11-Membered Macrocycles Containing the diars Moiety[1]

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Abstract: Six examples of the previously unknown tertiary-arsino macrocycles are described. These are the 2,10-dimethyl-2,10-diarsa-6-heterabicyclo[9.4.0]pentadeca-1(11),12,14-triene, where 6-hetera is phenylarsa, phenylphospha, thia, oxa, and methylaza, as well as 2,6,10-triphenyl-6-arsa-2,10-diphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene. The stereochemistry of some of the ligands is assigned on the basis of thermal complexation reactions with molybdenum hexacarbonyl.

Aside from carbon monoxide, tertiary phosphines are by far the most common neutral ligands for transition metals (TM).[2] Tertiary arsines have also received considerable attention as ligands for TM,[3] although not at the same level of intensity. Recent efforts have resulted in the synthesis and characterization of a number of multidentate macrocycles containing tertiary-phosphino ligating sites,[4] but to our knowledge there have been no reports of tertiary-arsino-containing macrocycles. We now report the synthesis and some TM complexation data of six such arsine-containing macrorings.

Results and Discussion

Scheme I outlines the synthesis of the arsino macrocycles **5–10**. Although 1,2-bis(dimethylarsino)benzene (**1**) is commercially available, due to its high cost, it was synthesized from dimethylarsine and 1,2-dichlorobenzene as reported.[5] The transformation from **1** to **2** proceeds in 40% yield over three steps, as described by Wild.[6] Treatment of **2** in THF with 2 equiv of *n*-butyllithium in hexane generates the bis(nucleophile) **3a** which is reacted with the bis(electrophile) **4** in boiling THF under high dilution conditions to give **5–9** in 20 to 50% isolated yields. Cycle **10** was obtained similarly from the previously described[4a,f] dilithio salt of 1,2-bis(phenylphosphino)benzene and **4a**. Species **10** is crystalline (mp 136.5–138 °C) whereas **5–9** are viscous oils at room temperature and all appear to be less susceptible to air oxidation than the corresponding phosphorus macrocycles.

Scheme I

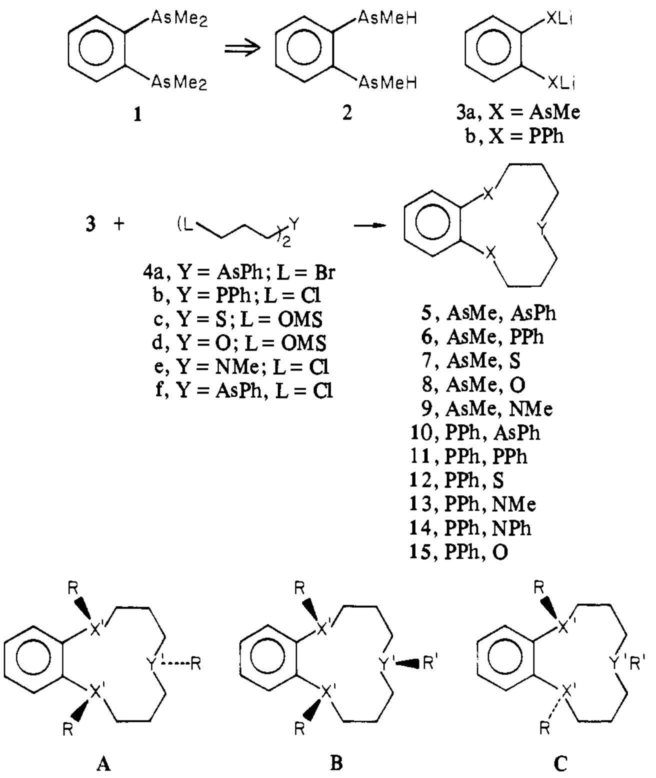

Table I. ^{13}C NMR Chemical Shifts of Methylene Carbon Atoms [X–C(1)–C(2)–C(3)–Y] and ^{1}H NMR Chemical Shifts of AsMe in Macrocycles 5–10[a]

	^{13}C				^{1}H
	C(1)	C(2)	C(3)	$AsCH_3$	$AsCH_3$
5A	34.6	24.6	29.6	9.2	1.17
5B	31.5	23.2	23.5	9.0	1.13
6A[b]	33.7	23.9	29.7	9.4	1.18
6B[b]	31.2	22.3	24.0	9.2	1.12
7	32.2	27.7	30.0	9.6	1.18
7C	33.9	26.7	28.1	8.6	1.16
8	28.7	27.3	70.3	10.1	1.10
9	28.6	24.7	41.5	9.3	1.18
10	31.5	23.5	29.2		

[a] Spectra determined on ca. 0.1 M solutions in $CDCl_3$. See Experimental Section for details. The chemical shift assignments for the ^{13}C data have not been rigorously established. [b] See Experimental Section for ^{13}C–^{31}P coupling constants.

Since the inversion barrier at an aryldialkylarsine is about 43 kcal/mol[7] and that at the corresponding phosphine is about 33 kcal/mol,[7,8] cycles **5**, **6** and **10** may exhibit three isomers (two meso and one *dl* pair, **A–C** Scheme I) and **7–9** two isomers (one meso, one *dl* pair, **A** ≡ **B**, **C**). In fact, we find that the crude products derived from the synthesis of **5** and **6** contain two isomers in each case, as evidenced particularly by ^{13}C NMR spectroscopy and thin-layer chromatography. In both cases, careful anaerobic chromatography on silica gel separated the isomers which we designate as **5A**, **5B** and **6A**, **6B**. As can be seen from Table I, selected ^{13}C and ^{1}H NMR chemical shifts are clearly different between each pair of isomers. Since all four of these materials are viscous oils, we do not have the luxury of determining the structures of these species by X-ray diffraction methods. We have established previously that when the 1,2-bis(phenylphosphino)-

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benzene moiety is incorporated in 11- and 14-membered rings the phenyl groups are always cis across the benzo fusion,[4a,c] and thermal equilibration does not generate the *trans*-Ph_2 isomers to any significant extent.[4c] In order to establish the structures of **5A**,**B** and **6A**,**B**, we have resorted to differences in transition-metal ligating ability of the **A** and **B** isomers. Previously we have determined that ligand **13** gives the *fac*-**13**·$Mo(CO)_3$ upon heating at 115 °C in toluene with 1 equiv of hexacarbonylmolybdenum for ca. 1 h, whereas **14** gives only *cis*-**14**·$Mo(CO)_4$ under similar conditions.[9] Similarly, **12** gave the corresponding tricarbonyl derivative, whereas **15** gave only the tetracarbonyl species.[10] More importantly, we have found that **11A**[11] with 1 equiv of $Mo(CO)_6$ in toluene at 115 °C for 1 h gives only *cis*-**11A**·$Mo(CO)_4$, which slowly (>24 h) and inefficiently converts to *fac*-**11B**·$Mo(CO)_3$. In contrast, **11B** rapidly (ca. 1 h) gives *fac*-**11B**·$Mo(CO)_3$ by using the above conditions.[10] We now find that isomers **5A** and **6A** give only the tetracarbonyl species whereas **5B** and **6B** give the *fac*-tricarbonyl derivatives under the conditions described above.[12] Thus we assign the **A** isomers as meso-trans and the **B** isomers as meso-cis, as depicted in Scheme I.

Although **10** can also have three isomers, **A**–**C**, our evidence indicates only one is formed since we observe no extraneous absorptions in the ^1H, ^{13}C, or ^{31}P NMR spectra. This material gives only the molybdenum tetracarbonyl derivative under our standard conditions, and thus we assign it as **10A**. Cycles **7**–**9** can exist in only two isomeric forms, $\mathbf{A} \equiv \mathbf{B}$[13] and **C**. In all three cases the crude product exhibited chromatographic and spectroscopic properties consistent with the presence of only one isomer. Upon vacuum distillation of **7**, which required a bath temperature of 235 °C, however, new absorptions were observed in the ^1H and ^{13}C NMR spectra of the distilled material (see Table I, entry **7C**). These new peaks were about 20% of the intensity of the original peaks which were still present in the distilled sample. Since the undistilled **7** readily gave the *fac*-$Mo(CO)_3$ derivative under standard conditions and since inspection of models indicates that it is sterically impossible to form the tricarbonyl derivative with the **C** isomer, we assign the undistilled material as $\mathbf{7A} \equiv \mathbf{7B}$. Although we have not been able to separate the minor component obtained after distillation, we believe it to be isomer **7C**. With macrocycles **8** and **9**, the spectroscopic properties were identical before and after distillation; apparently the lower distillation temperatures precluded isomerization. Species **8** gave only the molybdenum tetracarbonyl, whereas **9** gave the *fac*-tricarbonyl derivative, analogous to the behavior of **15** and **13**, respectively.[9,10] Thus here, as with **7**, we assign the isomers obtained as $\mathbf{8A} \equiv \mathbf{8B}$ and $\mathbf{9A} \equiv \mathbf{9B}$.

We have commented previously on the exclusive formation of the *cis*-bis(phenylphosphino)benzene moiety in the macrocyclization involving **3b**.[4a] Apparently a similar situation pertains in the key macrocyclization step involving **3a**. Obviously rather subtle conformational effects must be operative to give almost equal amounts of isomers **A** and **B** with **5** (3:2 respectively), predominantly **A** with **6** (5:1), and no detectable amount of **B** with **10**.

Experimental Section

General Methods. Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, AZ, or Galbraith Laboratories, Inc., Knoxville, TN.

Infrared (IR) spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer.

Proton magnetic resonance (^1H NMR) spectra were obtained on Perkin-Elmer R-12, Varian A-60, or Varian HA-100 instruments. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are reported in hertz. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Carbon-13 and phosphorus-31 NMR spectra were determined on a Bruker instrument at 22.6 and 36.4 MHz, respectively. Chemical shifts are given as parts per million relative to Me_4Si for ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield from 85% H_3PO_4 are defined as negative for the ^{31}P spectra. The ^{13}C and ^{31}P NMR spectra are proton decoupled.

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

Gas chromatographic analyses were performed on either a Varian Aerograph 2720 (thermal conductivity detector) or 2740 (flame ionization detector) instrument by using either 5% or 20% SE-30 on Gas Chrom Q, packed in stainless steel columns (6 ft × 0.188 in. or 6 ft × 0.125 in). Peak area measurements were obtained with the aid of a Vidar 6300 digital integrator.

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

The following compounds were prepared according to literature procedures or only minor modifications thereof: 1,2-bis(dimethylarsino)benzene (**1**),[5] 1,2-bis(methylarsino)benzene (**2**),[6] bis(3-chloropropyl)phenylphosphine (**4b**),[4a] 1,7-bis(methylsulfonyloxy)-4-oxaheptane (4d),[14] bis(3-chloropropyl)methylamine (**4e**).[15]

Bis(3-bromopropyl)phenylarsine (4a). To a mixture of 1,3-dibromopropane (127 g, 628 mmol) and phenylarsine[16] (4.4 g, 28 mmol) in THF (250 mL) at −78 °C was added dropwise a 2.4 M hexane solution of *n*-butyllithium (26 mL, 63 mmol). The resulting mixture was allowed to warm to room temperature and evaporated at 40 °C under high vacuum (dry ice cooled receiver). The residue was partitioned between ether (200 mL) and water (2 × 50 mL). The ether layer was washed with brine (100 mL), dried ($MgSO_4$), and concentrated to give a pale yellow oil (6.9 g) which was chromatographed on silica gel (120 g) by using dichloromethane–hexane (1:4 v/v) as eluant to yield a colorless oil (2.2 g, 20%): ^1H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 3.4 (m, 4 H), 1.85 (m, 8 H); mass spectrum, *m/e* 394 (M^+ for $^{79}Br^{79}Br$). This material was used without further purification in the macrocyclizations described below.

Bis[3-(methylsulfonyloxy)propyl] Sulfide (4c). A solution of methanesulfonyl chloride (2.82 g, 24.9 mmol) in dichloromethane (10 mL) was added dropwise to a solution of bis(3-hydroxypropyl) sulfide[17] (1.7 g, 11.3 mmol) and triethylamine (3.4 g, 33.9 mmol) in dichloromethane (50 mL) at −10 °C. The mixture was stirred for 1.5 h and then washed with water (2 × 50 mL) and brine (100 mL). The organic solution was dried and evaporated to give a brown oil which was chromatographed on silica gel (100 g) using chloroform–ethyl acetate (3:2 v/v) to give a colorless oil. This was crystallized from dichloromethane–pentane as a white solid (2.74 g, 80%): mp 42–43.5 °C; ^1H NMR ($CDCl_3$) δ 4.34 (t, J = 6 Hz, 4 H), 3.05 (s, 6 H), 2.67 (t, J = 6 Hz, 4 H), 2.04 (m, 4 H); mass spectrum, *m/e* 306 (M^+).

Anal. Calcd for $C_8H_{18}O_6S_3$: C, 31.36; H, 5.92. Found: C, 31.23; H, 6.01.

Bis(3-chloropropyl)phenylarsine (4f). Reaction of phenylarsine (4.95 g, 32.1 mmol) and 1-bromo-3-chloropropane (46 g, 292 mmol) as described for **4a** above gave, after the extractive and evaporative workup, a pale yellow oil (9.0 g, 91%): ^1H NMR ($CDCl_3$) δ 7.5 (m, 5 H), 3.6 (m, 4 H), 1.9 (m, 8 H); mass spectrum, *m/e* 305 (M^+ for ^{35}Cl–^{35}Cl). This material was used for the synthesis of **10** without further purification.

2,10-Dimethyl-6-phenyl-2,6,10-triarsabicyclo[9.4.0]pentadeca-1-(11),12,14-triene (5). The following description is typical of all the macrocyclizations carried out in this work. The dianion **3a** [from **2** (2.4 g, 9.35 mmol) and 2.4 M *n*-BuLi in hexane (9.5 mL, 22.8 mmol)] in THF (120 mL) and **4a** (3.9 g, 9.85 mmol) in THF (130 mL) were added dropwise (8–12 drops/min) simultaneously from two separate syringes via overflow dilution chambers to a round-bottom flask initially charged with 1.5 L of boiling THF. After the addition was complete, the reaction mixture was concentrated on a rotary evaporator. The residue was dissolved in ether (500 mL), washed with saturated aqueous ammonium chloride (100 mL), water (2 × 100 mL), and brine (100 mL), and dried. Upon concentration under vacuum a pale yellow, viscous oil (3.5 g) was

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[9] Kyba, E. P.; Brown, S. B. *Inorg. Chem.* **1980**, *19*, 2159–2162.

[10] This laboratory, unpublished results.

[11] The structure of **11A** has been established by X-ray crystallography.[4a]

[12] The metal carbonyl derivatives of these ligands will be described elsewhere.

[13] Obviously **9A** and **9B** are not equivalent, but rapid inversion at nitrogen makes them inseparable.

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[17] Bis(3-hydroxypropyl) sulfide was prepared from thiodipropanoic acid (Fairfield Chemical Co.) by a lithium aluminum hydride reduction in THF at 0 °C.

obtained. A careful anaerobic column chromatography on silica gel (100 g) with hexane–dichloromethane (3:1 v/v) as eluant gave two isomers of **5**. The chromatographically more mobile material, **5A** ($R_f = 0.36$, in the above solvent system), was obtained as a viscous oil (0.85 g, 18.5%): ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 9 H), 1.75 (m, 12 H), 1.17 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.7–127.8 (aromatic), 34.6, 29.6, 24.6, 9.2; mass spectrum, *m/e* 492 (M^+). The less mobile material, **5B** ($R_f = 0.28$), was also a colorless viscous oil (0.62 g, 14%): ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 9 H), 1.7 (m, 12 H), 1.13 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.5–127.4 (aromatic), 31.5, 23.5, 23.2, 9.0; mass spectrum *m/e* 492 (M^+). The ratio of **5A** to **5B** in the crude product was ca. 5:4 as shown by ^{1}H and ^{13}C NMR spectroscopy. Compound **5A**, upon refluxing with 1 equiv of $Mo(CO)_6$ in toluene for 2 h, gave solution (toluene) IR absorptions at 2010 and 1900 cm^{-1} (tetracarbonyl), whereas **5B** gave, under similar conditions, IR absorptions at 1950 and 1850 cm^{-1} (tricarbonyl).[18]

Anal. Calcd for $C_{20}H_{27}As_3$: C, 48.81; H, 5.53. Found for **5A**: C, 48.94; H, 5.43; for **5B**: C, 49.00; H, 5.62.

2,10-Dimethyl-6-phenyl-2,10-diarsa-6-phosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene (6). Reaction of **3a** (14.7 mmol) and **4b** (14.7 mmol) as described for **5** above gave, after the extractive and evaporative workup, a pale yellow oil (5.2 g). This was chromatographed on silica gel (250 g) by using dichloromethane–hexane (1:1 v/v) as eluant to give two isomeric compounds as viscous oils. **6A** (0.83 g, 13%, $R_f = 0.22$ in the above solvent system): ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 9 H), 1.8 (m, 12 H), 1.18 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.8–128.1 (aromatic), 33.7 (d, J = 13 Hz), 29.7 (d, J = 12 Hz), 23.9 (d, J = 17.6 Hz), 9.4 (s); ^{31}P NMR ($CDCl_3$) δ −27.01; mass spectrum, *m/e* 448 (M^+). **6B** (0.36 g, 6%, $R_f = 0.12$): ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 9 H), 1.7 (m, 12 H), 1.22 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.6–127.5 (aromatic), 31.2 (d, J = 8.5 Hz), 24.0 (d, J = 15 Hz), 22.3 (d, J = 10 Hz), 9.2 (s); ^{31}P NMR ($CDCl_3$) δ −21.22; mass spectrum, *m/e* 448 (M^+). The ratio of **6A** to **6B** in the crude product was ca. 5:1 as shown by ^{1}H and ^{31}P NMR spectra. Compound **6A** upon refluxing with 1 equiv of $Mo(CO)_6$ in toluene for 1.5 h gave toluene solution IR absorptions at 2010 and 1900 cm^{-1} (tetracarbonyl), whereas **6B** under similar conditions gave IR absorptions at 1950 and 1850 cm^{-1} (tricarbonyl).

Anal. Calcd for $C_{20}H_{27}As_2P$: C, 53.59; H, 6.07. Found for **6A**: C, 53.30; H, 5.90; for **6B**: C, 53.74; H, 5.96.

2,10-Dimethyl-2,10-diarsa-6-thiabicyclo[9.4.0]pentadeca-1(11),12,14-triene (7). Reaction of **3a** (13.18 mmol) and **4c** (13.18 mmol) as described for **5** above gave, after the extractive and evaporative workup, a light yellow oil (4.2 g) which was chromatographed on silica gel (150 g) by using dichloromethane–pentane (1:1 v/v) to yield a colorless oil (2.1 g, 43%): ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 4 H), 2.5 (m, 4 H), 1.8 (m, 8 H), 1.18 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.4, 130.5, 128.5, 32.2, 30.0, 27.7, 9.6; mass spectrum, *m/e* 372 (M^+). This material was distilled [155–157 °C (5 μm), bath temperature ca. 235 °C] to give a colorless liquid (1.8 g, 37%) which exhibited new, minor peaks in the ^{1}H and ^{13}C NMR spectra (see Table I, **7C**) in addition to those before distillation in a ratio of 1:4. The two materials could not be separated chromatographically. The undistilled **7** was heated at reflux with 1 equiv of $Mo(CO)_6$ in toluene for 1.5 h, at which point IR absorptions at 1950 and 1850 cm^{-1} only (tricarbonyl) were observed.

Anal. Calcd for $C_{14}H_{22}As_2S$: C, 45.17; H, 5.96. Found: C, 45.44; H, 5.79.

2,10-Dimethyl-2,10-diarsa-6-oxabicyclo[9.4.0]pentadeca-1(11),12,14-triene (8). Reaction of **3a** (20.93 mmol) and **4d** (20.93 mmol) as described for **5** above gave, after the extractive and evaporative workup, a colorless oil (5.88 g) which was chromatographed on silica gel (150 g) by using dichloromethane–hexane (1:1 v/v) as eluant to yield a colorless liquid (3.7 g, 50%). This material was distilled [126–128 °C (0.015 mm)] to give a viscous, colorless liquid (3.0 g, 40%): ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 4 H), 3.1 (m, 4 H), 1.9 (m, 8 H), 1.10 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 149.0, 130.3, 127.9, 70.3, 28.7, 27.3, 10.1; mass spectrum, *m/e* 356 (M^+).

Anal. Calcd for $C_{14}H_{22}As_2O$: C, 47.21; H, 6.23. Found: C, 47.39; H, 6.27.

2,6,10-Trimethyl-2,10-diarsa-6-azabicyclo[9.4.0]pentadeca-1-(11),12,14-triene (9). Reaction of **3a** (19.9 mmol) and **4e** (19.9 mmol) as described for **5** gave, after the extractive and evaporative workup, a pale yellow oil (6.0 g) which was chromatographed on alumina (150 g) by using dichloromethane–hexane (1:3 v/v) as eluant to give a colorless liquid (3.0 g, 41%). This was distilled [130–132 °C (10 μm)] to yield a colorless, viscous liquid (2.7 g, 36%); ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 4 H), 2.3 (m, 4 H), 2.0 (s, 3 H), 1.75 (m, 8 H), 1.15 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.8, 130.3, 127.9, 56.0, 41.5, 28.6, 24.7, 9.3; mass spectrum, *m/e* 369 (M^+).

Anal. Calcd for $C_{15}H_{25}As_2N$: C, 48.80; H, 6.83. Found: C, 48.81; H, 6.75.

2,6,10-Triphenyl-6-arsa-2,10-diphosphabicyclo[9.4.0]pentadeca-1-(11),12,14-triene (10). Reaction of **3b**[4a] (23.29 mmol) and **4f** (23.29 mmol) as described for **5** gave, after the extractive and evaporative workup, a white glass (10.2 g). This was crystallized from benzene–hexane and recrystallized from acetone to give a white, crystalline solid (3.5 g, 28%): mp 136.5–138 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 19 H), 2.7 (m, 4 H), 2.3 (m, 4 H), 1.95 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 142.0–127.6 (aromatic), 31.5 (t, J = 5 Hz), 29.2 (t, J = 6 Hz), 23.5 (t, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$) δ −31.58; mass spectrum, *m/e* 528 (M^+). When **10** was heated with a stoichiometric amount of $Mo(CO)_6$ in refluxing toluene for 1 h, absorptions in the IR spectrum at 2010 and 1900 cm^{-1} only were observed.

Anal. Calcd for $C_{30}H_{31}AsP_2$: C, 68.19; H, 5.91. Found: C, 67.87; H, 6.11.

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