

Polytertiary Phosphines and Arsines. VI. Some Metal
Complexes of the Mixed Phosphine-Diarsine
Bis(2-Diphenylarsinoethyl)phenylphosphine¹R.B. King and Pramesh N. Kapoor²

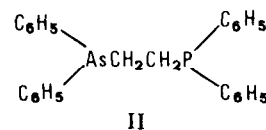
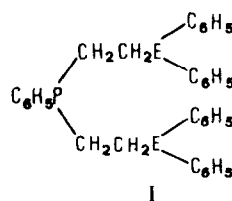
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The following metal complexes of the phosphine-diarsine $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ (abbreviated as Asf—Pf—Asf) can be prepared by procedures analogous to the preparation of the corresponding complexes of the triphosphine $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$: (1) Monoligate monometallic (Asf—Pf—Asf)M(CO) (COCH₃)(C₅H₅); (2) Biligate monometallic (Asf—Pf—Asf)M(CO)₂ (M = Cr and Mo) and $[(C_5H_5)Mo(CO)_2(Asf—Pf—Asf)][PF_6]$; (3) Triligate monometallic $[(Asf—Pf—Asf)MCl][PF_6]$ (M = Pd and Pt), (Asf—Pf—Asf)RhCl₃, (Asf—Pf—Asf)M(CO)₃ (M = Cr and Mo), and (Asf—Pf—Asf)Mn(CO)₅Br. Reaction of rhenium(III) chloride with Asf—Pf—Asf in boiling acetonitrile gives brown (Asf—Pf—Asf)₂Re₃Cl₉. Reaction of osmium tetroxide and hydrochloric acid with Asf—Pf—Asf in boiling ethanol gives the yellow-orange osmium(III) derivative (Asf—Pf—Asf)OsCl₃. Reaction of $[Rh(CO)_2Cl]_2$ with Asf—Pf—Asf in boiling toluene gives brown sparingly soluble (Asf—Pf—Asf)Rh₂(CO)₃Cl₂. Reaction of $CH_3Mo(CO)_3C_5H_5$ with Asf—Pf—Asf in acetonitrile at room temperature gives yellow monoligate monometallic (Asf—Pf—Asf)Mo(CO)₂(COCH₃)(C₅H₅) rather than a triligate trimetallic derivative. Similarly the reaction of $CH_3Mo(CO)_3C_5H_5$ with the phosphine-arsine $(C_6H_5)_2AsCH_2CH_2P(C_6H_5)_2$ (abbreviated as Asf—Pf) gives the yellow monometallic derivative (Asf—Pf)Mo(CO)₂(COCH₃)(C₅H₅) rather than a biligate bimetallic derivative.

Introduction

Recently³ we reported a survey of the metal complexes of the tritertiary phosphine bis(2-diphenylphosphinoethyl)phenylphosphine, $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (I: E = P; abbreviated as Pf—Pf—Pf). This paper reports a similar survey of the metal complexes of the closely related phosphine-diarsine⁴ bis(2-diphenylarsinoethyl)phenylphosphine, $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ (I: E = As; abbreviated as Asf—Pf—Asf). This work was undertaken in order to explore the effect of par-

tial substitution of arsenic for phosphorus in the complexing behavior of a potentially tridentate ligand.



Experimental Section

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, and (c) admitting to evacuated vessels containing organometallic compounds. All reactions described in this paper were carried out with magnetic stirring.

Materials. Triphenylarsine (M and T Chemical Company, Rahway, New Jersey) was converted to diphenylarsine by reduction with sodium in liquid ammonia.⁵ This diphenylarsine was converted to the ligands bis(2-diphenylarsinoethyl)phenylphosphine, $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ (I: E = As; abbreviated as Asf—Pf—Asf), and 1-diphenylarsino-2-diphenylphosphinoethane, $(C_6H_5)_2AsCH_2CH_2P(C_6H_5)_2$ (II: abbreviated as Asf—Pf) by the base-catalyzed addition of the diphenylarsine to phenyldivinylphosphine and diphenylvinylphosphine, respectively, as discussed in the first paper of this series.⁴ Platinum metal compounds were generally purchased from Englehard Industries, Newark, New Jersey. The following metal carbonyls were purchased from the indicated commercial sources: M(CO)₅ (M = Cr, Mo, and W) (Pressure Chemical Company, Pittsburgh, Pennsylvania), CH₃C₅H₄Mn(CO)₃ (Ethyl Corp., New York, New York), and Fe(CO)₅ (GAF, Corp., New York, New York). Rhenium trichloride was purchased from Shattuck Chemical Company, Denver, Colorado. The compounds Mn₂(CO)₁₀,⁶ Mn(CO)₅Br,^{7a} $[Rh(CO)_2Cl]_2$,⁸ CH₃Mo-

(1) For part V of this series see R.B. King and M. S. Saran, *Inorg. Chem.*, **10**, 1861 (1971).

(2) Post-doctoral research associate, 1968-1969, 1970-1971.

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Table I. New Metal Complexes of bis-(diphenylarsinoethyl)phenylphosphine Prepared in this work.

Compound ^a	Properties		Reactant	Preparation Solvent	Temp. ^c	Yield, %	Analyses, % ^d			
	Color	M.p. ^b					C	H	Cl or O	Other
[(Asf-Pf-Asf)PdCl ₂][PF ₆]	pale-yellow	253-254°	NaCl + PdCl ₂	H ₂ O/EtOH	80°(2)	70 ^{e f}	c. 44.9	3.7	3.9(Cl)	16.4(As)
[(Asf-Pf-Asf)PtCl ₂][PF ₆]	white	310-312°	K ₂ PtCl ₄	H ₂ O/EtOH	80°(6)	63 ^{e f}	f. 44.7	3.7	3.8(Cl)	16.7(As)
(Asf-Pf-Asf)RhCl ₃	orange	> 340°	RhCl ₃ · 3H ₂ O	EtOH	80°(20)	68 ^h	c. 40.9	3.3		11.4(F)
(Asf-Pf-Asf)OsCl ₃	yellow-orange	241-243°	OsO ₄ + HCl	EtOH	80°(10)	69 ^h	f. 41.8	3.6		11.1(F)
(Asf-Pf-Asf) ₂ Re ₂ Cl ₆	brown	232-234°	ReCl ₅	CH ₃ CN	85°(18)	42 ^h	c. 49.1	4.0	12.8(Cl)	18.0(As)
(Asf-Pf-Asf)Cr(CO) ₃	yellow	124-126°	C ₅ H ₅ Cr(CO) ₃	hexane	70°(30)	79 ^{i j}	f. 49.1	4.0	12.6(Cl)	17.8(As)
(Asf-Pf-Asf)Cr(CO) ₃	yellow	278-281°	Cr(CO) ₃ ^k	xylene	140°(80)	75 ^h	c. 44.4	3.6	11.6(Cl)	
(Asf-Pf-Asf)Mo(CO) ₃	white	142-143°	C ₅ H ₅ Mo(CO) ₃	hexane	70°(30)	86 ^j	f. 44.6	4.6	11.6(Cl)	
(Asf-Pf-Asf)Mo(CO) ₃	white	274-276°	Mo(CO) ₃ ^k	xylene	140°(72)	67 ^{h i}	c. 38.5	3.1	15.0(Cl)	
(Asf-Pf-Asf)Mn(CO) ₅ Br	yellow	223-224°	Mn(CO) ₅ Br	benzene	80°(60)	47 ⁱ	f. 39.1	3.5	13.2(Cl)	
(Asf-Pf-Asf)Rh ₂ (CO) ₄ Cl ₂	brown	275-278°	[Rh(CO) ₂ Cl] ₂	toluene	110°(16)	67 ^h	c. 58.0	4.2	8.4(O)	
(Asf-Pf-Asf)Mo(CO) ₂ (COMe)Cp	yellow	93-95°	MeMo(CO) ₃ Cp	CH ₃ CN	25°(100)	53 ⁱ	f. 57.9	4.5	8.0(O)	
[CpMo(CO) ₃ (Asf-Pf-Asf)][PF ₆]	brown-yellow	218-219°	CpMo(CO) ₃ Cl	C ₆ H ₆	25°(80)	57 ^e	c. 58.6	4.4	6.3(O)	
(Asf-Pf-Asf)Fe(CO)(COMe)Cp	orange	134-136°	MeFe(CO) ₃ Cp	CH ₃ CN	85°(10) ^{i m}	57	f. 59.4	4.9	6.8(O)	
							c. 55.0	4.0	7.8(O)	
							f. 55.8	4.4	7.6(O)	
							c. 55.4	4.1	6.0(O)	
							f. 56.3	4.4	6.3(O)	
							c. 53.2	4.1	3.9(O)	
							f. 53.4	4.0	4.0(O)	
							c. 45.2	3.4	4.9(O)	7.2(Cl)
							f. 44.7	3.9	5.3(O)	5.6(Cl)
							c. 58.5	4.7	5.4(O)	
							f. 59.5	4.7	6.6(O)	
							c. 50.0	3.9	3.2(O)	11.6(F)
							f. 49.7	3.7	2.8(O)	9.6(F)
							c. 61.9	5.1	3.9(O)	
							f. 62.1	5.0	4.1(O)	

^a The following abbreviations were used: Asf-Pf-Asf = bis(2-diphenylarsinoethyl)phenylphosphine; Cp = cyclopentadienyl; Me = methyl. ^b Melting points were taken in capillaries and are uncorrected. ^c The reaction time in hours at the indicated temperature is given in parentheses. ^d Micronalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Meade Microanalytical Laboratory, Amherst, Massachusetts. ^e Solvent (except water) was removed at 25°/25 mm. The residue was dissolved in acetone and treated with excess aqueous NH₄PF₆. The acetone was then removed at 25°/25 mm. The precipitated hexafluorophosphate salt was removed by filtration and dried. ^f The crude product was recrystallized from a mixture of acetone, benzene, and diethyl ether. ^g Calcd: F, 12.5. Found: F, 12.5. ^h The product precipitated from the reaction mixture upon cooling. It was removed by filtration, washed with the cold reaction solvent, and dried. ⁱ A concentrated dichloromethane solution of the crude product was chromatographed on a 2×50 cm. alumina column. The yellow band was eluted with mixtures of dichloromethane and hexane. Solvent was removed from the eluate at ~25°/25 mm. ^j The crude product was recrystallized from a mixture of dichloromethane and hexane. ^k The compounds (Asf-Pf-Asf)M(CO)₃ (M = Cr and Mo) were also obtained by stirring equivalent quantities of the cycloheptatriene complexes C₅H₅M(CO)₃ (M = Cr and Mo) and the Asf-Pf-Asf ligand in benzene at room temperature for 60 hr. Solvent was then removed at 25°/25 mm. and the crude product crystallized from a mixture of dichloromethane and hexane. ^l Some of the product precipitated from the reaction mixture upon cooling. Additional product was obtained by removal of the xylene (25°/0.1 mm) and addition of excess hexane. ^m The crude product was crystallized from a mixture of benzene and ethanol.

(CO)₃C₅H₅,^{7b} CH₃Fe(CO)₂C₅H₅,^{7c} and C₅H₅Mo(CO)₃Cl⁹ were prepared by the cited published procedures.

Preparation of Complexes of [(C₆H₅)₂AsCH₂CH₂]₂PC₆H₅ (Table I). The preparations of most of the complexes of the phosphine-diarsine [(C₆H₅)₂AsCH₂CH₂]₂PC₆H₅ followed procedures already reported³ for the preparation of analogous metal complexes of the tritertiary phosphine [(C₆H₅)₂PCH₂CH₂]₂PC₆H₅. Details of these reactions including reactant, solvent, temperature, time, and purification procedures are listed in Table I. The mole ratio of the ligand [(C₆H₅)₂AsCH₂CH₂]₂PC₆H₅ to the transition metal derivative in all cases was about 1:1.

Reaction of CH₃Mo(CO)₃C₅H₅ with [(C₆H₅)₂AsCH₂CH₂]₂PC₆H₅. A mixture of 0.5 g (1.92 mmoles) of CH₃Mo(CO)₃C₅H₅, 1.2 g (1.93 mmoles) of [(C₆H₅)₂AsCH₂CH₂]₂PC₆H₅, and 100 ml of acetonitrile was stirred for 100 hr at room temperature. A clear yellow solution was obtained. Solvent was removed from this solution at 25°/25 mm. A concentrated dichloromethane solution of the residue was chromatographed

on a 2×60 cm alumina column. The yellow band was eluted with a mixture of dichloromethane, hexane and acetone. Solvent was removed from the yellow eluate at 25°/25 mm to give 0.9 g (53% yield) of yellow (Asf-Pf-Asf)Mo(CO)₂(COCH₃)(C₅H₅) (Table I).

Reaction of CH₃Mo(CO)₃C₅H₅ with (C₆H₅)₂AsCH₂CH₂PC₆H₅. A mixture of 0.4 g (1.54 mmoles) of CH₃Mo(CO)₃C₅H₅, 0.7 g (1.58 mmoles) of (C₆H₅)₂AsCH₂CH₂PC₆H₅, and 100 ml of acetonitrile was stirred for 40 hr at room temperature. A clear yellow solution was obtained. Solvent was removed from this solution at 25°/25 mm to give an oil. A concentrated dichloromethane solution of this oil was chromatographed on a 2×60 cm alumina column made up in hexane. The resulting yellow band was eluted with hexane. Solvent was removed from the resulting eluate at 25°/25 mm to give another yellow oil. Crystallization of this oil from a mixture of dichloromethane and hexane gave 0.6 g (55% yield) of yellow crystalline (Asf-Pf)Mo(CO)₂(COCH₃)(C₅H₅), m.p. 132-133°. *Anal.* Calcd for C₃₅H₃₂AsMoO₃P: C, 59.8; H, 4.6; O, 6.8. Found: C, 59.5; H, 4.6; O, 6.8

(7) R. B. King, «Organometallic Syntheses», Vol. 1, Academic Press, New York, 1965, (a) p. 174; (b) p. 145; (c) p. 151.

(8) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8, 211 (1966).

(9) (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956); (b) R. B. King, K. H. Pannell, C. A. Eggers and L. W. Houk, *Inorg. Chem.*, 7, 2355 (1968).

Spectroscopic Studies. Infrared spectra of the metal carbonyl derivatives in the 2200-1500 cm⁻¹. ν(CO)

Table II. Infrared $\nu(\text{CO})$ Frequencies of the Metal Carbonyl Derivatives Prepared in this Work.

Compound	Medium ^a	$\nu(\text{CO})$ Frequencies, cm^{-1}
(Asf-Pf-Asf)Cr(CO) ₄	CH	2014(s), 1920(s), 1895(s,sh), 1889(s)
(Asf-Pf-Asf)Mo(CO) ₄	CH	2026(s), 1929(s), 1913(s), 1901(s)
(Asf-Pf-Asf)Cr(CO) ₃	CH ₂ Cl ₂	1930(s), 1842(s, br)
(Asf-Pf-Asf)Mo(CO) ₃	CH ₂ Cl ₂	1941(s), 1852(s, br)
(Asf-Pf-Asf)Mn(CO) ₅ Br	CH ₂ Cl ₂	1936(s), 1863(s)
(Asf-Pf-Asf)Rh ₂ (CO) ₄ Cl ₂	KBr	2062(m), 1973(s), 1953(s, sh)
(Asf-Pf-Asf)Mo(CO) ₂ (COMe)Cp	CH ₂ Cl ₂	1935(s), 1848(vs), 1620(m, sh) ^b , 1604(m) ^b
(Asf-Pf)Mo(CO) ₂ (COMe)Cp	CH ₂ Cl ₂	1935(s), 1846(vs), 1615(m, sh) ^b , 1607(m) ^b
(Asf-Pf-Asf)Fe(CO)(COMe)Cp	CH ₂ Cl ₂	1909(s), 1593(m) ^b
[CpMo(CO) ₂ (Asf-Pf-Asf)][PF ₆]	CH ₂ Cl ₂	1979(s), 1911(s)

^a CH = cyclohexane; ^b Acyl $\nu(\text{CO})$ frequency.

Table III. Proton N.M.R. Spectra of Cyclopentadienylmetal Complexes of the Phosphine-Arsines.

Compound	Solvent	Proton N.M.R. Spectrum, ^a τ			
		Phosphine-Arsine C ₆ H ₅	Ligand CH ₂	Other Ligands π -C ₅ H ₅	Ligands CH ₃ CO
(Asf-Pf-Asf)Mo(CO) ₂ (COMe)Cp	CDCl ₃	2.68 s	~7.9 br	5.16 s	7.43 s
(Asf-Pf)Mo(CO) ₂ (COMe)Cp	CDCl ₃	2.65, 2.72	~7.9 br	5.15 s	7.39 s
(Asf-Pf-Asf)Fe(CO)(COMe)Cp ^b	CDCl ₃	2.85	8.0-8.2 br	5.82	7.58
[CpMo(CO) ₂ (Asf-Pf-Asf)][PF ₆]	(CD ₃) ₂ CO	2.39 br, 2.72 br	7.22 br	4.99 s	—

^a The following abbreviations were used: s = singlet; br = broad. ^b This spectrum was broad apparently because of paramagnetic impurities.

region (Table II) were taken in the indicated media and were recorded on a Perkin-Elmer 621 spectrometer with grating optics. Proton n.m.r. spectra of the cyclopentadienylmetal carbonyl derivatives (Table III) were obtained on a Varian HA-100 n.m.r. spectrometer in the indicated solvents. The integrations of the n.m.r. spectra were consistent with the proposed formulations.

The following far infrared spectra (400-100 cm^{-1}) of the metal chloride complexes were obtained in Nujol mulls pressed between polyethylene plates and recorded on a Beckman IR-11 spectrometer: A. *Asf-Pf-Asf*: 315(m), 308(m), 297(w), 270(w), and 230(vw) cm^{-1} . B. [(*Asf-Pf-Asf*)PdCl][PF₆]: 343(m), 326(m), 317(w,sh), 293(vw), 284(w), and 232(m) cm^{-1} . C. [(*Asf-Pf-Asf*)PtCl][PF₆]: 372(w), 346(m), 337(vw), 328(w), 310(m), 288(w), 272(w), and 232(w) cm^{-1} . D. (*Asf-Pf-Asf*)RhCl₃: $\nu(\text{Rh-Cl})$ frequencies at 311(m) and 282(s) cm^{-1} . E. (*Asf-Pf-Asf*)OsCl₃: $\nu(\text{Os-Cl})$ frequencies at 327(m) and 305(s) cm^{-1} . F. (*Asf-Pf-Asf*)Re₃Cl₉: 358(m), 334(w), 305(w), and 207(w) cm^{-1} .

Physical Measurements. The following molar conductances were determined in ~0.0003 to 0.003 molar acetone solution at room temperature (~25°) using platinum electrodes and a Model 31 conductivity bridge manufactured by the Yellow Springs Instrument Company, Inc., Yellow Springs, Ohio: A. [(*Asf-Pf-Asf*)PdCl][PF₆]: 97 $\text{ohm}^{-1} \text{cm}^2/\text{mole}$. B. [(*Asf-Pf-Asf*)PtCl][PF₆]: 86 $\text{ohm}^{-1} \text{cm}^2/\text{mole}$. C. [C₅H₅Mo(CO)₂(*Asf-Pf-Asf*)] [PF₆]: 98 $\text{ohm}^{-1} \text{cm}^2/\text{mole}$.

The following magnetic susceptibilities were checked at room temperature in the solid state on an Alpha Scientific Model 9500 magnetic balance using the Faraday method: A. (*Asf-Pf-Asf*)OsCl₃: paramagnetic, but a field-dependent very paramagnetic impurity pre-

vented determination of a precise magnetic moment. B. (*Asf-Pf-Asf*)Re₃Cl₉: diamagnetic.

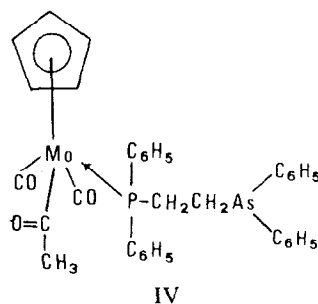
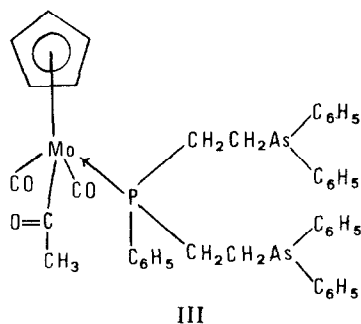
Discussion

The phosphine-diarsine *Asf-Pf-Asf* (I: E = As) forms the following monometallic complexes which correspond to previously reported³ monometallic complexes of the tritertiary phosphine *Pf-Pf-Pf* (I: E = P): (1) Monoligate monometallic: (*Asf-Pf-Asf*)Fe(CO)(COCH₃)(C₅H₅); (2) Biligate monometallic: (*Asf-Pf-Asf*)M(CO)₄ (M = Cr and Mo) and [C₅H₅Mo(CO)₂(*Asf-Pf-Asf*)] [PF₆]; (3) Triligate monometallic: [(*Asf-Pf-Asf*)MCl][PF₆] (M = Pd and Pt), (*Asf-Pf-Asf*)RhCl₃, (*Asf-Pf-Asf*)M(CO)₃ (M = Cr and Mo), and (*Asf-Pf-Asf*)Mn(CO)₂Br. In addition, a polymetallic rhenium compound of stoichiometry (*Asf-Pf-Asf*)₂Re₃Cl₉ which corresponded to the previously reported³ (*Pf-Pf-Pf*)₂Re₃Cl₉ could be prepared. As expected the colors, infrared spectra (Table II), and proton n.m.r. spectra (Table III) of these new *Asf-Pf-Asf* complexes were very similar to those of their *Pf-Pf-Pf* analogues³ and therefore they will not be discussed in detail.

In attempts to prepare bimetallic complexes of *Asf-Pf-Asf* (I: E = As) corresponding to the reported³ biligate bimetallic (*Pf-Pf-Pf*)Fe₂(CO)₂(C₅H₅)₂ and triligate bimetallic [(C₅H₅)₂Mn₂(CO)(NO)₂(*Pf-Pf-Pf*)] [PF₆], the reactions of *Asf-Pf-Asf* with [C₅H₅Fe(CO)₂]₂ and [C₅H₅Mn(CO)₂NO] [PF₆] were investigated under conditions which gave the *Pf-Pf-Pf* derivatives. However, in both of these cases only intractable decomposition products were obtained. This suggests a certain reluctance for the phosphine-diarsine *Asf-Pf-Asf* (I: E = As) to form bimetallic complexes as compared with the tritertiary phosphine

Pf–Pf–Pf (I: E = P). This reluctance for Asf–Pf–Asf to form bimetallic complexes may arise from the fact that the presence of only one phosphorus atom requires the second metal atom to bond to the Asf–Pf–Asf ligand through arsenic atoms, which are weaker donors than phosphorus atoms.

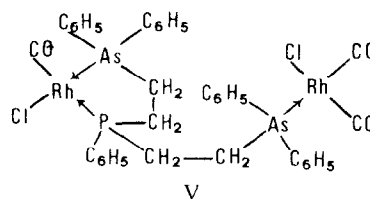
The trimetallic complexes (Pf–Pf–Pf)[Mo(CO)₂(COCH₃)(C₅H₅)₃] can be prepared by reaction of Pf–Pf–Pf with CH₃Mo(CO)₃C₅H₅ in acetonitrile at room temperature. An analogous reaction of Asf–Pf–Asf with CH₃Mo(CO)₃C₅H₅, even when the latter was present in excess, gave only (Asf–Pf–Asf)Mo(CO)₂(COCH₃)(C₅H₅), a monoligate monometallic derivative probably with structure III closely related to the iron complexes (tridentate)Fe(CO)(COCH₃)(C₅H₅) (tridentate = Asf–Pf–Asf or Pf–Pf–Pf). Apparently only the phosphorus atom in Asf–Pf–Asf can react with CH₃Mo(CO)₃C₅H₅ in acetonitrile at room temperature. This is consistent with the observation by Craig and Green¹⁰ that numerous trivalent phosphorus ligands including both tertiary phosphines and phosphites, but no trivalent arsenic ligands, can react with CH₃Mo(CO)₃C₅H₅ in acetonitrile at room temperature to form the corresponding LMo(CO)₂(COCH₃)(C₅H₅) derivatives. The monometallic derivative (Asf–Pf–Asf)Mo(CO)₂(COCH₃)(C₅H₅), as expected, exhibits a much greater solubility in organic solvents than the trimetallic derivative³ (Pf–Pf–Pf)[Mo(CO)₂(COCH₃)(C₅H₅)₃].



The apparent ability of CH₃Mo(CO)₃C₅H₅ in aceto-

nitrile solution to react selectively with the trivalent phosphorus atoms in mixed phosphine-arsines is further suggested by the reaction of the phosphine-arsine (C₆H₅)₂AsCH₂CH₂P(C₆H₅)₂ with CH₃Mo(CO)₃C₅H₅ in acetonitrile to give the monometallic derivative (Asf–Pf–Asf)Mo(CO)₂(COCH₃)(C₅H₅) (IV) rather than a bimetallic derivative like the closely related ditertiary phosphine (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂.¹¹

This work demonstrates that bimetallic and trimetallic derivatives of the phosphine-diarsine [(C₆H₅)₂AsCH₂CH₂]₂PC₆H₅ (I: E = As) cannot be prepared by procedures analogous to those successful for the preparation of bimetallic and trimetallic derivatives of the tritertiary phosphine [(C₆H₅)₂PCH₂CH₂]₂PC₆H₅ (I: E = P) apparently because of the lower donor ability of arsenic relative to phosphorus. However, reaction of Asf–Pf–Asf (I: E = As) with [Rh(CO)₂Cl]₂ in boiling toluene gives an insoluble brown solid of stoichiometry (Asf–Pf–Asf)Rh₂(CO)₃Cl₂. This may be the triligate bimetallic derivative V with two square planar rhodium(I) atoms. However, the insolubility of this complex prevents its detailed characterization. In particular, alternative polymeric formulations cannot be excluded at the present time. Related rhodium carbonyl chloride derivatives of ditertiary phosphines have been reported.¹²



The one other difference between the chemistry of Asf–Pf–Asf and Pf–Pf–Pf occurs in their reactions with a mixture of osmium tetroxide and excess hydrochloric acid in ethanol solution. The reaction of the tritertiary phosphine Pf–Pf–Pf (I: E = P) with this reagent gives the osmium(IV) derivative³ (Pf–Pf–Pf)OsCl₄. However, the reaction of the phosphine-diarsine Asf–Pf–Asf (I: E = As) with this reagent results in further reduction to give the osmium(III) derivative (Asf–Pf–Asf)OsCl₃. The reason for this difference is not clear at the present time.

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