7, −32.0; HRMS m/e 580.1662 (calcd m/e 580.1672).

***cis*-2,10-Diphenyl-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene 6-Sulfide (19).** A stirred solution of **18** (3.64 g, 6.269 mmol) in THF (120 mL) was cooled to −78 °C and treated with a 0.32 M THF solution of potassium naphthalenide (59.0 mL, 18.9 mmol). The reaction mixture was stirred at −78 °C for 30 min, followed by slow addition to an aqueous THF solution (200 mL of H_2O/THF, 1:1 v/v). The THF solution was separated, and the aqueous solution was extracted with diethyl ether (2 × 50 mL). The combined organic extracts were dried and concentrated. The residue was heated at 70 °C under high vacuum to remove methylnaphthalene, naphthalene, and their derivatives

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to give **7** as a viscous oil (2.84 g, 100%): ^{1}H NMR δ 7.1–7.8 (m, 14 H), 1.3–2.8 (m, 13 H); ^{13}C NMR (partial) δ 146.7 (t, J = 9 Hz), 140.0 (t, J = 3 Hz), 133.2 (t, J = 3 Hz), 29.7 (m), 23.6 (m), 19.5 (m); ^{31}P NMR δ 21.0 (^{1}H coupled, J = 446 Hz), −30.5 (s); HRMS m/e 440.103 91 (calcd m/e 440.104 63).

***cis*-2,10-Diphenyl-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1-(11),12,14-triene (2a).** Trimethylsilyl chloride (5.0 g, 46.0 mmol) was added to a stirred solution of lithium aluminum hydride (1.74 g, 45.8 mmol) in THF (50 mL) at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for 2 h. A solution of phosphine sulfide **19** (2.84 g, 6.44 mmol) in THF (30 mL) was added to the above reducing mixture at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Water (5 mL) and saturated aqueous ammonium chloride (20 mL) were added, and the two layers were separated. The aqueous layer was extracted with diethyl ether (2 × 50 mL), and the combined organic extracts were dried and concentrated. The residue was chromatographed on alumina with benzene/hexane (1:1 v/v) as eluent. The filtrate was concentrated to give **2a** as a clear, colorless oil (2.0 g, 78%): ^{1}H NMR δ 6.83–7.92 (m, 14 H), 1.13–2.33 (m, 12 H); ^{13}C NMR δ 147.1 (t, J = 10.5 Hz), 141.0 (t, J = 2.5 Hz), 133.2, 131.3 (t, J = 8.5 Hz), 129.5, 128.2 (t, J = 2.5 Hz), 127.3, 30.30 (m), 25.2 (m), 20.5 (m); ^{31}P NMR δ −27.0, −64.9 (^{1}H coupled, J = 203 Hz), −30.0, −73.3 (^{1}H coupled, J = 210 Hz) (peak height ratio 2:2:3:3); IR (benzene) 2267 cm^{-1} (P–H stretch); HRMS m/e 408.131 59 (calcd m/e 408.132 56).

Diethyl(1-naphthylmethyl)phosphine (10a). A solution of phosphine **16** (3.47 g, 19.95 mmol) and ethyl bromide (6.9 g, 63.3 mmol) in THF (50 mL) was treated with a 2.52 M hexane solution of *n*-BuLi (7.9 mL, 19.9 mmol) at −78 °C. The resulting mixture was stirred at low temperature for 30 min, and then treated with a THF solution of 0.80 M lithium diisopropylamide (25.0 mL, 20.0 mmol). The reaction mixture was stirred at −78 °C for another 30 min and then quenched with degassed water (30 mL). The organic layer was separated, and the aqueous solution was extracted with diethyl ether (2 × 20 mL). The combined organic extracts were dried and concentrated. The residue was distilled under high vacuum to give **10a** as a clear, colorless air-sensitive liquid (3.81 g, 83%): bp 115–117 °C (20 μm); ^{1}H NMR δ 7.17–8.25 (m, 7 H), 3.1 (s, 2 H), 1.15–1.40 (m, 4 H), 0.77–1.1 (m, 6 H); ^{13}C NMR (partial) δ 31.9 (d, J = 17.7 Hz), 19.5 (d, J = 13.8 Hz), 9.5 (d, J = 13.4 Hz); ^{31}P NMR δ −16.8; HRMS m/e 230.121 94 (calcd m/e 230.122 43).

Diethyl(1-naphthylmethyl)phosphine Sulfide (10b). A stirred solution of phosphine **10a** (545.3 mg, 2.37 mmol) in THF (10 mL) was treated with sulfur (95.0 mg, 0.37 mmol) at room temperature. The reaction was stirred until all the solid disappeared. After concentration of the reaction mixture, the residue was chromatographed on silica gel (10 g) with hexane, followed by ethyl acetate. The ethyl acetate eluent gave product **10b** as a white solid (610 mg, 98%): mp 78.5–79.5 °C; ^{1}H NMR δ 7.32–8.26 (m, 7 H), 3.87 (d, J = 14 Hz, 2 H), 1.6–2.0 (m, 4 H), 1.0–1.4 (m, 6 H); ^{13}C NMR δ 133.9 (d, J = 2.5 Hz), 131.9 (d, J = 3.7 Hz), 128.8, 128.4 (d, J = 8.5 Hz), 128.3, 127.9 (d, J = 3.5 Hz), 126.2 (d, J = 0.8 Hz), 125.8, 125.2 (d, J = 3.8 Hz), 123.9 (d, J = 1.6 Hz), 35.8 (d, J = 45.1 Hz), 23.1 (d, J = 51.2 Hz), 6.4 (d, J = 4.5 Hz); ^{31}P NMR δ 53.9; HRMS m/e 262.095 16 (calcd m/e 262.094 50).

Reaction of Diethyl(1-naphthylmethyl)phosphine (10a) and *meso*-1,2-Bis(methylphenylphosphino)benzene (9) with Sodium Naphthalenide. A mixture of **9** (558 mg, 1.73 mmol) and **10a** (398.1 mg, 1.73 mmol) in THF (10 mL) was treated with a 0.896 M THF solution of sodium naphthalenide (3.9 mL, 3.5 mmol) at −78 °C. After the solution was warmed to room temperature (1 h), the following ^{31}P NMR spectrum was recorded: δ −17.6 (**10a**), −27.4 (Ph_2PMe), −55.1 (Et_2PH) (lit.[17] δ −55.5), −71.3 (PhPHMe) (lit.[18] δ −72.3); peak height ratio 4:3:9:6.

Reaction of Diethyl(1-naphthylmethyl)phosphine Sulfide (10b) and *meso*-1,2-Bis(methylphenylphosphino)benzene (9) with Sodium Naphthalenide. A mixture of **10b** (290 mg, 1.1 mmol) and **9** (57.3 mg, 0.178 mmol) in THF (3 mL) was treated with 0.896 M THF solution of sodium naphthalenide (3.5 mL, 3.136 mmol) at −78 °C. The resulting mixture was stirred for 1 h at low temperature and quenched with water (1 mL). The organic layer was separated and concentrated, and the residue was dissolved in $CDCl_3$ to give the following spectroscopic data: ^{31}P NMR δ 32.0 (^{1}H coupled, J_{P-H} = 434 Hz) (lit.[19] δ 31.0 (^{1}H coupled, J_{P-H} = 437 Hz)), −35.4 (**9**); ^{1}H NMR δ 2.5 (s, CH_3Nph-1).

(*cis*-2,10-Diphenyl-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1-(11),12,14-triene-κ^3P)(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) Hexafluorophosphate (21). To a solution of phosphine **2a** (40.8 mg, 0.10 mmol) in dichloromethane (1 mL) was added a solution of bis(bicyclo-[2.2.1]hepta-2,5-diene)rhodium(I) hexafluorophosphate (43.1 mg, 0.10 mmol) in dichloromethane (1 mL) at room temperature. The solution was concentrated, and the residue was pumped under vacuum overnight to give a brown solid (72.4 mg, 97%): ^{1}H NMR (CD_2Cl_2) δ 6.75–8.85 (m, 14 H), 0.45–3.15 (m, 21 H); ^{31}P NMR (CD_2Cl_2) δ 55.2 (dd, J_{P-P} = 24.0 Hz, J_{Rh-P} = 119.6 Hz), −49.4 (dt, J_{P-P} = 24.0 Hz, J_{Rh-P} = 112.3 Hz), −107.6 (sept, J= 710 Hz).

Anal. Calcd for $C_{31}H_{35}P_4F_6Rh$: C, 49.75; H, 4.71. Found: C, 49.45; H, 4.71.

***fac*-(*cis*-2,10-Diphenyl-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1-(11),12,14-triene-κ^3P)tricarbonylmolybdenum(0) (22).** A solution of **2a** (36.0 mg, 0.088 mmol) in toluene (2.5 mL) was added to $Mo(CO)_6$ (23.4 mg, 0.089 mmol), and resulting mixture was heated under reflux for 3 h. The filtered solution was allowed to cool to room temperature to give **22** as yellow solid (15.0 mg, 29%): mp 170–180 °C dec; IR (CH_2Cl_2) 2300 (vw), 1950 (s), 1901 (w), 1860 (s) cm^{-1}; ^{1}H NMR δ 8.0–7.0 (m, 14), 3.0–1.0 (br m, 12); ^{31}P NMR (CD_2Cl_2) δ 50.6 (d, J = 30 Hz, ^{1}H coupled, J = 330 Hz), −35.2 (t, J = 30 Hz, ^{1}H coupled, J = 347 Hz); HRMS m/e 584.0228 (calcd m/e 584.0241, for $C_{27}H_{27}O_3P_3{}^{92}Mo$).

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Registry No. **2a** (isomer 1), 95784-83-1; **2a** (isomer 2), 95840-53-2; **8b**, 95784-79-5; **8c**, 95784-80-8; **9**, 77410-05-0; **10a**, 95784-84-2; **10b**, 4519-81-7; **11**, 6372-48-1; **12**, 1486-28-8; **13**, 627-49-6; **14**, 6591-06-6; **15**, 1466-24-6; **16**, 95784-78-4; **17** dianion, 95784-85-3; **18**, 95784-81-9; **19**, 95784-82-0; **21**, 95797-87-8; **22**, 95784-77-3; $Mo(CO)_6$, 13939-06-5; $Br(CH_2)_3Cl$, 109-70-6; EtBr, 74-96-4; bis(bicyclo[2.2.1]hepta-2,5-diene)-rhodium(I) hexafluorophosphate, 38816-56-7; 1-methylnaphthalene, 90-12-0; 1,2-bis(phenylphosphino)benzene, 38023-29-9.

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