Acknowledgment. We wish to thank Professor Pierre Laszlo for helpful discussions concerning virtual coupling. Support for the Cornell Nuclear Magnetic Resonance Facility from the National Science Foundation Instrumentation Program (Grants CHE-79-04825 and PCM-80-18643) and the National Institutes of Health (Grant DHHS 08SORR02002A)) is gratefully acknowledged. The FT-IR spectrometer was obtained with support from the National Science Foundation (Grant CHE-83-04659).

Contribution from the Department of Chemistry,
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Contrasting Behaviors of Phosphorus and Arsenic in a Polycyclic Framework Favoring Pnictogen Square Pyramidality

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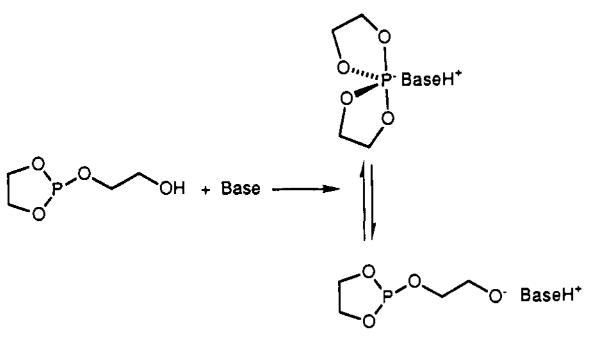
The preparations of the novel polycyclic compounds $ZPn(OCH_2)_2CHCHCH_2O(CH_2OH)$ and $ZPn(OCH_2)_2C(CH_2)_xCCH_2O(CH_2OH)$ ($Z = W(CO)_5$, $Mn(CO)_4Br$, $Fe(CO)_4$, $CpFe(CO)_2^+$, $CpCoI_2$, $Ni(CO)_3$, $Pn = P$, $x = 1-4$; Z = lone pair, $Pn = As$, $x = 2, 3$) and also $ZP(OCH_2)_2CHCH_2CH_2O$ ($Z = W(CO)_5$, $CpFe(CO)_2^+$, $Ni(CO)_3$) are reported. The phosphorus compounds possessing a pendant alcohol group displayed no tendency to coordinate the alcoholic oxygen from 223 to 350 K, even under deprotonation conditions. This was also true where Z = lone pair, O, S, Se, and Ph_3C^+. Also reported are the preparations of $As(OCH_2)_2CHCHCH_2O(CH_2OH)$ and $As(OCH_2)_2C(CH_2)_xCCH_2O(CH_2OH)$ ($x = 2, 3$). The first and second ($x = 2$) of these compounds are fluxional on the ^1H and ^{13}C NMR time scales, presumably owing to the larger size of the pnictogen. A mechanism for the fluxionality, which involves a square-pyramidal transition state, is discussed. The molecular structures of $CpCoI_2L$ ($L = P(OCH_2)_3CMe$ and $P(OCH_2)_2C(CH_2)_3CCH_2O(CH_2OH)$) determined by X-ray means are presented. The former was found to exhibit a monoclinc space group $P2_1/n$ with $a = 9.474$ (2) Å, $b = 8.346$ (3) Å, $c = 19.416$ (5) Å, $Z = 4$, and $\beta = 102.81$ (2)°. The latter compound was found to exhibit a monoclinic space group $P2_1/c$ with $a = 7.758$ (3) Å, $b = 19.327$ (4) Å, $c = 11.958$ (2) Å, $Z = 4$, and $\beta = 97.28$ (2)°. The Co–P distances in these complexes are 2.140 (1) and 2.140 (3) Å, respectively.

Introduction

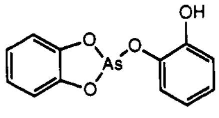
The small energy increase in the square-pyramidal (SP) geometry relative to the trigonal-bipyramidal (TBP) geometry represents an excited state in pentacoordinate pnictogen compounds undergoing Berry pseudorotation.[1] Even in reactions of species such as phosphoranyl radicals and phosphoranide anions containing one and two electrons, respectively, in the fifth ligand site, SP intermediates are believed to be present[2] as a result of Berry pseudorotation.[3] Recently a number of SP phosphorus, arsenic, and antimony compounds, stabilized by steric and electronic factors introduced by the ligands, have been prepared and structured by others.[4]

The deprotonation of phosphites containing pendant alcohol groups has been reported to yield stable phosphoranide anions that exist in equilibrium with the phosphite species as shown in reaction 1.[5,6] Although in the one instance in which such a phosphoranide anion has been structurally characterized[7] the phosphorus experiences a TBP coordination geometry, the energy barrier between the TBP and the SP geometries is probably small.[8]



(1)

The equilibrium between tricoordinate and pentacoordinate forms of hydrospiroarsoranes can be observed in the ^1H NMR spectrum of aromatic **1**.[9] In compounds containing saturated



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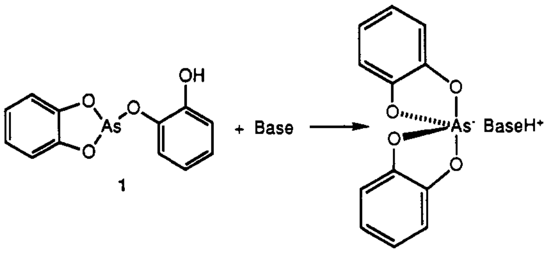
five-membered rings, however, only the tricoordinate form is detectable.[9] Reaction of the equilibrium mixture with base yields the arsoranide anion in reaction 2.



(2)

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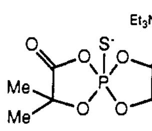
The pentavalent phosphorus anions **2–5** also equilibrate with their tetracoordinate counterparts.[10] Compounds **6–9**, which have been recently reported, are in the tetracoordinate form in the solid state.[11] In solution, however, these compounds rapidly undergo conversion to the stable pentacoordinate form with no detectable tetracoordinate form remaining. Recently we described the conversion of alcohols **10a–e** to the polycyclic systems **11–15**.[12]



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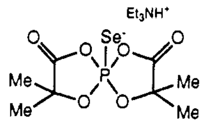

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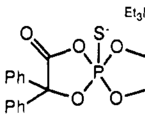

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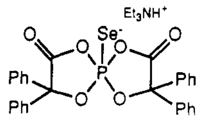

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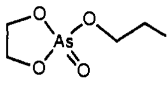

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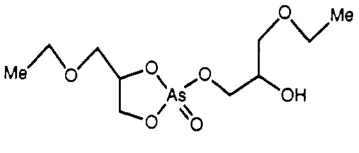

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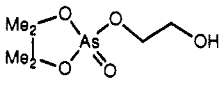

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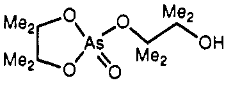

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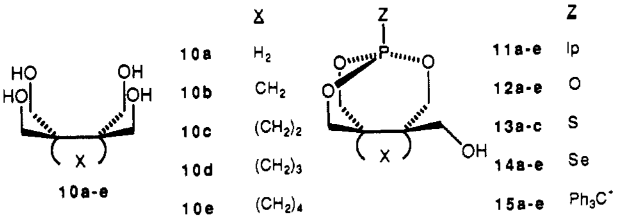
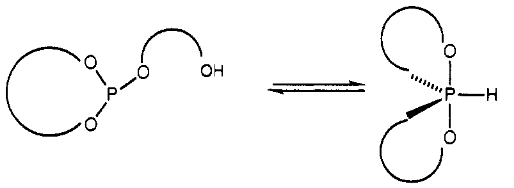




(3)

Table I. ^{31}P NMR Spectral Data (Chemical Shifts (ppm) and Coupling Constants[a] (Hz)) for Compounds **20–29**

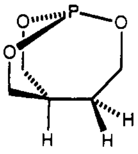
		compound series				
compound		a	b	c	d	e
20[b]	128 [417][d]					
21a–d[b]		129 [419][d]	130 [401][d]	131 [405][d]	130 [413][d]	
22[b]	157					
23a–c[b]		165	165	167		
24[b]	162					
25a–e[c]		159	160	161	162	160
26a–e[b]		136	138	137	140	137
27a–e[b]		136	138	137	140	137
28[b]	157					
29a–e[b]		165	163	159	162	163

[a] In brackets. [b] CDCl$_3$. [c] Acetonitrile. [d] ^1J(PW).

Table II. Reaction Yields of Compounds **18a–c** and **20–29**

compound	% yield	compound	% yield
18a	33.8	**25c**	90.1
18b	45.5	**25d**	91.5
18c	44.1	**25e**	85.4
20	72.9	**26**	82.5
21a	68.1	**27a**	79.3
21b	51.2	**27b**	72.0
21c	70.4	**27c**	75.0
21d	70.0	**27d**	72.8
22	53.0	**27e**	70.2
23a	49.5	**28**	40.2
23b	34.0	**29a**	37.6
23c	51.5	**29b**	29.2
24	92.6	**29c**	38.2
25a	87.3	**29d**	38.4
25b	77.4	**29e**	31.2

Although the equilibrium between tricoordinate and pentacoordinate tautomers depicted in reaction 3 is known for dioxaphospholanes[13] and dioxaphosphorinanes[14,15] containing pendant alcohol groups, phosphites **11a–e** and their derivatives **12a–e**, **13a–c**, **14a–e**, and **15a–e** show no sign of similar equilibria involving square-pyramidal species. Furthermore, compounds **4a–e** possess base properties, coupling constants, and NMR resonances comparable to the model phosphites **16** and **17**. The NMR spectroscopic properties of **12a–e**, **13a–c**, **14a–e**, and **15a–e** are also similar to the derivatives of **16** and **17** with corresponding Z groups on phosphorus.[12]



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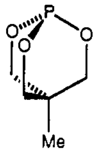
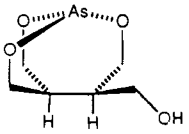
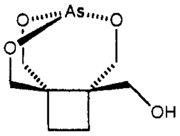


17

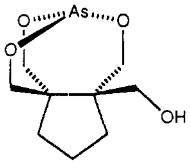
We report here the preparation of several metal complexes of **11a–e** to determine whether phosphorus coordination by the oxygen of the pendant alcohol group could be encouraged by draining electron density from phosphorus through coordination of this atom to a metal. The reactions of phosphites **11a–e** and their derivatives with a number of bases have also been carried out in an unsuccessful attempt to prepare SP phosphoranide anions. In addition, we report the preparation and characterization of the arsenic compounds **18a–c**. We show that these compounds react with base to give NMR spectra consistent with the formation of fluxional square-pyramidal arsoranide anions in solution.



18a



18b



18c

Experimental Section

Physical Measurements. NMR spectra were obtained on Nicolet NT-300 (^{1}H), Bruker WM-200 (^{13}C), and Bruker WM-300 (^{31}P) in-

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struments at room temperature. The ^{31}P NMR data of the compounds described in this paper are presented in Table I. Because the ^{1}H and ^{13}C spectra of the vast majority of the new compounds prepared herein are very similar to those of **11a–e**, **12a–e**, **13a–c**, **14a–e**, and **15a–e** presented elsewhere,[12] and in the interest of space considerations, spectral parameters appear in the supplementary material. These spectral data are included in this section, however, for the other new compounds. Variable-temperature NMR measurements were recorded on a Bruker WM-200 instrument. These spectra were recorded in acetonitrile-d_3 solutions over the temperature range 223–350 K. Chemical shifts are given in ppm (positive downfield) relative to internal Me_4Si (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P) standards. High resolution mass spectral data were recorded on a Kratos MS-50 spectrometer.

Compounds **11–16**,[12] **17**,[16] $W(CO)_5(THF)$,[17] $Mn(CO)_5Br$,[18] $Fe_3(CO)_{12}$,[19] $[CpFe(CO)_2(THF)][BF_4]$,[20] $CpCo(CO)I_2$,[21] $As(NMe_2)_3$,[22] and $N(CH_2CH_2NMe)_3P$ (**19**)[23] were prepared as described previously. All reactions were performed with the strict exclusion of moisture unless otherwise described. Solvents were dried by standard methods and distilled before use. All other chemicals were used as received. Reaction yields of the following new compounds are presented in Table II.

W(CO)$_5$(16) (20), W(CO)$_5$(11a) (21a), W(CO)$_5$(11b) (21b), W(CO)$_5$(11c) (21c), and W(CO)$_5$(11d) (21d). These complexes were prepared by using the same general procedure. In a typical synthesis, a sample of the appropriate ligand (**11a–d** or **16**) (ca. 1.1 mmol) in a 250-mL round-bottom flask was added a solution of $W(CO)_5(THF)$ in 150 mL of THF prepared from $W(CO)_6$ (ca. 1.2 mmol). This solution was stirred for 3 h at room temperature and the solvent removed under vacuum. The resulting white solid was purified by silica gel chromatography using ethyl acetate as the eluent. After unreacted $W(CO)_6$ was collected, the product eluted and removal of the solvent under vacuum gave pure product.

***cis*-Mn(CO)$_4$Br(11a) (22).** To a 50-mL round-bottom flask containing $Mn(CO)_5Br$ (0.4313 g, 1.569 mmol) and **11a** (0.2754 g, 1.546 mmol) was added 25 mL of THF. The resulting solution was stirred for 3 h at room temperature and the solvent removed under vacuum to give a pale yellow solid. The product was purified by silica gel chromatography using ethyl acetate as the eluent giving pure **22** (IR(CH_2Cl_2, cm^{-1}) 2108, 2029, 1974 (ν(CO))).

Fe(CO)$_4$(11a) (23a), Fe(CO)$_4$(11b) (23b), and **Fe(CO)$_4$(11c) (23c).** These complexes were prepared by using the same method. In a typical reaction, a mixture of $Fe_3(CO)_{12}$ (ca. 0.87 mmol) and the appropriate ligand (ca. 2.6 mmol) in 50 mL of benzene was heated to reflux for 3 h. The solvent was removed under vacuum and the solid residue extracted with three 25-mL portions of hot hexane. The hexane extracts were combined and the solvent removed under vacuum to give pure product.

[CpFe(CO)$_2$(16)][BF$_4$] (24), [CpFe(CO)$_2$(11a)][BF$_4$] (25a), [CpFe(CO)$_2$(11b)][BF$_4$] (25b), [CpFe(CO)$_2$(11c)][BF$_4$] (25c), [CpFe(CO)$_2$(11d)][BF$_4$] (25d), and [CpFe(CO)$_2$(11e)][BF$_4$] (25e). All of these complexes were prepared by using the same method. In a typical reaction, to a 50-mL round-bottom flask containing $[CpFe(CO)_2(THF)][BF_4]$ (ca 1.0 mmol) and the appropriate ligand (ca. 1.0 mmol) was added 25 mL of THF. The solution was then stirred for 30 min and hexane added to precipitate the product. Filtration of the cream-colored solid gave pure product.

CpCo(17)I$_2$ (26), CpCo(11a)I$_2$ (27a), CpCo(11b)I$_2$ (27b), CpCo(11c)I$_2$ (27c), CpCo(11d)I$_2$ (27d), and CpCo(11e)I$_2$ (27e). These complexes were prepared by using the same synthetic procedure. To a solution of $CpCo(CO)I_2$ (ca. 1.9 mmol) in 10 mL of CH_2Cl_2 was added dropwise a solution of the appropriate ligand (1.9 mmol) in 5 mL of CH_2Cl_2 over a period of 3 h. The solution was stirred an additional hour and the solvent removed under vacuum. The crude product was then purified by silica gel chromatography using ethyl acetate as the eluent and the purple product band collected. Removal of the solvent gave pure product (**26**).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 3 H, Me), 3.96 (d, ^3J(HCOP) = 12.92 Hz, 6 H, H_2COP), 5.25 (s, 5 H, Cp). ^{13}C NMR (300 MHz, $CDCl_3$) δ 17.53 (s, Me), 41.88 (d, $C(CH_2)_3$), 63.19 (d, CH_2O), 87.67 (s, Cp).

Ni(CO)$_3$(16) (28), Ni(CO)$_3$(11a) (29a), Ni(CO)$_3$(11b) (29b), Ni(CO)$_3$(11c) (29c), Ni(CO)$_3$(11d) (29d), and Ni(CO)$_3$(11e) (29e). To a solution of the appropriate ligand (ca. 1.1 mmol) in 20 mL of $CHCl_3$ was added $Ni(CO)_4$ (ca. 1.2 mmol) in one portion by syringe. The solution was stirred for 16 h and the solvent reduced to ca. 3 mL. Addition of hexane to precipitate the product followed by filtration gave the white solid product.

4-(Hydroxymethyl)-1-arsa-2,7,8-trioxatricyclo[3.2.2.0^{1,5}]nonane (18a). To a suspension of **10a** (0.6346 g, 4.226 mmol) in 25 mL of THF was added in one portion $As(NMe)_2)_3$ (0.8762 g, 4.230 mmol). The reaction mixture was then heated to 65 °C for 3 h. Upon cooling to room temperature the solvent was removed under vacuum and the crude solid product purified by silica gel chromatography using ethyl acetate as the eluent. Removal of the solvent from the product fraction gave pure white solid **18a**. ^{1}H NMR (300 MHz, DMSO) δ 2.12 (m, $^3J(H_fCCH_a)$ = 6.82 Hz, $^3J(H_fCCH_{a'})$ = 7.30 Hz, $^3J(H_fCCH_c)$ = 4.67 Hz, $^3J(H_fCCH_{c'})$ = 9.56 Hz, 1 H, H_f), 2.15 (m, $^3J(H_eCCH_b)$ = 1.93 Hz, $^3J(H_eCCH_{b'})$ = 4.67 Hz, $^3J(H_eCCH_d)$ = 1.92 Hz, $^3J(H_eCCH_{d'})$ = 3.57 Hz, 1 H, H_e), 3.34 (m, $^2J(H_{a'}CH_a)$ = 10.63 Hz, $^3J(H_{a'}COH)$ = 5.25 Hz, $^3J(H_{a'}CCH_f)$ = 7.30 Hz, 1 H, $H_{a'}$), 3.39 (m, $^2J(H_aCH_{a'})$ = 10.63 Hz, $^3J(H_aCOH)$ = 5.25, $^3J(H_aCCH_f)$ = 6.82 Hz, 1 H, H_a), 3.85 (dd, $^2J(H_{c'}CH_c)$ = 11.73 Hz, $^3J(H_{c'}CCH_f)$ = 9.56 Hz, ^{1}H, $H_{c'}$, 3.89 (m, $^2J(H_dCH_{d'})$ = 10.36 Hz, $^4J(H_dCCH_b)$ = 2.86 Hz, $^3J(H_dCCH_e)$ = 1.92 Hz, 1 H, H_d), 4.05 (dd, $^2J(H_cCH_{c'})$ = 11.73 Hz, $^3J(H_cCCH_f)$ = 4.67 Hz, 1 H, H_c), 4.14 (dd, $^2J(H_{b'}CH_b)$ = 10.72 Hz, $^3J(H_{b'}CCH_e$ = 4.67 Hz, 1 H, $H_{b'}$, 4.20 (m, $^2J(H_bCH_{b'})$ = 10.72 Hz, $^4J(H_bCCCH_d)$ = 2.86 Hz, $^3J(H_bCCH_e)$ = 1.93 Hz, 1 H, H_b), 4.31 (dd, $^2J(H_{d'}CH_d)$ = 10.36 Hz, $^3J(H_dCCH_e)$ = 3.57 Hz, 1 H, $H_{d'}$). ^{13}C NMR (300 MHz, DMSO) δ 38.26 (s, C_e), 49.69 (s, C_f), 62.61 (s, C_a), 64.19 (s, C_d), 65.55 (s, C_c), 70.41 (s, C_b). High resolution MS (EI, 70 eV) *m/e* calcd for $C_6H_{12}O_4As$ 222.995 16, found 222.995 20.

4-(Hydroxymethyl)-1-arsa-2,9,10-trioxatricyclo[5.2.2.0^{4,7}]undecane (18b). To a suspension of **10c** (0.4705 g, 2.670 mmol) in 25 mL of THF was added to one portion $As(NMe_2)_3$ (0.5539 g, 2.674 mmol). The mixture was heated to 65 °C for 3 h and then allowed to cool to room temperature. The solvent was removed under vacuum and the crude product subjected to silica gel chromatography using ethylene acetate as the eluent. Removal of the solvent from the product fraction gave pure **18b**. ^{1}H NMR (300 MHz, DMSO) δ 1.60 (m, 4 H, ring CH_2), 3.77 (d, $^2J(H_{d'}CH_d)$ = 10.17 Hz, 1 H, $H_{d'}$), 3.84 (dd, $^2J(H_{a'}CH_a)$ = 10.09 Hz, $^3J(H_{a'}COH)$ = 5.30 Hz, 1 H, $H_{a'}$), 3.86 (dd, $^2J(H_dCH_{d'})$ = 10.17 Hz, $^3J(H_dCCCH_b)$ = 3.37 Hz, 1 H, H_d), 3.94 (dd, $^2J(H_aCH_{a'})$ = 10.09 Hz, $^3J(H_aCOH)$ = 5.30 Hz, 1 H, H_a), 3.98 (d, $^2J)H_{b'}CH_b)$ = 10.55 Hz, 1 H, $H_{b'}$), 4.00 (d, $^2J(H_cCH_{c'})$ = 11.12 Hz, 1 H, H_c) 4.09 (d, $^2J(H_{c'}CH_c)$ = 11.12 Hz, 1 H, $H_{c'}$), 4.61 (dd, $^2J(H_bCH_{b'})$ = 10.55 Hz, $^4J(H_bCCCH_d)$ = 3.37 Hz, 1 H, H_b). ^{13}C NMR (300 MHz, DMSO) δ 22.25 (s, C_h), 22.36 (s, C_g), 46.23 (s, C_e), 49.16 (s, C_f), 62.94 (s, C_a), 68.18 (s, C_d), 69.53 (s, C_c), 73.16 (s, C_b). High resolution MS (EI, 70 eV) *m/e* calcd for $C_8H_{14}O_4As$ 249.010 81, found 249.010 92.

4-(Hydroxymethyl)-1-arsa-2,10,11-trioxatricyclo[6.2.2.0^{4,8}]dodecane (18c). To a suspension of **10d** (0.6706 g, 3.525 mmol) in 25 mL of THF was added in one portion $As(NMe_2)_3$ (0.7313 g, 3.530 mmol). The reaction mixture was heated to 65 °C for 3 h and allowed to cool to room temperature. The solvent was removed under vacuum and the crude product purified by silica gel chromatography using ethyl acetate as the eluent. Removal of the solvent from the product-containing fraction gave pure **18c**. ^{1}H NMR (300 MHz, DMSO) δ 1.93 (m, 6 H, ring CH_2), 3.82 (d, $^2J(H_{b'}CH_b)$ = 10.43 Hz, 1 H, $H_{b'}$), 3.84 (dd, $^2J(H_{a'}CH_a)$ = 10.58 Hz, $^3J(H_{a'}COH)$ = 5.30 1 H, $H_{a'}$), 3.89 (d, $^2J(H_{d'}CH_d)$ = 10.80 Hz, 1 H, $H_{d'}$), 3.99 (dd, $^2J(H_dCH_{d'})$ = 10.80 Hz, $^4J(H_dCCCH_b)$ = 3.52 Hz, 1 H, H_d), 4.11 (d, $^2J(H_cCH_{c'})$ = 11.59 Hz, 1 H, H_c), 4.35 (dd, $^2J(H_aCH_{a'})$ = 10.58 Hz, $^3J(H_aCOH)$ = 5.30 Hz, 1 H, H_a), 4.39 (dd, $^2J(H_bCH_{b'})$ = 10.43 Hz, $^4J(H_bCCCH_d)$ = 3.52 Hz, 1 H, H_b), 4.57 (d, $^2J(H_{c'}CH_c)$ = 11.59 Hz, 1 H, $H_{c'}$). ^{13}C NMR (300 MHz, DMSO) δ 21.20 (s, C_i), 30.93 (S, C_h), 34.56 (s, C_g), 50.19 (s, C_e), 56.43 (s, C_f), 60.68 (s, C_a), 66.83 (s, C_d), 68.72 (s, C_c), 73.80 (s, C_b). High resolution MS (EI, 70 eV) *m/e* calcd for $C_9H_{16}O_4As$ 263.026 46, found 263.026 08.

Deprotonation Reactions. A number of bases in arbitrary stoichiometric excesses were used in the deprotonation of the compounds described above and four procedures were followed depending on the base: (1) In the case of Et_3N, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and pyridine, a solution containing a large (20-fold) excess of base in benzene-d_6 was syringed under nitrogen into an NMR tube containing a weighed amount of the reagent to be deprotonated. The resulting mixture was analyzed by ^{1}H and ^{31}P NMR spectroscopy. (2) For the bases NaH and KH a 2-fold excess of the base was placed in a 10-mL round-bottom flask containing a weighed amount of the compound to be deprotonated. THF (10 mL) was added and the mixture stirred for 1 h. The mixture was filtered and the filtrate placed in an NMR tube containing a small amount of benzene-d_6. All manipulations were carried out in an argon-

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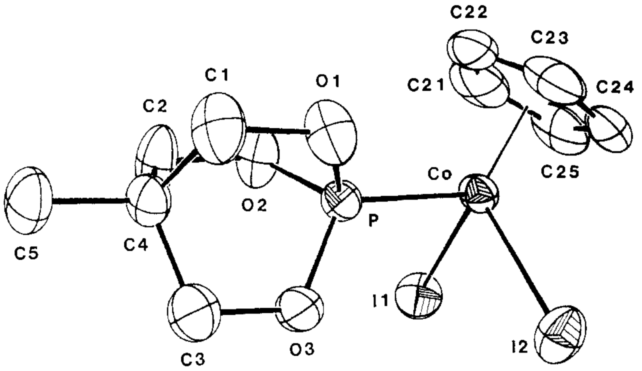

Figure 1. ORTEP drawing of **26** with ellipsoids at the 50% probability level.

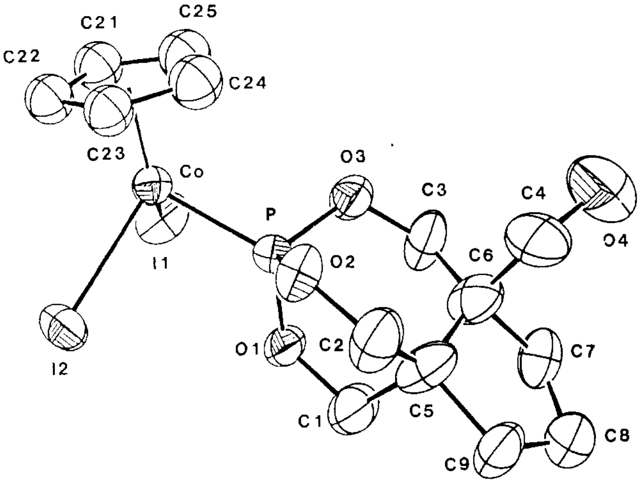

Figure 2. ORTEP drawing of **27d** with ellipsoids at the 50% probability level.

Table III. Crystallographic Data for **26** and **27**

compound	**26**	**27d**
chem formula	$C_{10}H_{14}O_3CoPI_2$	$C_{14}H_{19}O_4CoPI_2$
mol wt	525.9	596.03
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.474 (2)	7.758 (3)
b, Å	8.346 (3)	19.327 (4)
c, Å	19.416 (5)	11.958 (2)
β, deg	102.81 (2)	97.28 (2)
vol, Å^3	1497 (1)	177 (1)
d_{calcd}, g/cm^3	2.33	2.23
Z	4	4
λ	Mo Kα	Mo Kα
μ, cm^{-1}	53.26	45.0
cryst size, mm	0.20 × 0.20 × 0.22	0.20 × 0.20 × 0.15
reflns coll	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
no. of reflns coll	3413	2323
no. of unique data with $F^2 > 2\sigma(F^2)$	2420	1419
range, deg	0–55	0–45
final R, %	2.85	3.41
final R_w, %	3.74	4.29
GOF[a]	0.913	0.929
no. of var	154	168
temp, °C	22 ± 1	22 ± 1
mode	$\omega-2\theta$	ω scans
max transm factor	1.287	1.0
min transm factor	0.696	0.869

[a] The goodness of fit is defined as $[w(F_o - F_c)^2/(n_o - n_u)]^{1/2}$, where n_o and n_u denote the number of data and variables, respectively.

Table IV. Positional Parameters for $CpCo(\mathbf{17})I_2$, **26**, and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
I(1)	−0.04076 (4)	0.14468 (4)	0.36216 (2)	3.732 (6)
I(2)	0.23066 (4)	−0.18899 (5)	0.43169 (2)	4.118 (7)
Co	−0.03433 (6)	−0.16287 (7)	0.36324 (3)	2.60 (1)
P	0.0229 (1)	−0.1671 (1)	0.26264 (5)	2.44 (2)
O(1)	0.0417 (4)	−0.3424 (4)	0.2338 (2)	4.08 (7)
O(2)	−0.0962 (3)	−0.0926 (4)	0.2005 (2)	3.60 (6)
O(3)	0.1659 (3)	−0.0796 (5)	0.2547 (2)	4.56 (8)
C(1)	0.0687 (6)	−0.3469 (6)	0.1618 (3)	4.4 (1)
C(2)	−0.0605 (5)	−0.0934 (8)	0.1315 (2)	4.5 (1)
C(3)	0.1998 (6)	−0.0912 (9)	0.1851 (3)	5.4 (1)
C(4)	0.080 (5)	−0.1797 (6)	0.1341 (2)	3.03 (8)
C(5)	0.1156 (6)	−0.1873 (8)	0.0614 (2)	4.3 (1)
C(21)	−0.2543 (6)	−0.1854 (8)	0.3498 (4)	5.9 (1)
C(22)	−0.1958 (6)	−0.3226 (7)	0.3246 (3)	5.1 (1)
C(23)	−0.0965 (7)	−0.3896 (6)	0.3813 (3)	5.2 (1)
C(24)	−0.0990 (7)	−0.2963 (8)	0.4413 (3)	5.7 (1)
C(25)	−0.1934 (6)	−0.1718 (7)	0.4224 (3)	5.4 (1)
H(1)	−0.0090	−0.4009	0.1313	5*
H(2)	0.1564	−0.4028	0.1627	5*
H(3)	−0.0520	0.0139	0.1167	5*
H(4)	−0.1354	−0.1459	0.0987	5*
H(5)	0.2884	−0.1474	0.1891	7*
H(6)	0.2091	0.0136	0.1675	7*
H(7)	0.0405	−0.2429	0.0298	5*
H(8)	0.1233	−0.0817	0.0443	5*
H(9)	0.2046	−0.2421	0.0645	5*
H(10)	−0.3230	−0.1144	0.3235	7*
H(11)	−0.2194	−0.3623	0.2775	6*
H(12)	−0.0379	−0.4813	0.3796	6*
H(13)	−0.0438	−0.3166	0.4876	7*
H(14)	−0.2140	−0.0904	0.4529	7*

[a] B values with an asterisk were refined anisotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) = bc(\cos\alpha)B(2,3)]$.

flushed glovebag. This solution was analyzed by ^{1}H and ^{31}P NMR spectroscopy. (3) Deprotonation using *n*-BuLi was accomplished by syringing 3 equiv of a 22% solution of *n*-BuLi in hexane into an NMR tube containing ca. 0.1 mmol of the compound to be deprotonated dissolved in ca. 1 mL of a THF/benzene-d_6 mixture (90/10) at -78 °C under argon. The resulting products were analyzed by ^{1}H and ^{31}P NMR spectroscopy. (4) In the case of base $N(CH_2CH_2NMe)_3P$ (**19**), 1 equiv of the base and 1 equiv of the compound to be deprotonated were placed in an NMR tube to which 2 mL of acetonitrile-d_3 was added to dissolve the mixture. The products of the deprotonation were analyzed by ^{1}H and ^{31}P NMR spectroscopy.

X-ray Diffraction Data. The same general procedure was used for both structure determinations described here. A purple crystal of **26** or **27d**, grown by slow evaporation of solvent from saturated CH_2Cl_2 solutions, was mounted on a glass fiber and centered on an Enraf-Nonius CAD4 diffractometer. Cell dimensions and the orientation matrix were obtained from least-squares refinement using setting angles of 25 reflections in the range $25 < 2\theta < 34°$. During data collection, three representative reflections were checked every 60 min as orientation and intensity standards. Since the change in intensity was less than the error in the measurements, no decay correction was applied. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections, based on a series of ψ scans, were initially applied to the data. Refinement of the structure was carried out using the SHELX76 package.[24] Scattering factors were obtained from the usual sources.[25]

In both structures, 25 reflections chosen from a rotation photograph were indexed to give the appropriate unit cell, which subsequent solution of the structure showed to be of a specific symmetry. The structure was solved with the use of over 3000 unique reflections in both cases with $I > 2\sigma(I)$.

Structure Solution and Refinement for 26 and 27d. Both structures were solved by direct methods. All iodine, cobalt, and phosphorus atoms were located from a direct methods E map. The remainder of the nonhydrogen atoms were located by alternate least-squares and difference Fourier procedures. Hydrogen atoms were then used in calculated positions for structure factor calculations only. Isotropic thermal parameters for the hydrogen atoms were set at 1.30 times the value of the isotropic equivalent of the thermal parameter for the attached carbon atom. Following least-squares convergence of all atoms with isotropic thermal

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Table V. Positional Parameters for CpCo(**11d**)I_2, **27d**, and Their Estimated Standard Deviations

atom	x	y	z	B^a, Å^2
I(1)	0.2047 (1)	0.17365 (4)	0.17052 (6)	5.35 (2)
I(2)	−0.17097 (9)	0.08977 (4)	0.29632 (7)	4.52 (2)
Co	0.1588 (2)	0.10230 (7)	0.3453 (1)	3.12 (3)
P	0.2036 (4)	0.0085 (1)	0.2584 (2)	3.10 (7)
O(1)	0.105 (1)	−0.0034 (3)	0.1353 (6)	4.1 (2)
O(2)	0.153 (1)	−0.0578 (4)	0.3262 (6)	4.4 (2)
O(3)	0.4027 (9)	−0.0024 (4)	0.2454 (7)	4.4 (2)
O(4)	0.674 (1)	−0.1617 (6)	0.222 (1)	9.4 (4)
C(1)	0.085 (2)	−0.0728 (7)	0.088 (1)	7.5 (5)
C(2)	0.137 (2)	−0.1257 (6)	0.273 (1)	5.7 (4)
C(3)	0.452 (2)	−0.0428 (6)	0.153 (1)	5.5 (4)
C(4)	0.492 (2)	−0.1609 (8)	0.248 (1)	7.8 (5)
C(5)	0.199 (2)	−0.1273 (7)	0.162 (1)	5.6 (4)
C(6)	0.385 (2)	−0.1140 (7)	0.147 (1)	5.5 (4)
C(7)	0.407 (2)	−0.1480 (7)	0.030 (1)	6.3 (4)
C(8)	0.287 (2)	−0.2095 (8)	0.021 (1)	7.6 (5)
C(9)	0.153 (2)	−0.1989 (6)	0.106 (1)	5.7 (4)
C(21)	0.278 (1)	0.1805 (3)	0.4480 (8)	4.8 (3)*
C(22)	0.130 (1)	0.1565 (3)	0.4954 (8)	4.4 (2)*
C(23)	0.152 (1)	0.0845 (3)	0.5168 (8)	4.2 (2)
C(24)	0.313 (1)	0.0641 (3)	0.4828 (8)	5.1 (3)*
C(25)	0.391 (1)	0.1233 (3)	0.4402 (8)	5.4 (3)*

[a] B values with an asterisk used in calculated positions for structure factor calculations only. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) = bc(\cos\alpha)B(2,3)]$.

Table VI. Selected Bond Distances and Angles in CpCo(**17**)I_2, **26**[a]

Bond Distances (Å)			
Co–I(1)	2.5676 (7)	P–O(2)	1.585 (3)
Co–I(2)	2.5762 (6)	P–O(3)	1.577 (4)
Co–P	2.140 (1)	O(2)–C(2)	1.452 (6)
Co–C(21)	2.051 (5)	O(3)–C(3)	1.459 (7)
Co–C(22)	2.042 (6)	C(1)–C(4)	1.508 (7)
Co–C(23)	2.035 (6)	C(2)–C(4)	1.510 (7)
Co–C(24)	2.080 (6)	C(3)–C(4)	1.518 (7)
Co–C(25)	2.089 (6)	C(4)–C(5)	1.522 (7)
P–O(1)	1.590 (3)		
Bond Angles (deg)			
I(1)–Co–I(2)	96.17 (2)	P–O(3)–C(3)	115.5 (3)
I(1)–Co–P	91.11 (4)	O(1)–C(1)–C(4)	110.9 (4)
I(2)–Co–P	93.12 (3)	O(2)–C(2)–C(4)	111.0 (4)
Co–P–O(1)	114.0 (1)	O(3)–C(3)–C(4)	110.6 (4)
Co–P–O(2)	114.0 (1)	C(1)–C(4)–C(2)	108.5 (4)
Co–P–O(3)	118.6 (1)	C(1)–C(4)–C(3)	108.8 (4)
O(1)–P–O(2)	102.1 (2)	C(1)–C(4)–C(5)	109.9 (4)
O(1)–P–O(3)	103.0 (2)	C(2)–C(4)–C(3)	108.3 (4)
O(2)–P–O(3)	103.1 (2)	C(2)–C(4)–C(5)	111.2 (4)
P–O(1)–C(1)	114.4 (3)	C(3)–C(4)–C(5)	110.0 (4)
P–O(2)–C(2)	115.3 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Selected Bond Distances and Angles in CpCo(**11d**)I_2, **27d**[a]

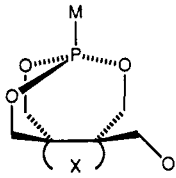
Bond Distances (Å)			
I(1)–Co	2.566 (2)	O(2)–C(2)	1.45 (1)
I(2)–Co	2.563 (2)	O(3)–C(3)	1.45 (2)
Co–P	2.140 (3)	O(4)–C(4)	1.48 (2)
Co–C(21)	2.089 (7)	C(1)–C(5)	1.57 (2)
Co–C(22)	2.113 (9)	C(2)–C(5)	1.47 (2)
Co–C(23)	2.087 (9)	C(3)–C(6)	1.47 (2)
Co–C(24)	2.046 (8)	C(4)–C(6)	1.64 (2)
Co–C(25)	2.047 (8)	C(5)–C(6)	1.50 (2)
P–O(1)	1.589 (7)	C(5)–C(9)	1.56 (2)
P–O(2)	1.591 (8)	C(6)–C(7)	1.58 (2)
P–O(3)	1.586 (8)	C(7)–C(8)	1.51 (2)
O(1)–C(1)	1.45 (1)	C(8)–C(9)	1.56 (2)
Bond Angles (deg)			
I(1)–Co–I(2)	95.86 (5)	C(1)–C(5)–C(2)	106 (1)
I(1)–Co–P	90.70 (9)	C(1)–C(5)–C(6)	108 (1)
I(2)–Co–P	91.59 (9)	C(1)–C(5)–C(9)	106 (1)
Co–P–O(1)	118.9 (2)	C(2)–C(5)–C(6)	122 (1)
Co–P–O(2)	111.7 (2)	C(2)–C(5)–C(9)	109 (1)
Co–P–O(3)	112.3 (3)	C(6)–C(5)–C(9)	106 (1)
O(1)–P–O(2)	103.6 (4)	C(3)–C(6)–C(4)	110 (1)
O(1)–P–O(3)	104.6 (5)	C(3)–C(6)–C(5)	120 (1)
O(2)–P–O(3)	104.5 (4)	C(3)–C(6)–C(7)	111 (1)
P–O(1)–C(1)	120.3 (8)	C(4)–C(6)–C(5)	103 (1)
P–O(2)–C(2)	121.1 (7)	C(4)–C(6)–C(7)	109 (1)
P–O(3)–C(3)	120.2 (7)	C(5)–C)6)–C(7)	104 (1)
O(1)–C(1)–C(5)	112 (1)	C(6)–C(7)–C(8)	105 (1)
O(2)–C(2)–C(5)	113 (1)	C(7)–C(8)–C(9)	108 (1)
O(3)–C(3)–C(6)	114 (1)	C(5)–C(9)–C(8)	105 (1)
O(4)–C(4)–C(6)	105 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

parameters, a numerical absorption correction was applied giving correction factors ranging from 0.696 to 1.287. The crystal data for both structures are summarized in Table III. The positional parameters are given in Tables IV and V for **26** and **27d**, respectively. Selected bond lengths and angles for these respective compounds are given in Tables VI and VII. The ORTEP diagrams of **26** and **27d** are presented in Figures 1 and 2, respectively.

Results and Discussion

Syntheses. The metal complexes of phosphites **11a–e** were prepared by standard procedures described in the Experimental Section. Complexes of the phosphite ester **16** with the metal fragments $W(CO)_5$ (**20**), $[CpFe(CO)_2]^+$ (**24**), and $Ni(CO)_3$ (**28**) were prepared as model compounds since **16** contains no pendant alcohol arm. Reaction of the appropriate alcohol with $As(NMe_2)_3$ (reaction 4) gave **18a–c**, which are arsenic analogues of **11a**, **11c**, and **11d**, respectively.



	M
21a-d	$W(CO)_5$
22	$Mn(CO)_4Br$ (L = **11a**)
23a-c	$Fe(CO)_4$
25a-c	$CpFe(CO)_2^+$
27a-e	$CpCoI_2$
29a-e	$Ni(CO)_3$

$$\mathbf{10a},\ \mathbf{10c},\ \text{or}\ \mathbf{10d} + As(NMe_2)_3 \rightarrow \mathbf{18a},\ \mathbf{18b},\ \text{or}\ \mathbf{18c} + 3HNMe_2 \quad (4)$$

NMR Spectra. As discussed previously for **11a–e**, **12a–e**, **13a–c**, **14a–e**, and **15a–e**,[12] the appearance of the ^1H and ^{13}C NMR spectra of these compounds should be simplified if they were present in the pentacoordinate form, which is of higher symmetry as shown in Figure 3 for **11a–e**. As with all of the aforementioned compounds, all of the complexes of **11a–e** display ^1H and ^{13}C NMR spectra that are consistent with the absence of detectable amounts of pentacoordinate phosphorus. Thus ligation of the oxygen of the pendant alcohol group to the phosphorus would be expected to labilize the alcoholic proton, giving rise to an anionic pentacoordinate phosphorus ligand, or a neutral form of the ligand in which rapid migration of the proton from one oxygen to the neighboring one could occur. Variable-temperature NMR studies on complexes **25a–c** and **27a–e** over the range of 223–350 K left the ^1H and ^{13}C spectra unchanged.

Typically, ^{31}P shifts for complexes containing pentacoordinate phosphorus appear much further upfield than their tetracoordinate counterparts.[26] For **30** and **31**, the ^{31}P NMR signals appeared at 67 and 73 ppm, respectively, while typical $Mn(CO)_5$ and $Co(CO)_3(PPh_3)$ complexes of phosphite esters resonate at ca. 130

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(26) Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987.

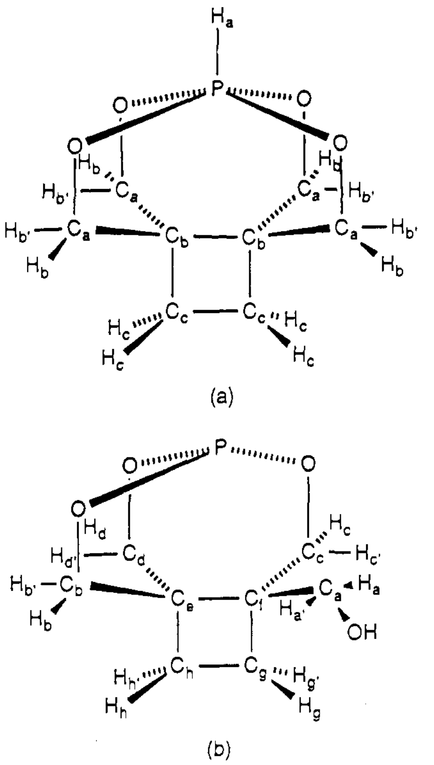
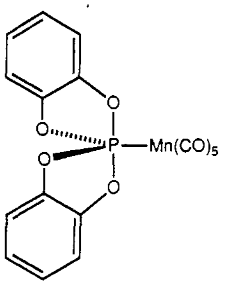


Figure 3. Pentacoordinate (a) and tricoordinate (b) forms of **11a–e**.

and ca. 120 ppm, respectively.[27,28] Similar comparisons can be made with complexes of **32** and those of $P(NR_2)_3$.[29] Examination



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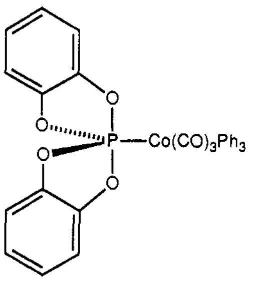

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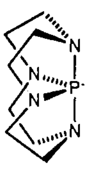


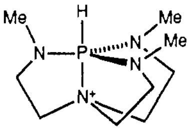
32

of the ^{31}P NMR chemical shifts of the metal complexes of **11a–e** reveals that their chemical shifts are in the typical range for tetracoordinate phosphite complexes.[30] In addition, the shifts for the complexes of **11a–e** compare well with the resonances observed in complexes of **16** (Table I) which lack a pendant alcohol group with which to form pentacoordinate phosphorus ligands.

The arsenite esters **18a–c** yield ^{1}H NMR spectra that are very similar to those of the phosphorus analogues **11a**, **11c**, and **11d**. Variable-temperature experiments performed on the former compounds showed no evidence of a tricoordinate–pentacoordinate tautomeric equilibrium. No changes in the ^{1}H NMR spectra were observed over the range of 223–350 K. The absence of couplings due to the substitution of phosphorus by arsenic in **18a–c** greatly simplifies their splitting patterns with respect to the corresponding phosphite esters and allowed facile assignment of their proton spectra. As in **11a,c,d** and their derivatives,[12] comparison of the proton–proton coupling constants of **18a** with those of **18b** and **18c** indicates that little change takes place in the carbon backbone in going from one arsenic derivative to another. All of the coupling constants compare well with one another and are consistent with a tricoordinate structure. Compounds **18b** and **18c** contain b proton resonances that appear substantially downfield with respect to their other methylene protons, while in **18a** this proton resonance is well within the range defined by the other seven methylene protons. This suggests that, as in **11a–e**,[12] twisting occurs around the methine–methine C–C bond in **18a**, which would inhibit interaction between the alcohol arm and the b proton. As was pointed out earlier,[12] such an interaction is favored in relatively rigid structures such as **18b** and **18c**.

The ^{13}C NMR spectra of **18a–c** are also very similar to those of **11a**, **11c**, and **11d**, respectively, including the inequivalence of all of the carbon atoms in the three arsenite esters, corroborating the tricoordinate nature of these compounds. No signals assignable to pentacoordinate arsenic species were detected. Variable-temperature NMR spectra were recorded in the range of 223–350 K and no changes in the ^{13}C resonances were observed for any of the three arsenites **18a–c**. Little change in the chemical shifts of the carbon resonances occurs in going from **18a** to **18c**, although carbon b exhibits a downfield shift in **18b** and in **18c** that is not present in **18a**. Again, this observation can be attributed to the hydrogen bonding interaction of the oxygen of the alcoholic arm of **18b** and **18c** with proton b in solution, thereby shifting the b carbon resonance to lower field.

Deprotonation Studies. ^{1}H, ^{13}C, and ^{3}P NMR spectra consistent with tri- or tetracoordinate species with pendant alkoxide groups were obtained from reactions of **11a–e**, **12a–e**, **13a–c**, **14a–e**, and **15a–e** with NaH and KH. Although the reactions of these bases with the metal complexes of **11a–e** resulted in their decomposition, the ^{1}H NMR spectra of these reaction mixtures proved that the phosphite ester ligands remained intact. In none of the reactions of *n*-BuLi did the **11a–e** framework remain intact, however. Nucleophilic attack on phosphorus by the negatively charged *n*-Bu group was found to occur, giving *n*-Bu_3P. Thus *n*-Bu_3P could be detected in both the ^{1}H and ^{3}P NMR spectra, and small amounts of the parent tetraalcohols **10a–e** were seen in the ^{1}H NMR spectra of the reaction mixtures. This reaction is similar to that reported for PhLi with $P(OEt)_3$, which gives PPh_3 in 80% yield.[31] Reaction of **11a–e** and its derivatives with the strong base **19** confirmed the deprotonation of these compounds. Thus the stable cation **33** is formed, giving characteristic ^{1}H, ^{13}C, and ^{31}P NMR



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spectra easily differentiated from **19**.[23,32] In all of the deprotonation reactions performed using **19** as the base, both **19** and **33** are detected in the ^{1}H, ^{13}C, and ^{31}P NMR spectra. Except for the disappearance of the OH proton in the ^{1}H NMR spectra, no significant changes are observed in the ^{1}H, ^{13}C, and ^{31}P NMR spectra of **11a–e** or any of their derivatives, indicating that these compounds do not form tetracoordinate or pentacoordinate phosphorus anions, respectively, upon deprotonation. In reactions of **19** with the metal derivatives of **11a–e**, displacement of CO was observed in addition to deprotonation. The evolution of gas and the appearance of ^2J(PMP) coupling accompanied by new downfield signals in the ^{31}P NMR spectra confirmed the displacement of CO ligands by **19**. Moreover, **19** appears to displace **11a–e** from the metal fragments, resulting in the appearance of ^{31}P resonances for free phosphite ester ligand in the *111–120* ppm region. Variable temperature (223–350 K) and ^{31}P NMR studies of deprotonation reactions using the bases pyridine, DBU, and **19** showed no detectable evidence for pentacoordinate phosphorus

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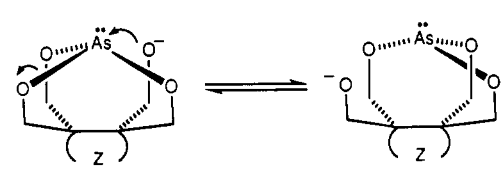
species or for fluxionality of the alkoxy groups.

Deprotonations of the arsenic compounds **18a–c** were also carried out. In reactions with pyridine and DBU, no change was observed in the room-temperature ^{1}H NMR spectra of **18a–c**. In variable-temperature ^{1}H NMR experiments performed with DBU and **18a**, however, the resonances of the eight methylene protons a–d broadened as the temperatures rose, giving rise to one broad resonance at 350 K. However, similar experiments performed on **18b** and **18c** showed no detectable change in the ^{1}H NMR spectrum. ^{31}P NMR spectra of reaction mixtures containing **19** and one of the compounds **18a–c** contained resonances due to both the starting material **19** and its conjugate acid **33**, confirming that deprotonation of the arsenic species had occurred. The ^{1}H NMR spectrum of the reaction mixture containing **18c** and **19** was very similar to the ^{1}H NMR spectrum of the starting arsenite **18c**, except for the additional signals due to **19** and **33**. No change in the splitting pattern of the protons of **18c** was detected from 223 to 350 K in variable-temperature NMR studies of this reaction mixture. The room-temperature ^{1}H NMR spectrum of the reaction of **18a** with **19**, however, contained a single broad resonance in the methylene proton region of **18a** and a single resonance for the methine protons. Variable-temperature ^{1}H NMR experiments failed to cause any change in the spectrum of this reaction mixture over the range of 223–350 K. Analysis of the reaction mixture using ^{13}C NMR showed only two broad resonances at 65 and 25 ppm due to the four methylene and two methine carbons, respectively. These data are consistent with a fluxional system in which the deprotonated alcoholic arms is exchanging with the remaining alkoxy arms bound to the arsenic. The reaction of **18b** with **19** also resulted in broad resonances for the a–d protons of the methylene arms and for the ring methylene protons at room temperature. Variable-temperature ^{1}H NMR spectroscopy performed on this reaction mixture yielded signals similar to the starting tricoordinate form of **18b** at 223 K, while at room temperature and above the sample contained single broad signals for protons a–d and for the protons of the cyclobutane ring. At room temperature the ^{13}C NMR spectrum of this reaction mixture displayed eight carbon signals characteristic of the tricoordinate form of **18b**. These signals, however, are much broader than those of the starting material, although the signals due to **19** and **33** are relatively sharp. Variable-temperature ^{13}C NMR studies performed on this reaction mixture yielded eight sharp signals for the deprotonated form of **18b** at 223 K. At 350 K there appeared a single broad resonance at ca. 47 ppm for the quaternary carbon atoms, and a single sharp resonance at 23.53 ppm for the remaining methylene carbons of the cyclobutane ring. As with **18a**, these data are consistent with a fluxional anions species in which the four alkoxy arms are exchanging. As the temperature is lowered, this exchange becomes slow and the ^{1}H NMR spectrum resembles that of the tricoordinate starting material. The deprotonations of **18a** and **18b** by **19** have been shown to be reversible by the addition of a small amount of water to these samples. Thus upon protonation, the ^{1}H NMR spectra of these reaction mixtures match those of the starting arsenite esters. Addition of more **19** to these samples again yield ^{1}H NMR spectra similar to those of the deprotonated arsenite esters discussed above.

A rationale is now suggested for the relative ease with which the arsenite esters **18a** and **18b** become fluxional compared with the analogous and nearly analogous phosphorus compounds discussed here, which in all cases appear to be static structures. The large size of arsenic compared with phosphorus is expected to allow chelation of four oxygen groups in the transition state with less strain in the polycyclic structure and less ligand–ligand repulsion around the arsenic. This effect apparently outweighs the greater pnictogen–oxygen bond strength expected with phosphorus. It is of interest to speculate on the mechanism of the fluxionality of **18a** and of deprotonated **18a** and **18b**. Nucleophilic attack of the oxygen of a pendant CH$_2$OH or CH$_2$O$^-$ arm could conceivably displace an equivalent moiety from either a trans (reaction 5) or a cis (reaction 6) position. If such a displacement occurs from a trans position, the displaced arm would attack at the same site to displace the original arm to begin the process over again.



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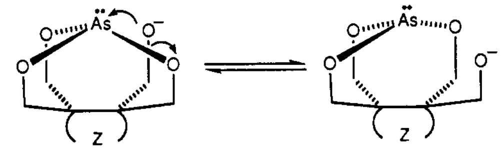
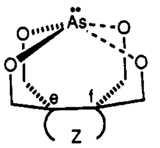


(6)

Because this type of fluxionality involves only one pair of trans related arms of the system with the other pair always remaining bonded, more complex ^{1}H and ^{13}C NMR spectra would be expected because of the low C_1 symmetry of the system. With cis displacement, however, all of the alkoxy arms can become involved, giving effective C_{2v} symmetry on the NMR time scale.

The differences in the spectral results obtained from the reactions of **18a**, **18b** and **18c** with **19** are attributable to the stereochemical properties of the tertiary/quaternary C–C backbone in **18a–c**. For exchange of the arsenic-bound and unbound alkoxy arms, these compounds must proceed through a transition state in which the substituents on carbons e and f are in an eclipsed conformation. In the case of **18c**, the preference of the cyclopentane ring for a puckered conformation inhibits the formation of such eclipsing. For **18b**, on the other hand, the relatively low energy difference between the puckered and planar forms of cyclobutane easily permit this eclipsing and thus exchange of the alkoxy arms is favored. At reduced temperatures, however, the puckered form is apparently favored and the exchange is slow on the NMR time scale. Compound **18a**, which contains no carbocyclic ring, has the lowest barrier to the eclipsed conformation of any of the three arsenite esters, and exchange of the alkoxy arms is observed over the entire temperature range studied. It should be noted that never under any of the conditions employed was fluxionality sufficiently rapid to yield the simple AB ^{1}H NMR pattern expected for **18b** or the ABX pattern expected for **18a**.



Structural Studies. The structure of complex **26** shown in Figure 1 contains a single ligand, **17**, bound to a CpCoI$_2$ metal fragment. The effect of the coordination of the phosphite ligand to the metal fragment on its P—O bond lengths is roughly equivalent to that caused by the presence of a P=O in the structure of **34**.[33] The P—O distances in **26**, shown in Table VI, compare well with those of **34**. The phosphite ester, **35**, can be taken as a model for **17**, and the P—O distances in the former are ca. 1.615 Å.[34] Comparisons of the remaining bond lengths of the ligand in **26** with those of **34** and **35** indicate that within experimental error, little change occurs in the carbon backbone upon coordination of phosphite **17** to the metal in **26**. Likewise the bond angles within **26**, **34**, and **35** are equivalent within experimental error. These results parallel those found in other structurally characterized complexes of **17**, in which little change in the ligand bond lengths is seen upon coordination to a metal.

Examination of the Co–P–O bond angles in **26** shows that the complex contains two equivalent angles (114.0 (1)°) and one slightly larger angle (118.6 (1)°), indicating that the ligand is tilting slightly away from the two large iodine atoms of the molecule. In the X-ray structure of **36**, which we recently carried out,[35] this effect is also observed. In **26** the geometry around the

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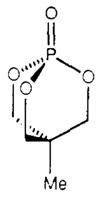

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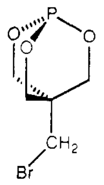

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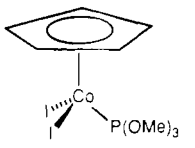

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cobalt atom can be considered pseudooctahedral with the cyclopentadienyl ring occupying one face of the octahedron. Accordingly, the I–Co–I (96.17 (2)°) and I–Co–P angles (93.11 (4)° and 93.12 (3)°) are all nearly 90°. The Co–P bond length (2.140 (1) Å) is slightly shorter than that in **36** (2.160 (1) Å) and this shortening is accompanied by a slight lengthening of one of the Co–I bonds (2.5762 (6) Å) with respect to those of **36** (2.5704 (6) and 2.5717 (6) Å).

Complex **27d**, shown in Figure 2, contains a single ligand **11d** bound to a CpCoI$_2$ metal fragment. As in the case of **26**, the carbon backbone of the phosphite ligand in **27d** remains largely unchanged upon coordination to the metal, and the structure of the phosphite ligand in **27d** is similar to that of the phosphate **12d**[12] within experimental error. The effect of the phosphate oxygen on the P–O bond lengths is nearly the same as coordination of the phosphorus to the metal fragment as shown by comparison of the P–O distances in **27d**, presented in Table VII, with those of **12d**.[12] Further comparison of the remaining C–O and C–C bond lengths shows that they too are eqivalent within experimental error. A comparison of the bond angles of **27d** with those of **12d** indicates significant differences between the two structures, however. Examination of the O–P–O angles of the two structures shows **27d** to contain slightly smaller angles (103.6 (4)°, 104.6 (5)°, and 104.5 (4)°) in comparison with the analogous angles of **12d** (105.9 (1)°, 107.1 (2)°, and 106.4 (2)°). The decrease in the O–P–O angles in **27d** is accompanied by an increase in the C(2)–C(5)–C(6) and C(3)–C(6)–C(5) angles (122 (1)° and 120 (1)°, respectively) compared with those of **12d** (115.1 (3)° and 115.2 (3)°, respectively). The remaining bond angles of the two structures, however, are all equivalent within experimental error.

A comparison of the structure of **27d** with the structures of **26** and **27** reveals that the average of the P–O–C bond angles in **27d** (ca. 120°) is unexpectedly closer to that in **36**, which contains an acyclic ligand (ca. 122°), than in **26**, which also contains a bicyclic ligand (ca. 115°). On the other hand the weak Lewis basicities of **11a–e** compare favorably with bicyclic **17** rather than with the considerably more basic acyclic P(OMe)$_3$.[12] These results substantiate that conclusion that the variation in electronic properties seen in relatively unstrained phosphite esters is dominated by the conformation of the alkoxy groups rather than by P–O–C bond angles.

In **27d** the angles about the cobalt(III) are ca. 90° (95.86 (5)°, 90.70 (9)°, and 91.59 (9)°), indicating a pseudooctahedral geometry around the metal center. The Co–I bond distances (2.563 (2) and 2.566 (2) Å) are somewhat shorter than both of those in **26** (2.5676 (7) and 2.5762 (6) Å) and in **36** (2.5704 (6) ad 2.5717 (6) Å). The Co–P bond distance (2.140 (3) Å) is the same within experimental error as that in **26** (2.140 (1) Å) and slightly shorter than that in **36** (2.160 (1) Å).

Conclusions. It has been demonstrated that the metal complexes of **11a–e** synthesized here do not exhibit a tautomeric equilibrium between tetrahedral tetracoordinate and SP pentacoordinate forms in solution. In the deprotonation of **11a–e** and their derivatives and metal complexes using several different bases, no changes in their ^{1}H, ^{13}C, and ^{31}P NMR spectra were observed, which could be taken as evidence for the formation of a SP pentacoordinate species. Although in solution the arsenite esters **18a–c** yield NMR spectra characteristic of tricoordinate species, deprotonation of **18a** and **18b** results in ^{1}H and ^{13}C NMR data consistent with a fluxional anion in which all of the alkoxy arms exchange rapidly. Because **18c** does not exhibit this fluxionality, it is proposed that the higher energy of the envelope form of the cyclopentane ring over the puckered conformation is sufficient to inhibit fluxionality.

Acknowledgment. We thank the National Science Foundation for grant support to Dr. John G. Verkade, and we thank Dr. Lee Daniels of the Iowa State University Molecular Structure Laboratory for the structural determinations by X-ray means.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths, and angles for **26** and **27d** and ^{1}H and ^{13}C NMR data for **18** and **20–29** (35 pages); tables of observed and calculated structure factors for **26** and **27d** (20 pages). Ordering information is given on any current masthead page.

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(35) Davis, R. V.; Miller, L. L.; Johnson, D. C.; Daniels, L. M.; Verkade, J. G., work in progress.