Transition-Metal-Substituted Acyl Phosphanes and Phosphaalkenes. 33.[1] Transition-Metal-Substituted Arsaalkenes. 3.[2] Reactivity of Metallodisilylphosphanes and -arsanes $(\eta^5\text{-}C_5Me_5)(CO)_2M{-}E(SiMe_3)_2$ (M = Fe, Ru; E = P, As) toward Carbon Disulfide. Formation of Metallophosphaalkenes, Metalloarsaalkenes, and 1,3,4-Thiadiphospholes

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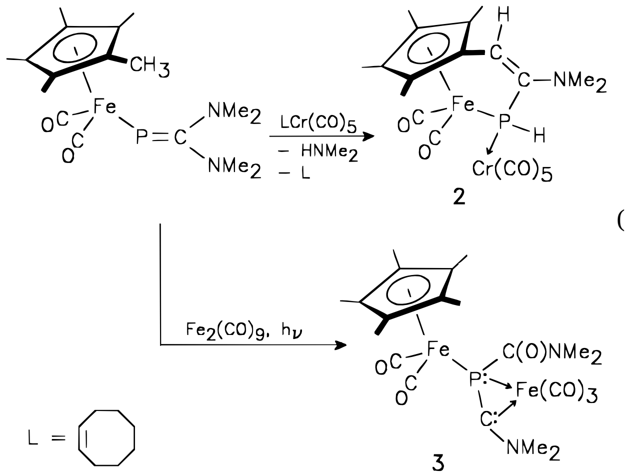
Reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2$ (**4a**) with carbon disulfide afforded the unstable metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}C[SSiMe_3]_2$ (**5a**), which decomposed to the doubly metalated 1,3,4-thiadiphosphole **8a** by extrusion of bis(trimethylsilyl)sulfide. The transient metallophosphaalkene **5a** was intercepted as the isolable $[(CO)_5Cr]$-adduct **6a** by treatment with $[(Z)\text{-cyclooctene}]Cr(CO)_5$. Similarly, the metallodisilylarsanes $(\eta^5\text{-}C_5Me_5)(CO)_2M{-}As(SiMe_3)_2$ (M = Fe, Ru) (**11a,b**) were converted to stable metalloarsaalkenes **12a,b** by exposure to CS_2. Pentacarbonylchromium complexes **13a,b** were accessible by reaction with $[(Z)\text{-cyclooctene}]Cr(CO)_5$. The X-ray structure analysis of **13a** revealed the molecule as the first η^1-arsaalkene complex.

Introduction

The chemistry of compounds with low-coordinate phosphorus, such as phosphaalkenes and phosphaalkynes, rapidly developed within the last two decades,[3] and still is of considerable continuing interest.

Transition-metal-substituted phosphaalkenes of the type $L_nM{-}P{=}CR^1R^2$ are polyfunctional molecules with an extraordinary rich chemistry.[4] The compound $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2$ (**1**)[5] undergoes a number of cycloadditions with electron-deficient alkenes, alkynes, azo compounds, diazoesters,[4] and 4-arylsydnones.[1] The ligating behavior of **1** is also unusual, as shown by the synthesis of complexes **2** and **3** from **1**, eq 1, and $[(Z)\text{-cyclooctene}]Cr(CO)_5$ or $Fe_2(CO)_9$, respectively.[6]



(1)

In view of the rich chemistry displayed by **1**, the quest for other heavily-functionalized metallophosphaalkenes is obvious. In this paper, we describe the synthesis of metallophosphaalkenes and metalloarsaalkenes $[M]{-}E{=}C(SSiMe_3)_2$ ($[M] = (\eta^5\text{-}C_5Me_5)(CO)_2Fe$, $(\eta^5\text{-}C_5Me_5)(CO)_2Ru$; E = P, As) and their conversion into pentacarbonylchromium adducts and into a metalated 1,3,4-thiadiphosphole.

Results and Discussion

Reaction of metallodisilylphosphane $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2$ (**4a**)[7] with an equimolar amount of carbon disulfide in *n*-pentane at 20 °C produced metallophosphaalkene **5a**, as indicated by a singlet at δ 509 ppm in the $^{31}P\{^1H\}$ NMR spectrum. For comparison, the respective resonance of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ was observed at δ 641.5 ppm.[8] Compound **5a** could not be isolated from the dark reaction mixture without

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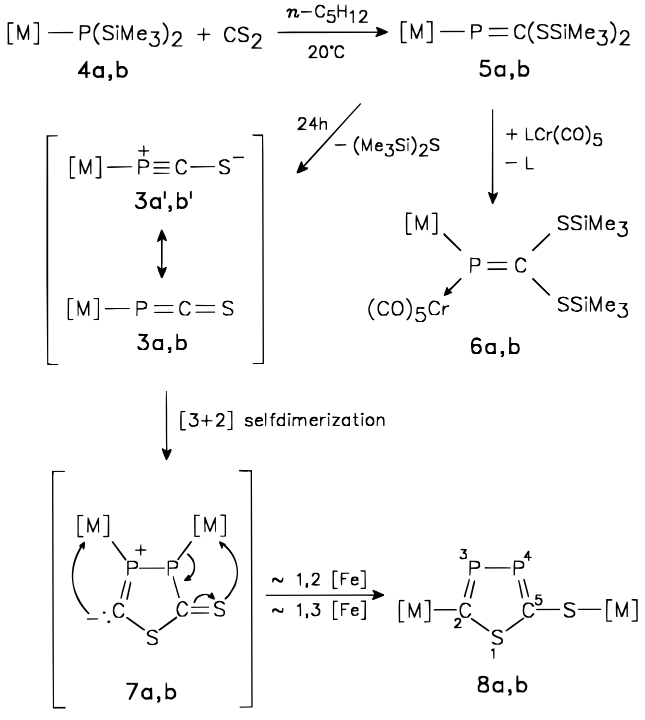
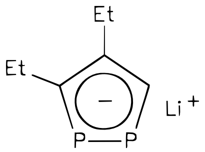
Scheme 1



[M] = (η^5–C_5Me_5)$(CO)_2M$; M = Fe, Ru
L = (*Z*)–cyclooctene

decomposition. The metallophosphaalkene, however, was intercepted as a stable pentacarbonylchromium complex **6a** by treatment of the fresh reaction mixture with [(*Z*)-cyclooctene]Cr$(CO)_5$.[9] During complex formation, the singlet of **5a** in the $^{31}P\{^1H\}$ NMR spectrum was replaced by a singlet at δ 465.7 ppm. The relatively small high-field shift of 43.3 ppm is consistant with an η^1-ligation of the phosphorus atom of **5a** to the chromium center in **6a** (Scheme 1).

After the reaction mixture obtained from **4a** and CS_2 was stirred for 24 h at ambient temperature, the singlet of metallophosphaalkene **5a** had disappeared. Work up by column chromatography at silanized silica, with benzene as an eluent, afforded a brown zone from which 1,3,4-thiadiphosphole **8a** was isolated as a dark red powder. The $^{31}P\{^1H\}$ NMR spectrum of this compound displayed the signal of an AB spin system in the characteristic region of P═C double bonds ($\delta_A = 310.6$, $\delta_B = 317.6$ ppm, $^1J_{AB} = 411.8$ Hz). The large coupling constant agrees with a PP bond, as was also observed in 1,2-diphospholides such as **9** ($^1J_{PP} = 436$ Hz).[10]



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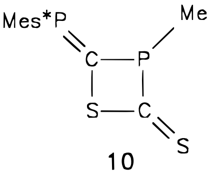

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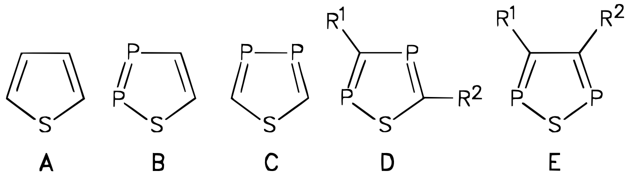
In the $^{13}C\{^1H\}$ NMR spectrum of **8a**, the ring carbon atoms resonate as doublets of doublets in the low-field region typical for P═C systems ($\delta = 208.2$ ppm, $^1J_{PC} = 89.0$, $^2J_{PC} = 12.5$ Hz and $\delta = 209.3$ ppm, $^1J_{PC} = 108.5$, $^2J_{PC} = 7.2$ Hz). A singlet at $\delta = 215.8$ ppm and a doublet at $\delta = 216.2$ ppm ($^3J_{PC} = 5.2$ Hz) are due to the carbonyls of the two chemical and magnetically different [(η^5-C_5Me_5)$(CO)_2$Fe] groups. The IR spectrum (KBr) of **8a** is dominated by two intense ν(CO) bands at $\nu = 2003$ and 1949 cm^{-1}. The formation of the 1,3,4-thiadiphosphole **8a** may be explained by a [3 + 2] self-dimerization of transient metallophosphathioketene **3a** to give the zwitterionic heterocycle **7a**. Sigmatropic [1,2] and [1,3] migrations of the [(η^5-C_5Me_5)$(CO)_2$Fe] units afforded the final product. Neither the hypothetical metallophosphathioketene **3a** nor the intermediate ring **7a** could be detected spectroscopically. Whereas no stable monomeric organothiophosphaketenes were known until recently, Becker et al. recently reported the synthesis and X-ray structure determination of $[Li(DME)_3]^+$-$[P\equiv C-S]^-$.[11] Attempts by Appel et al. to synthesize the kinetically-stabilized Mes*P═C═S resulted in the formation of dimer **10**.[12]

The replacement of two CH units in thiophene **A** by phosphorus atoms formally leads to four isomeric thiadiphospholes (**B**–**E**). Only representatives of the types



D and **E** are known, namely the poorly characterized 4,5-bis(trifluoromethyl)-1,2,3-thiadiphosphole (type **E**)[13] and four 1,2,4-thiadiphospholes of the type **D** ($R^1 = Me_3SiS$, $R^2 = Me_3Si$;[14] $R^1 = R^2 = Me_3SiO$;[15] $R^1 = R^2 = Ph$;[16] $R^1 = R^2 = t$Bu[17,18]). Compound **8a** is the first example of a 1,3,4-thiadiphosphole (type **C**).

The reaction of (η^5-C_5Me_5)$(CO)_2RuP(SiMe_3)_2$ (**4b**)[19] with CS_2 lead to an unstable rutheniophosphaalkene (**5b**), which according to ^{31}P NMR evidence decomposed to a number of unknown compounds within hours. In only 2 of the 10 experiments was an AB pattern observed ($\delta_A = 294.2$, $\delta_B = 312.3$, $^1J_{AB} = 408.0$ Hz), which would be expected for 1,3,4-thiadiphosphole **8b**. It was not possible to increase the ratio of this compound nor was it possible to isolate it without decomposition. In line with the iron analogue **5a**, rutheniophosphaalkene **5b** was easily converted into its stable orange crystalline pentacarbonylchromium adduct **6b** by treatment with [(*Z*)-cyclooctene]Cr$(CO)_5$. During this process, the singlet at $\delta_{^{31}P} = 475.3$ of **5b** was upfield-shifted to $\delta = 438.2$ ppm.

In view to the well-developed chemistry of phosphaalkenes, the chemistry of arsaalkenes has only been

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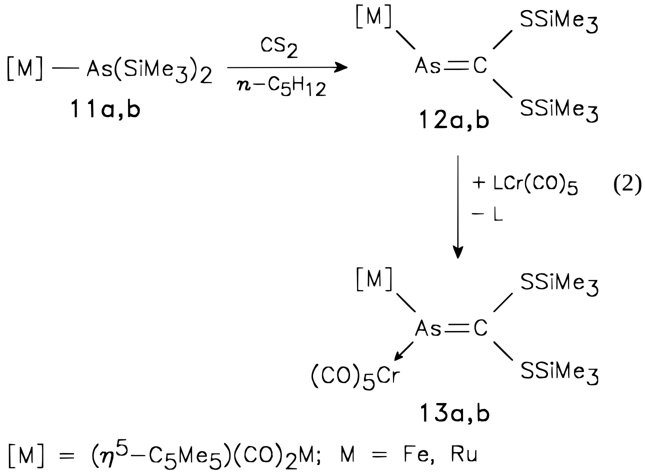
poorly investigated.[20] We were interested in the question as to whether the chemistry of arsaalkenes just resembles that of their phosphorus analogues or, perhaps, display characteristics of their own.

The reaction of the metallodisilylarsanes **11a,b**[21] with carbon disulfide furnished the metalloarsaalkenes as dark brown (**12a**) or orange red (**12b**) isolable compounds in yields up to 80%, eq 2. No tendency to eliminate $(Me_3Si)_2S$ with formation of hypothetical [M]—As=C=S and oligomers thereof was observed. This is surprising because usually arsaalkenes are less stable than the corresponding phosphorus analogues. The coordination of **12a,b** to the $[Cr(CO)_5]$ fragment with production of dark red crystalline **13a** and orange **13b** was analogously achieved with [(*Z*)-cyclooctene]$Cr(CO)_5$.



The $^{13}C\{^1H\}$ NMR spectra of the pentacarbonylchromium complexes **6a** and **6b** display doublets at 174.3 ($^1J_{PC} = 35.4$ Hz) and δ 171.3 ($^1J_{PC} = 28.0$ Hz) which are readily assigned the carbon atom of the PC bond. The corresponding resonances of the As=C unit in **13a** and **13b** are considerably deshielded ($\delta = 191.9$ (s) and 187.9 (s), respectively). The η^1-ligation of the free metalloarsaalkenes **12a** ($\delta_{As=C} = 177.4$) and **12b** ($\delta_{As=C} = 175.2$) to the $[Cr(CO)_5]$ fragment are also accompanied by marked low-field shifts ($\Delta\delta = 12.7-14.5$ ppm). The electron-withdrawing effect of the $[Cr(CO)_5]$ unit is reflected in high-field shifts for the iron carbonyl and ruthenium carbonyl groups in going from **12a** to **13a** ($\Delta\delta_{^{13}CO} = 1.5$ ppm) and from **12b** to **13b** ($\Delta\delta_{^{13}CO} = 2.1$ ppm). The resonances of the equatorial carbonyl ligands of the $[Cr(CO)_5]$ group in **6a**, **6b**, **13a** and **13b** are observed at $\delta = 218.8-219.0$ ppm, whereas absorptions at $\delta = 225.3-226.1$ ppm are due to the axial CO ligands. Four intense bands for the carbonyl stretching modes are consonant with a local symmetry lower than C_{4v} at the $[Cr(CO)_5]$ unit. Absorptions in the region of $\nu = 2052-1908$ cm^{-1} reveal the metallophosphaalkenes and metalloarsaalkenes as a powerful donor ligand comparable to $CF_3P=C(F)NMe_2$ in its $[Cr(CO)_5]$ complex ($\nu = 2055$ (w), 1985 (w), 1940 (vs), 1930 (s), 1912 (s) cm^{-1}.[22] In $Cr(CO)_5(PMe_3)$, for example, carbonyl stretching frequencies are registered at $\nu = 2062.7$, 1949.0, and 1937.5 cm^{-1}.[23]

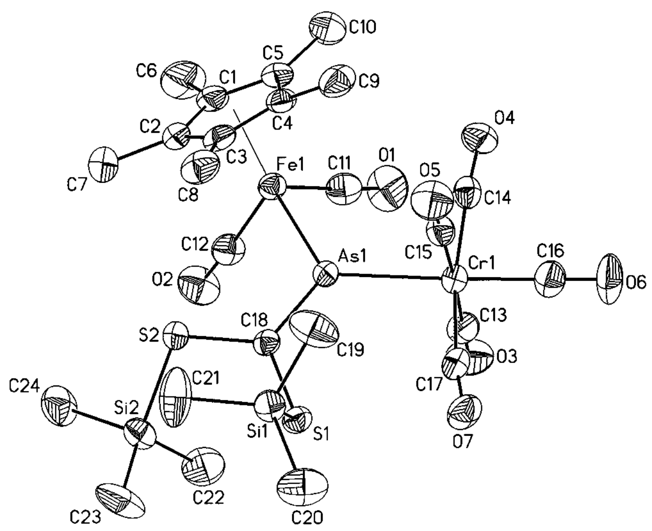
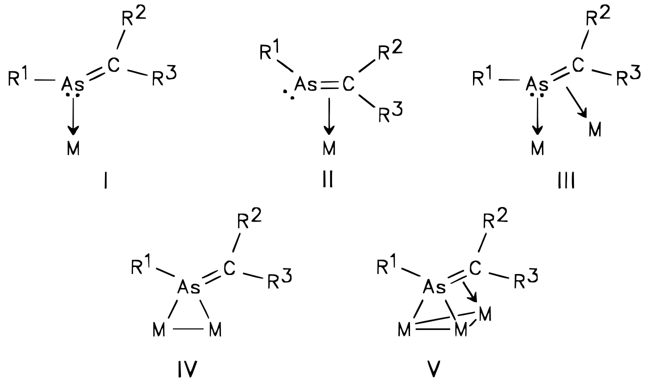
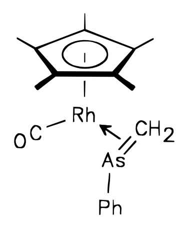


Figure 1. Molecular structure of **13a**.

The withdrawal of electron density from the $(\eta^5-C_5Me_5)(CO)_2M$ fragment by $[Cr(CO)_5]$ leads to high-frequency shifts ($\Delta\nu = 12-18$ cm^{-1}) of the iron and ruthenium carbonyl stretches in **12a,b** and **13a,b**. Like phosphaalkenes,[24] arsaalkene ligands in transition metal complexes are expected to be involved in at least five basic modes of coordination (**I**−**V**). Despite two decades of research, only one transition-metal arsaalkene complex is described in the literature. Complex **14** features an η^2-bonded arsaalkene ligand, which in the free form is still unknown and presumably highly labile toward oligomerization.[25] Thus, compounds **13a,b** are the first coordination compounds with an η^1-ligated arsaalkene.





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X-ray Structure Analysis of 13a. Single crystals of **13a** were grown from toluene at −30 °C. The results of the structural determination are shown in Figure 1.

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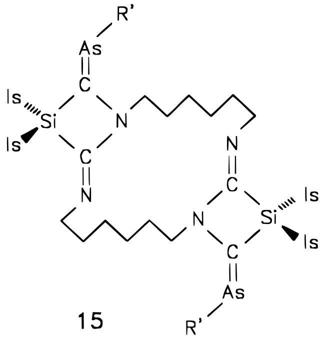
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 13a

As(1)−C(18)	1.800(5)	As(1)−Fe(1)	2.3711(9)
As(1)−Cr(1)	2.5240(10)	Fe(1)−C(12)	1.758(7)
Fe(1)−C(11)	1.777(8)	Fe(1)−C(1)	2.087(6)
Fe(1)−C(4)	2.112(5)	Fe(1)−C(5)	2.114(6)
Fe(1)−C(2)	2.132(6)	Fe(1)−C(3)	2.138(6)
Cr(1)−C(16)	1.840(7)	Cr(1)−C(15)	1.871(7)
Cr(2)−C(14)	1.879(7)	Cr(1)−C(17)	1.892(7)
Cr(1)−C(13)	1.899(7)	S(1)−C(18)	1.777(5)
S(1)−Si(1)	2.166(2)	S(2)−C(18)	1.773(5)
S(2)−Si(2)	2.170(2)	Si(1)−C(19)	1.834(7)
Si(1)−C(20)	1.834(7)	Si(1)−C(21)	1.844(7)
Si(2)−C(24)	1.836(7)	Si(2)−C(22)	1.836(8)
Si(2)−C(23)	1.848(7)	O(1)−C(11)	1.129(7)
O(2)−C(12)	1.146(7)	O(3)−C(13)	1.135(7)
O(4)−C(14)	1.154(7)	O(5)−C(15)	1.161(7)
O(6)−C(16)	1.154(7)	O(7)−C(17)	1.149(7)
C(1)−C(5)	1.424(8)	C(1)−C(2)	1.430(8)
C(2)−C(3)	1.396(8)	C(3)−C(4)	1.413(8)
C(4)−C(5)	1.408(8)		
C(18)−As(1)−Fe(1)	113.0(2)	C(18)−As(1)−Cr(1)	122.1(2)
Fe(1)−As(1)−Cr(1)	124.57(4)	C(12)−Fe(1)−C(11)	90.3(3)
C(12)−Fe(1)−As(1)	92.1(2)	C(11)−Fe(1)−As(1)	90.3(2)
C(16)−Cr(1)−C(15)	91.9(3)	C(16)−Cr(1)−C(14)	86.1(3)
C(15)−Cr(1)−C(14)	89.0(3)	C(16)−Cr(1)−C(17)	85.4(3)
C(15)−Cr(1)−C(17)	88.8(3)	C(14)−Cr(1)−C(17)	171.1(3)
C(16)−Cr(1)−C(13)	91.3(3)	C(15)−Cr(1)−C(13)	176.7(3)
C(14)−Cr(1)−C(13)	91.3(3)	C(17)−Cr(1)−C(13)	91.4(3)
C(16)−Cr(1)−As(1)	175.0(2)	C(15)−Cr(1)−As(1)	90.9(2)
C(14)−Cr(1)−As(1)	89.8(2)	C(17)−Cr(1)−As(1)	98.8(2)
C(13)−Cr(1)−As(1)	85.8(2)	C(18)−S(1)−Si(1)	104.8(2)
C(18)−S(2)−Si(2)	108.1(2)	O(1)−C(11)−Fe(1)	176.9(6)
O(2)−C(12)−Fe(1)	173.0(6)	O(3)−C(13)−Cr(1)	179.0(6)
O(4)−C(14)−Cr(1)	174.5(5)	O(5)−C(15)−Cr(1)	179.5(6)
O(6)−C(16)−Cr(1)	179.9(8)	O(7)−C(17)−Cr(1)	170.9(5)
S(2)−C(18)−S(1)	117.4(3)	S(2)−C(18)−As(1)	121.5(3)
S(1)−C(18)−As(1)	121.1(3)		

Selected bond lengths and angles for the compound are given in Table 1. The analysis confirms the presence of a ferrioarsaalkene with an unsupported As═C double bond, in which a [Cr(CO)$_5$] fragment is attached to the trigonal-planar arsenic atom via its lone pair. The bond distance As(1)−C(18) (1.800(5) Å) is close to the theoretical value of 1.79 Å calculated for HAs═CH$_2$.[26] The As═C bond lengths in the eight structurally-characterized arsaalkenes vary from 1.816(6) Å in **15**[27] to 1.921(3) Å in cyclic **16**.[28] The calculated value for an As−C single bond is 1.96 Å.[29] The Fe−As bond (2.3711(9) Å) is slightly shortened as compared to the ones in (η^5-C$_5$Me$_5$)(CO)$_2$Fe−As[Cr(CO)$_5$]═P−Mes* (2.389(1) Å)[30] and in (η^5-C$_5$H$_5$)(CO)$_2$Fe−As═C(OSiMe$_3$)(*t*Bu) (2.407(1) Å).[21]



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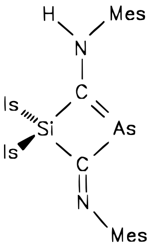

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Is = 2,4,6-iPr$_3$C$_6$H$_2$
R' = iPr$_3$Si

The Cr−As bond (2.5240(10) Å) in **13a** is elongated in comparison to the Cr−As distances in (η^5-C$_5$Me$_5$)(CO)$_2$-Fe−As[Cr(CO)$_5$]═P−Mes* (2.494(1) Å)[30] and in Mes*−As═As−[Cr(CO)$_5$] CH(SiMe$_3$)$_2$ (2.454(1) Å).[31] Like in all the structurally studied arsaalkenes, the tricoordinate carbon atom of the As═C bond in **13a** is planar. The angle Fe(1)−As(1)−C(18) of 113.0(2)° is amidst the corresponding angles in (η^5-C$_5$H$_5$)(CO)$_2$FeAs═C-(OSiMe$_3$)$_2$(*t*Bu) (111.4(1)°)[21] and (η^5-C$_5$Me$_5$)(CO)$_2$FeAs═C-(NMe$_2$)$_2$ (116.2(3)°).[2] Despite the differing steric bulk of the substituents at atom As(1), the angles As(1)−C(18)−S(1) (121.1(3)°) and As(1)−C(18)−S(2) (121.5(3)°) are equal. The arsenic atom is located at the apex of a distorted octahedron. Due to the steric requirements of the arsaalkene ligand, the equatorial carbonyl ligands are pushed back toward the axial CO group, as evident by the angles C(14)−Cr(1)−C(17) = 171.1(3)° and C(13)−Cr(1)−C(15) = 176.7(3)°. A marked deviation from linearity is also observed for one CO ligand at the iron center (O(1)−C(11)−Fe(1) = 173.0(6)°).

Experimental Section

All operations were performed with standard Schlenk techniques in an oxygen-free Ar atmosphere. Solvents were dried by standard methods and freshly distilled under argon. Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer, and the ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in C$_6$D$_6$ at 22 °C on Bruker AM Advance DRX 500, Bruker AC 250 P, and Bruker AC 100 instruments, standards, SiMe$_4$ (^{1}H, ^{13}C) and external 85% H$_3$PO$_4$ (^{31}P). Elemental analyses were performed in the microanalytical laboratory of our department. Mass spectra were obtained with a Varian MAT-CH5-DF spectrometer.

Metallodisilylphosphanes (η^5-C$_5$Me$_5$)(CO)$_2$FeP(SiMe$_3$)$_2$ (**4a**),[7] (η^5-C$_5$Me$_5$)(CO)$_2$RuP(SiMe$_3$)$_2$ (**4b**),[19] the metallodisilylarsane (η^5-C$_5$Me$_5$)(CO)$_2$FeAs(SiMe$_3$)$_2$ (**11a**),[21] (η^5-C$_5$Me$_5$)(CO)$_2$RuBr,[19] LiAs(SiMe$_3$)$_2$,[32] and [(*Z*)-cyclooctene]Cr(CO)$_5$[9] were synthesized according to the literature. Carbon disulfide and silanized silica (Merck) were purchased commercially.

Preparation of Compounds. (η^5-C$_5$Me$_5$)(CO)$_2$FeP[Cr(CO)$_5$]═C(SSiMe$_3$)$_2$ (6a). A solution of 1.24 g (2.91 mmol) of **4a** and 0.18 mL (2.91 mmol) of CS$_2$ in 20 mL of benzene was stirred at 20 °C until the singlet of **4a** at $\delta = -216.8$ ppm was completely replaced by a singlet at $\delta = 509$ ppm. Then a solution of 0.88 g (2.91 mmol) of [(*Z*)-cyclooctene]Cr(CO)$_5$ in 10 mL of benzene was added dropwise with stirring. The reaction mixture continued to stir at 20 °C until the ^{31}P{^{1}H} NMR spectrum of the solution only displayed a singlet at $\delta = 465.7$ ppm. The solution was filtered through a pad of Na$_2$SO$_4$, and the clear filtrate was evaporated to dryness. The black, powder residue was washed with *n*-pentane (5 × 10 mL) and then crystallized from a toluene/pentane mixture to give 0.80 g (40%) of **6a**. ^{1}H NMR δ: 0.47 (s, 18H, Si(CH$_3$)$_3$), 1.46 (s, 15H, C$_5$(CH$_3$)$_5$). ^{13}C{^{1}H} NMR δ: 1.1 (s, Si(CH$_3$)$_3$), 1.4 (s, Si(CH$_3$)$_3$), 9.4 (s, C$_5$(*C*H$_3$)$_5$), 98.1 (s, *C*$_5$(CH$_3$)$_5$), 174.3 (d, $^1J_{PC}$ = 35.4 Hz, P═C), 213.9 (s, FeCO), 218.9 (d, $^2J_{PC}$ = 12.5 Hz, CrCO$_{eq}$), 225.3 (d, $^2J_{PC}$ = 4.3 Hz, CrCO$_{ax}$). ^{31}P{^{1}H} NMR δ: 465.7 (s). IR (KBr, cm^{-1}) ν: 2050 (s, ν[Cr(CO)]), 2013 (s, ν[Fe(CO)]), 1965 (s, ν[Fe(CO)]), 1936 (vs, ν[Cr(CO)]), 1919 (sh, ν[Cr-

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(CO)]), 1909 (vs, ν[Cr(CO)), 1640 (w), 1484 (w), 1454 (w), 1428 (w), 1410 (w), 1387 (m), 1245 (m, δ(SiMe$_3$)), 1161 (w), 1074 (w), 1027 (w), 846 (s, ρ(SiMe$_3$)), 816 (m), 756 (w). MSLSIMS (*p*-nitrobenzylalcohol) *m*/*z*: 665 (M$^+$ − CO). Anal. Calcd for $C_{24}H_{33}CrFeO_7PS_2Si_2$ (692.64): C, 41.61; H, 4.81; Fe, 8.06. Found: C, 41.72; H, 4.78; Fe, 8.15.

2-[(η^5-C$_5$Me$_5$)(CO)$_2$Fe]-5-[(η^5-C$_5$Me$_5$)(CO)$_2$FeS]-1,3,4-thiadiphosphole (8a). A sample of 2.75 g (6.48 mmol) of **4a** was dissolved in 50 mL of *n*-pentane, and to the chilled solution (−30 °C) a solution of 0.39 mL (6.48 mmol) of CS$_2$ in 30 mL of *n*-pentane was added. The reaction mixture continued to stir at 20 °C until the ^{31}P{^{1}H} NMR spectrum of the red-black solution only showed a singlet at δ = 509 ppm. The solution was filtered through a pad of Na$_2$SO$_4$ (l = 2 cm), and the filtrate was evaporated to dryness. The brown residue was chromatographed on silanized silica with benzene as the eluent. A brown zone developed, which was eluted with 80 mL of benzene. From the brown elute, 1.20 g (29%) of **8a** was isolated as a red-brown powder. ^{1}H NMR δ: 1.32 (s, 15H, C$_5$(CH$_3$)$_5$), 1.37 (s, 15H, C$_5$(CH$_3$)$_5$). ^{13}C{^{1}H} NMR δ: 9.1 (s, C$_5$(*C*H$_3$)$_5$), 96.5 (s, *C*$_5$(CH$_3$)$_5$), 208.2 (dd, $^1J_{PC}$ = 89.0 Hz, $^2J_{PC}$ = 12.5 Hz, C=P), 209.3 (dd, $^1J_{PC}$ = 108.5 Hz, $^2J_{PC}$ = 7.2 Hz, C=P), 215.8 (s, SFe(CO)$_2$), 216.2 (d, $^3J_{PC}$ = 5.2 Hz, C−Fe(*C*O)$_2$). ^{31}P{^{1}H} NMR δ: AB signal δ_A = 310.6, δ_B = 317.6 ($^1J_{AB}$ = 411.8 Hz). MS/LSIMS *m*/*z*: 644 (M$^+$), 588 (M$^+$ − 2CO), 532 (M$^+$ − 4CO), 446 ((C$_5$Me$_5$)$_2$Fe$_2$S$_2$)$^+$. IR (KBr, cm^{-1}) ν: 2003 (vs, ν(CO)), 1949 (vs, ν(CO)), 1489 (w), 1473 (w), 1465 (w), 1457 (w), 1430 (w), 1381 (m), 1339 (w), 1252 (w), 1162 (w), 1074 (w), 1026 (m), 987 (w), 964 (w), 898 (w), 850 (w), 799 (w), 619 (w), 592 (m), 575 (m), 559 (w), 544 (w), 500 (w), 492 (w), 457 (w), 443 (w), 419 (w), 408 (w). Anal. Calcd for $C_{26}H_{30}Fe_2O_4P_2S_2$ (644.31): C, 48.49; H, 4.70. Found: C, 48.50; H, 4.99.

(η^5-C$_5$Me$_5$)(CO)$_2$RuP[Cr(CO)$_5$]=C(SSiMe$_3$)$_2$ (6b). A solution of 0.09 mL (1.47 mmol) of CS$_2$ in 5 mL of *n*-pentane was added dropwise to a chilled solution (−20 °C) of 0.69 g (1.47 mmol) of (η^5-C$_5$Me$_5$)(CO)$_2$RuP(SiMe$_3$)$_2$ (**4b**) in 20 mL of *n*-pentane. When warmed up to ambient temperature, the orange solution turned deep red. After 4 h of stirring at 20 °C, the ^{31}P{^{1}H} NMR spectrum showed a singlet at δ = 474.8 ppm. The reaction mixture was cooled to −30 °C before a solution of 0.30 g (1.47 mmol) of [(*Z*)-cyclooctene]Cr(CO)$_5$ in 20 mL of *n*-pentane was added. When warmed up to 20 °C, an orange-red precipitate formed. After the slurry was stirred for 90 min, the precipitate was filtered off and the filter cake was washed with 50 mL of *n*-pentane. Crystallization of the solid from 5 mL of diethyl ether at −30 °C yielded 0.35 g (32%) of **6b** as hexagonal orange crystals. ^{1}H NMR δ: 0.46 (s, 9H, Si(CH$_3$)$_3$), 0.47 (s, 9H, Si(CH$_3$)$_3$), 1.60 (s, 15H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR δ: 1.3 (s, Si(CH$_3$)$_3$), 1.4 (s, Si(CH$_3$)$_3$), 9.8 (C$_5$(*C*H$_3$)$_5$), 101.6 (s, *C*$_5$(CH$_3$)$_5$), 171.3 (d, $^1J_{PC}$ = 28.0 Hz, P=C), 200.4 (Ru(CO)), 218.8 ([d, $^2J_{PC}$ = 12.5 Hz, Cr(CO)$_{eq}$), 225.5 (s, Cr(CO)$_{ax}$). ^{31}P{^{1}H} NMR δ: 438.2 (s). ^{29}Si{^{1}H} NMR δ: 15.5 (s, Si(CH$_3$)$_3$), 15.9 (s, Si(CH$_3$)$_3$). IR (Nujol, cm^{-1}) ν: 2047 (s, ν(CrCO)), 2020 (s, ν(RuCO)), 1978 (s, ν(RuCO)), 1968 (s, ν(CrCO)), 1932 (vs, ν(CrCO)), 1920 (vs, ν(CrCO)), 1261 (m), 1249 (m, δ(SiMe$_3$)), 1094 (w), 1077 (w), 1028 (w), 846 (m, ρ(SiMe$_3$)), 812 (w), 752 (w), 665 (m), 645 (m), 628 (w), 559 (w), 536 (w), 510 (w), 464 (w), 442 (w), 413 (w). Anal. Calcd for $C_{24}H_{33}CrO_7PRuS_2Si_2$(737.65): C, 39.01; H, 4.51. Found: C, 38.83; H, 4.47.

In one experiment it was tried to obtain ^{1}H NMR spectroscopic data of the unstable precursor (η^5-C$_5$Me$_5$)(CO)$_2$Ru−P=C(SSiMe$_3$)$_2$. Thus, a solution of 0.08 g (0.17 mmol) of **4b** in 2.5 mL of (C$_6$D$_6$) was treated with 0.01 mL (0.17 mmol) of CS$_2$ at 10 °C. From the resulting red solution, a ^{1}H NMR spectrum showed three resonances at δ 0.50 (s, 9H, Si(CH$_3$)$_3$), 0.56 (s, 9H, Si(CH$_3$)$_3$), and 1.56 (s, 15H, C$_5$(CH$_3$)$_5$). The ^{31}P{^{1}H} NMR resonances was registered as a singlet at δ = 475.3 ppm.

2-[(η^5-C$_5$Me$_5$)(CO)$_2$Ru]-5-[(η^5-C$_5$Me$_5$)(CO)$_2$RuS]-1,3,4-thiadiphosphole (8b). A mixture of 1.25 g (2.66 mmol) of (η^5-C$_5$Me$_5$)(CO)$_2$RuP(SiMe$_3$)$_2$ (**4b**) and 0.16 mL (2.66 mmol) of CS$_2$ in 50 mL of *n*-pentane was stirred 4 h at 20 °C. The solution was filtered and concentrated to ca 15 mL. Upon storing overnight at −30 °C, a black precipitate separated, which was filtered off (0.33 g). All attempts to purify this material by crystallization or chromatography failed. ^{1}H NMR δ: 1.46 (s, 15H, C$_5$(CH$_3$)$_5$), 1.57 (s, 15H, C$_5$(CH$_3$)$_5$). ^{31}P{^{1}H} NMR: δ_A = 294.2, δ_B = 312.3 ($^1J_{AB}$ = 408.0 Hz).

(η^5-C$_5$Me$_5$)(CO)$_2$FeAs=C(SSiMe$_3$)$_2$ (12a). A solution of 0.22 mL (3.62 mmol) of CS$_2$ was added to the red-brown solution of 1.88 g (3.62 mmol) of (η^5-C$_5$Me$_5$)(CO)$_2$FeAs(SiMe$_3$)$_2$ (**11a**) in 40 mL of *n*-pentane at −20 °C. The solution was slowly warmed up to room temperature and then stirred at 40 °C for 8 h. After the solution was cooled to 20 °C, volatiles were removed *in vacuo* to yield a viscous brown-black oil (1.57 g, ca 80%) of impure **12a**. All attempts to obtain a pure crystalline product failed. ^{1}H NMR δ: 0.46 (s, 9H, Si(CH$_3$)$_3$), 0.50 (s, 9H, Si(CH$_3$)$_3$), 1.44 (s, 15H, C$_5$(CH$_3$)$_5$). ^{13}C{^{1}H} NMR δ: 0.9 (s, Si(CH$_3$)$_3$), 1.6 (s, Si(CH$_3$)$_3$), 9.3 (s, C$_5$(*C*H$_3$)$_5$), 95.7 (s, *C*$_5$(CH$_3$)$_5$), 177.4 (s, As=C), 215.8 (s, FeCO). ^{29}Si{^{1}H} NMR δ: 12.5 (s, Si(CH$_3$)$_3$), 13.4 (s, Si(CH$_3$)$_3$). IR (Nujol, cm^{-1}) ν: 1991 (vs, νFe(CO)), 1947 (vs, νFe(CO)), 1260 (m), 1247 (m, δ(SiMe$_3$), 1095 (w), 1074 (w), 1028 (w), 878 (w), 842 (s, ρ(SiMe$_3$)), 799 (m), 753 (w), 693 (w), 630 (w), 581 (m), 545 (w), 506 (w), 459 (w), 396 (w). Anal. Calcd for $C_{19}H_{33}AsFeO_2S_2Si_2$ (544.54): C, 41.91; H, 6.11. Found: C, 40.89; H, 6.17.

(η^5-C$_5$Me$_5$)(CO)$_2$FeAs[Cr(CO)$_5$]=C(SSiMe$_3$)$_2$ (13a). Metalloarsaalkene **12a** was prepared from 1.56 g (3.33 mmol) of (η^5-C$_5$Me$_5$)(CO)$_2$FeAs(SiMe$_3$)$_2$ (**4a**) and 0.26 mL (3.33 mmol) of CS$_2$ in 50 mL of *n*-pentane at −30 °C. To this mixture a solution of 1.01 g (3.33 mmol) of [(*Z*)-cyclooctene]Cr(CO)$_5$ in 30 mL of *n*-pentane was added dropwise. Warming up to ambient temperature led to the formation of a dark red precipitate. After the slurry was stirred for an additional 90 min, a dark red solid was isolated by filtration. After being washed with 50 mL of *n*-pentane, the filter cake was crystallized from 10 mL of toluene at −30 °C to afford 1.73 g (71%) of **13a** as dark red diamond-shaped crystals. ^{1}H NMR δ: 0.44 (s, 9H, Si(CH$_3$)$_3$), 0.46 (s, 9H, Si(CH$_3$)$_3$), 1.46 (s, 15H, C$_5$(CH$_3$)$_5$). ^{13}C{^{1}H} NMR δ: 1.0 (s, Si(CH$_3$)$_2$), 9.6 (s, C$_5$(*C*H$_3$)$_5$), 97.4 (s, *C*$_5$(CH$_3$)$_5$), 191.9 (s, As=C), 214.3 (s, FeCO), 219.0 (s, CrCO$_{eq}$), 226.1 (s, CrCO$_{ax}$). ^{29}Si{^{1}H} NMR δ: 15.5 (s, SiMe$_3$), 16.3 (s, SiMe$_3$). IR (Nujol, cm^{-1}): 2048 (s, ν(CrCO)), 2009 (s, ν(FeCO)), 1962 (s, ν(FeCO)), 1940 (vs, ν(CrCO)), 1920 (vs, ν(CrCO)), 1908 (vs, ν(CrCO)), 1259 (w), 1244 (m, δ(SiMe$_3$)), 1092 (w), 1075 (w), 1027 (w), 844 (ρ(SiMe$_3$)), 819 (m), 754 (w), 668 (m), 653 (m), 626 (w), 582 (w), 563 (w), 542 (w), 518 (w), 464 (w), 452 (w), 418 (w). Anal. Calcd for $C_{24}H_{33}AsCrFeO_7S_2Si_2$ (737.65): C, 39.14; H, 4.52. Found: C, 38.84; H, 4.42.

(η^5-C$_5$Me$_5$)(CO)$_2$RuAs(SiMe$_3$)$_2$ (4b). A sample of solid (η^5-C$_5$Me$_5$)(CO)$_2$RuBr (3.72 g, 10.0 mmol) was added to well-stirred solution of LiAs(SiMe$_3$)$_2$·3.1 THF (4.51 g, 10.0 mmol) in 50 mL of *n*-pentane at −30 °C. The mixture was slowly warmed up to 20 °C, and stirring was continued for 90 min, whereupon a tan precipitate separated. All volatiles were removed *in vacuo*, and the residue was extracted repeatedly with a total of 100 mL of *n*-pentane. After filtration, the extract was concentrated to 20 mL and stored at −30 °C overnight. Orange crystals of (η^5-C$_5$Me$_5$)(CO)$_2$RuAs(SiMe$_3$)$_2$ separated (3.26 g, 64%). ^{1}H NMR δ: 0.59 (s, 18H, Si(CH$_3$)$_3$), 1.64 (s, 15H, C$_5$(CH$_3$)$_5$). ^{13}C{^{1}H} NMR δ: 5.4 (s, SiCH$_3$), 9.9 (s, C$_5$(*C*H$_3$)$_5$), 99.5 (s, *C*$_5$(CH$_3$)$_5$), 205.1 (s, CO). ^{29}Si{^{1}H} NMR: 3.9 (s, Si(CH$_3$)$_3$). IR (Nujol, cm^{-1}) ν: 1986 (vs, ν(CO)), 1947 (vs, ν(CO)), 1240 (m, δ(SiMe$_3$)), 1072 (w), 1029 (w), 849 (m), 832 (s, ρ(SiMe$_3$)), 743 (w), 683 (m), 619 (w), 594 (w), 585 (w), 561 (m), 537 (w), 515 (w), 484 (w), 424 (w), 376 (w). Anal. Calcd for $C_{18}H_{33}AsO_2RuSi_2$ (513.62): C, 42.09; H, 6.48. Found: C, 41.91; H, 6.37.

(η^5-C$_5$Me$_5$)(CO)$_2$RuAs=C(SSiMe$_3$)$_2$ (12b). At −30 °C, the solutions of 1.23 g (2.40 mmol) of (η^5-C$_5$Me$_5$)(CO)$_2$RuAs(SiMe$_3$)$_2$ **4b** in 50 mL of *n*-pentane and 0.15 mL (2.40 mmol) of CS$_2$ in 20 mL of *n*-pentane were combined and slowly warmed up to 20 °C. The mixture continued to stir at 40 °C for 4 h. Removal of the volatiles *in vacuo* gave 1.09 g (77%) of orange-red waxy **12b**, which could not be crystallized. ^{1}H NMR δ: 0.51 (s, 9H,

$Si(CH_3)_3$), 0.54 (s, 9H, $Si(CH_3)_3$), 1.55 (s, 15H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR δ: 0.9 (s, $SiCH_3$), 1.7 (s, $SiCH_3$), 9.6 (s, $C_5(\mathit{C}H_3)_5$), 99.4 (s, $\mathit{C}_5(CH_3)_5$), 175.2 (s, As=C), 202.7 (s, CO). $^{29}Si\{^1H\}$ NMR δ: 12.5 (s, $Si(CH_3)_3$), 13.4 (s, $Si(CH_3)_3$). IR (Nujol, cm^{-1}) ν: 2010 (vs, ν(CO)), 1957 (vs, ν(CO)), 1249 (m, δ(SiMe$_3$)), 1072 (w), 1029 (w), 990 (w), 935 (w), 882 (w), 842 (m, ρ(SiMe$_3$)), 753 (w), 629 (w), 578 (m), 556 (m), 538 (w), 508 (w), 489 (w), 468 (w), 434 (w). Anal. Calcd for $C_{19}H_{33}O_2RuS_2Si_2$ (589.82): C, 38.70; H, 5.64. Found: C, 38.00; H, 5.33.

(η^5-C$_5$Me$_5$)(CO)$_2$RuAs[Cr(CO)$_5$]=C(SSiMe$_3$)$_2$ (13b). Compound **12b** was prepared from (η^5-C$_5$Me$_5$)(CO)$_2$RuAs(SiMe$_3$)$_2$ (1.13 g, 2.20 mmol) and CS_2 (0.13 mL, 2.20 mmol) in 50 mL of *n*-pentane as described before. To the chilled solution (−30 °C) a solution of [(*Z*)-cyclooctene]Cr(CO)$_5$ (0.67g, 2.20 mmol) in 20 mL of *n*-pentane was added dropwise with stirring. An orange precipitate separated spontaneously. After the slurry was warmed to 20 °C, it was filtered and the filter cake was washed with *n*-pentane (50 mL). Crystallization from 10 mL of toluene at −30 °C for 16 h afforded orange diamond-shaped crystalline **13b** (1.33, 77%). ^1H NMR δ: 0.43 (s, 9H, $Si(CH_3)_3$), 0.46 (s, 9H, $Si(CH_3)_3$), 1.60 (s, 15H, $C_5(CH_3)_3$). $^{13}C\{^1H\}$ NMR δ: 0.9 (s, $SiCH_3$), 1.1 (s, $SiCH_3$), 10.0 (s, $C_5(\mathit{C}H_3)_5$), 100.9 (s, $\mathit{C}_5(CH_3)_5$), 187.9 (s, As=C), 200.6 (s, RuCO), 218.9 (s, $CrCO_{eq}$), 226.1 (s, $CrCO_{ax}$). $^{29}Si\{^1H\}$ NMR δ: 15.5 (s, $Si(CH_3)_3$), 15.9 (s, $Si(CH_3)_3$). IR (Nujol, cm^{-1}) ν: 2050 (s, ν(CrCO)), 2022 (s, ν(RuCO)), 1971 (s, ν(RuCO)), 1940 (vs, ν(CrCO)), 1919 (vs, ν(CrCO)), 1909 (vs, ν(CrCO)), 1260 (w), 1244 (m, δ(SiMe$_3$)), 1074 (w), 1029 (w), 843 (m, ρ(SiMe$_3$)), 819 (m), 753 (w), 668 (m), 652 (m), 626 (w), 557 (w), 535 (w), 506 (w), 463 (w), 452 (w). Anal. Calcd for $C_{24}H_{33}AsCrO_7RuS_2Si_2$ (781.60): C, 36.87; H, 4.25. Found: C, 36.83; H, 4.24.

X-ray Crystal Structure Determination of 13a. Single crystals of **13a** were grown from toluene at −30 °C. A dark red crystal with the approximate dimensions of 0.35 × 0.29 × 0.27 mm^3 was measured on a Siemens SMART CCD area detector system with three axis geometry with Mo Kα radiation at 298 K. Crystal data and refinement details: cell dimensions $a = 10.2072(3)$ Å, $b = 12.3595(3)$ Å, $c = 14.4912(3)$ Å, $\alpha = 93.7110(10)°$, $\beta = 106.4520(10)°$, $\gamma = 103.3900(10)°$, $V = 1688.92(7)$ Å^3 (refined from all reflections > $20\sigma(F)$), $Z = 2$, $d_{calcd} = 1.448$ g cm^{-3}, $\mu = 1.954$ mm^{-1}, space group $P\bar{1}$, hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\phi = 0$, 88, and 180°) at a detector distance of 5.891 cm ($2\theta_{max} = 54.1°$), data reduction with the SAINT program (V4.028, Siemens) by which more than 97% of a data are covered, decay correction (<2%) by repeated collection of 50 frames at the end of the data collection, empirical absorption correction with redundant data (SADABS program, Siemens) max/min transmission 1.000/0.465, *R*(merg) before/after correction 0.0918/0.0371. There were 7435 intensities read, 5435 unique and 3550 observed [$I > 2\sigma(I)$] ($R_{int} = 0.0385$). Structure solution and refinement on F^2 with SHELXTL-Plus version. 5.03/Iris (Siemens), 344 parameters, hydrogen atoms treated as riding groups with a 1.2-fold (1.5-fold for methyl groups) isotropic *U* value of the equivalent *U* value of the corresponding C atom. R1 = 0.0551, wR2 = 0.1253, GooF(F^2) = 0.939, $w^{-1} = \sigma^2(F_o^2)+(0.0607P)^2 + 0.0P$, where $P = [(\max F_o^2,0) + 2F_c^2)]/3$, max/min residual electron densities 1.140 and −0.679 e Å^{-1}.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **13a** (6 pages). Ordering information is given on any current masthead page.

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