Transition Metal Substituted Phosphaalkenes, 40[+] Transition Metal Substituted Arsaalkenes, 6[+]

Reactivity of Ferriophosphaalkene [(η^5-C_5Me_5)(CO)$_2$Fe–P=C(NMe$_2$)$_2$] and Ferrioarsaalkene [(η^5-C_5Me_5)(CO)$_2$Fe–As=C(NMe$_2$)$_2$] Towards Trimethylaluminium, -gallium and -indium

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday

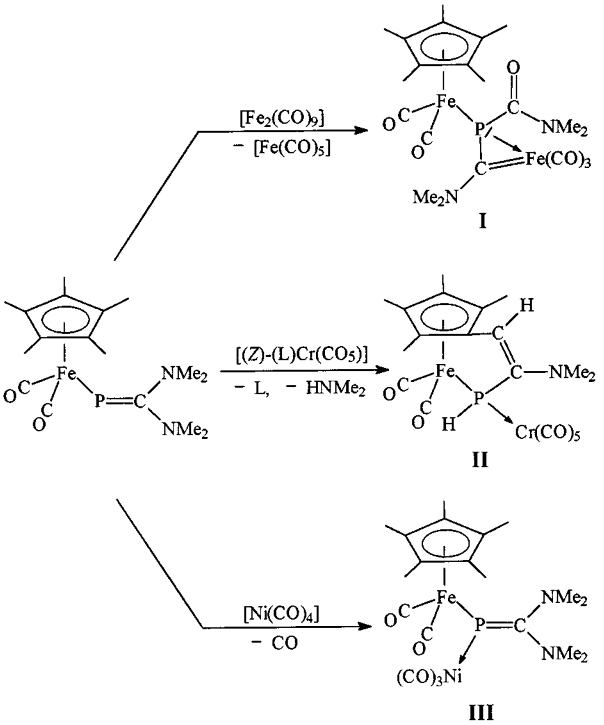
Keywords: Arsaalkenes / Phosphaalkenes / Aluminium / Gallium / Indium

Reaction of equimolar amounts of the ferriophosphaalkene [(η^5-C_5Me_5)(CO)$_2$FeP=C(NMe$_2$)$_2$] (**1a**) or the ferrioarsaalkene [(η^5-C_5Me_5)(CO)$_2$FeAs=C(NMe$_2$)$_2$] (**1b**) with trimethylaluminium, trimethylgallium and trimethylindium afforded the adducts [(η^5-C_5Me_5)(CO)$_2$FeE{MMe$_3$}C(NMe$_2$)$_2$] with E = P; M = Al (**2a**), Ga (**3a**), In (**4a**) and E = As; M = Al (**2b**), Ga (**3b**), and In (**4b**). These compounds feature η^1-coordination of the phosphaalkene or the arsaalkene ligand towards the Lewis acid via the pnictogen atom. The molecular structures of **2a** and **3a** were elucidated by X-ray diffraction analyses.

Introduction

During the course of our investigations on the chemical properties of metallophospha- and metalloarsaalkenes [(η^5-C_5Me_5)(CO)$_2$FeE=C(NMe$_2$)$_2$] (E = P, As)[1][2] we have studied their reactivity towards transition metal carbonyls. Whereas the treatment of the arsalkene with [Ni(CO)$_4$], [Fe$_2$(CO)$_9$] or [(*Z*)-cyclooctene)Cr(CO)$_5$] afforded adducts of the type [(η^5-C_5Me_5)(CO)$_2$FeAs{M(CO)$_n$}C(NMe$_2$)$_2$] ([M(CO)$_n$ = [Ni(CO)$_3$], [Fe(CO)$_4$], [Cr(CO)$_5$])[3] the corresponding phosphaalkene and [Fe$_2$(CO)$_9$] or [(*Z*)-cyclooctene)Cr(CO)$_5$] gave rise to the formation of complexes **I** and **II**.[4]

With nickel carbonyl adduct **III** was obtained.[4] Moreover, the metallophosphaalkene was converted by [(η^5-C_5H_5)(CO)$_2$Rh] into a complex analogous to **II** ([(η^5-C_5H_5)(CO)Rh] instead of [Cr(CO)$_5$]) the arsaalkene was disintegrated to the η^2-diarsene complex [{(η^5-C_5Me_5)(CO)$_2$Fe-As}$_2$Rh(CO)(η^5-C_5H_5)].[5] In view of these results it was obvious to extent our studies on the reactivity of the title compounds to electrophiles derived from main group metals.



Scheme 1

Results and Discussion

Treatment of **1a** and **1b** with equimolar amounts of AlMe$_3$, GaMe$_3$ and InMe$_3$ in *n*-pentane in the temperature range −78 °C to 20 °C afforded the trimethylmetal adducts **2a,b**, **3a,b** and **4a,b** as air- and moisture sensitive solids, whereas **1a** and **1b** appeared to be inert towards Al(*i*Pr)$_3$. Solutions of compound **2b** in benzene completely decomposed at 20 °C within a few hours. The stability of the remaining adducts in solution was sufficient to provide satisfactory NMR spectra. Purification of the obtained compounds was achieved by recrystallization from *n*-pentane at −28 °C. In the IR spectra (KBr) of adducts **2a,b, 3a,b** and

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[+] Part 39; part 5: L. Weber, M. H. Scheffer, H.-G. Stammler, B. Neumann, *Inorg. Chim. Acta*, in the press.

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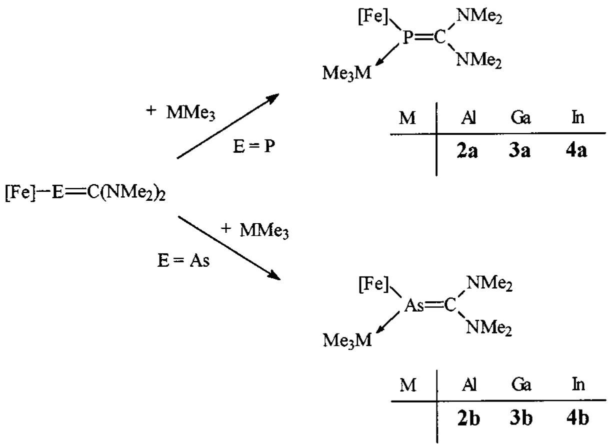
4a,b intense bands at $\tilde{\nu} = 1991-2000$ and $1931-1951$ cm^{-1} were assigned to the stretching modes of the terminal carbonyls of the $[Fe(CO)_2]$ unit. Hypsochromic shifts of 10−27 cm^{-1} of these bands with respect to **1a** and **1b** indicate a significant withdrawal of electron density from the organophosphorus or the organoarsenic ligand by the Lewis acids.



Scheme 2

The $^{13}C\{^1H\}$-NMR spectra of the phosphaalkene and arsaalkene adducts showed resonances at $\delta = 219.4-220.8$ for the carbonyl carbon atoms, which are only slightly shielded when compared to the starting materials **1a** and **1b**. The resonance for the methylene carbon atom in the phosphaalkene adducts appeared as doublet at $\delta = 203.0-204.5$, and thus is slightly shifted to low-field relative to **1b** ($\delta = 202.4$). Adduct formation was accompanied by a decrease of the $^1J_{PC}$ coupling constant from 97.0 Hz in **1a** to 75.8−80.6 Hz in **2a**-**4a**. In a corresponding $[Ni(CO)_3]$ adduct a similar $^1J_{PC}$ coupling was measured ($^1J_{PC}$ = 77.7 Hz),[4] whereas smaller coupling constants ranging from 59.0 to 67.4 Hz were registered upon protonation, alkylation and silylation of **1a**.[6] The methylene carbon atom of **1b** ($\delta = 214.8$) is shifted upfield to $\delta = 211.7$ (**3b**) and 211.9 (**4b**) upon adduct formation. The $^{31}P\{^1H\}$-NMR spectra of the adducts **2a**, **3a** and **4a** are characterized by singlets at $\delta = -12.1$, 14.5 and 22.2, which are strongly deshielded with respect to **1a** ($\delta = 135.5$).

X-ray Structural Analysis of 2a

To ensure that the metallophosphaalkene is bonded to the metal through the phosphorus atom and to establish the stereochemistry within the ligand an X-ray structural determination of **2a** was undertaken.

An ORTEP drawing of **2a** is shown in Figure 1, also selected bond lengths and angles . The analysis shows that η^1-coordination of the ferriophosphaalkene to trimethylaluminium by virtue of the phosphorus lone pair results in a significant distortion of the organophosphorus ligand. Thus, the phosphorus atom is now trigonal-pyramidally coordinated (sum of angles 340.0°). This value is between those of the corresponding adducts of **1a** to the $[Ni(CO)_3]$ (335.8°)[4] and to the $[Cr(CO)_5]$ units (346.1°).[7] The phosphorus atom forms single bonds to the atoms Fe, Al and C(16). In comparison to **1a** [1.709(5) Å] the PC bond is elongated to 1.779(3) Å, a situation which was also evident in the $[Ni(CO)_3]$ adduct [1.770(5) Å].[4] The iron−phosphorus bond length [2.3174(9) Å] is similar to the one in **1a** [2.325(2) Å].[1] The P−Al bond length of 2.5077(12) Å may be compared to the P−Al distances in the number of adducts of phosphanes and $AlMe_3$ such as $Me_3Al-PH(t\text{-}Bu)CH_2CH_2(t\text{Bu})HP-AlMe_3$ [2.533(3) Å],[8] $Me_3Al-P(Ph)_2CH_2CH_2(Ph_2)P-AlMe_3$ [2.544(4) Å][9] and $Me_3Al-P(Ph)_2CH_2CH_2P(Ph)[AlMe_3]CH_2CH_2(Ph)_2P-AlMe_3$ [2.504(6) and 2.535(7) Å].[8]

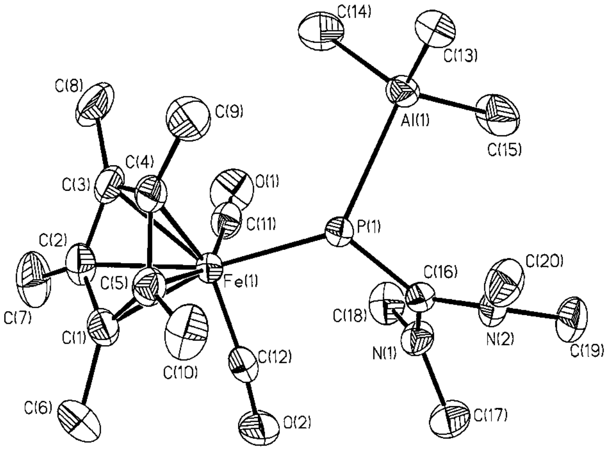


Figure 1. Molecular structure of **2a** in the crystal. Selected bond lengths [Å] and angles [deg]: Fe(1)−C(12) 1.754(3), Fe(1)−C(11) 1.761(3), Fe(1)−P(1) 2.3174(9), Al(1)−C(15) 1.980(4), Al(1)−C(14) 1.984(4), Al(1)−C(13) 1.988(4), Al(1)−P(1) 2.5077(12), P(1)−C(16) 1.779(3), O(1)−C(11) 1.142(4), O(2)−C(12) 1.151(4), N(1)−C(16) 1.358(4), N(1)−C(18) 1.447(4), N(1)−C(17) 1.470(4), N(2)−C(16) 1.363(4), N(2)−C(20) 1.457(4), N(2)−C(19) 1.465(4); C(12)−Fe(1)−C(11) 97.01(16), C(12)−Fe(1)−P(1) 92.08(11), C(11)−Fe(1)−P(1) 92.84(10), C(15)−Al(1)−C(14) 111.87(19), C(15)−Al(1)−C(13) 111.33(18), C(14)−Al(1)−C(13) 112.71(16), C(15)−Al(1)−P(1) 107.58(12), C(14)−Al(1)−P(1) 107.04(12), C(13)−Al(1)−P(1) 105.90(11), C(16)−P(1)−Fe(1) 116.45(10), Fe(1)−P(1)−Al(1) 124.13(4), C(16)−N(1)−C(18) 122.5(3), C(16)−N(1)−C(17) 122.5(3), C(18)−N(1)−C(17) 114.9(3), C(16)−N(2)−C(20) 122.5(3), C(16)−N(2)−C(19) 121.7(3), C(20)−N(2)−C(19) 113.5(3), O(1)−C(11)−Fe(1) 175.6(3), O(2)−C(12)−Fe(1) 174.6(3), N(1)−C(16)−N(2) 115.2(3), N(1)−C(16)−P(1) 126.0(2), N(2)−C(16)−P(1) 118.8(2)

The methylene carbon atom C(16) of **2a** is trigonal planar (sum of angles 360.0°). The same is true for nitrogen atom N(1) (sum of angles 359.9°), whereas atom N(2) slightly deviates from planarity (sum of angles 357.7°). Relatively short carbon−nitrogen bonds C(16)−N(1) [1.358(4) Å] and C(16)−N(2) [1.363(4) Å] indicate effective π-coordination of the lone pair of electrons on the nitrogen atoms with C(16).

In the crystal molecule **2a** adopts a conformation with an orthogonal orientation of the bond P(1)−Al(1) and the vector Cp*−Fe (where Cp* is the centre of the C_5Me_5 ring [torsion angle Cp*−Fe(1)−P(1)−Al(1) = −90.1°]. According to a Newman projection of **2a** (Figure 2) the lone pair at the phosphorus atom is presumably directed towards the

C_5Me_5 ring, leading to a nearly eclipsed position of the vectors Fe(1)−C(12)−O(2) and P(1)−C(16) [torsion angle C(12)−Fe(1)−P(1)−C(16) = 14.5°].

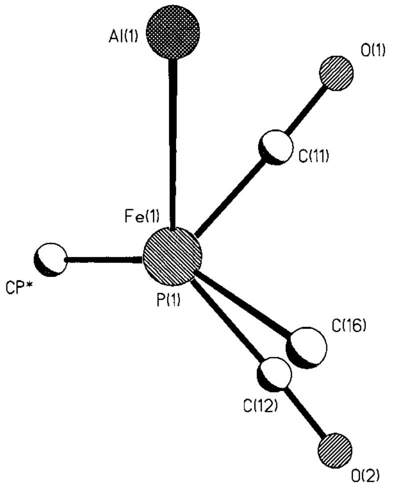


Figure 2. Newman projection of **2a** with view along the P(1)−Fe(1) vector

X-ray Structural Analysis of 3a

The molecular structure in the crystal of the $GaMe_3$ adduct of **1a**, as determined by X-ray diffraction analysis (Figure 3), is closely related to the structure of **2a**. The trigonal-pyramidal phosphorus atom (sum of angles = 340.3°) and the single bond lengths P(1)−C(16) of 1.780(4) Å and Fe(1)−P(1) of 2.3233(17) Å are well comparable in **3a** and **2a**. The Ga−P and Al−P atomic distances are the same within experimental error, which was also observed in the bis-adducts of diphos with $AlMe_3$ and $GaMe_3$. Thus, in $[Me_3GaP(Ph)_2CH_2CH_2P(Ph)_2GaMe_3]$ the Ga−P bond lengths were determined to 2.546(4) Å.[9] Generally, Ga−P bonds in molecules with tetra-coordinate gallium and phosphorus range from 2.347(5) Å in $[(Me_3Si)_3P{-}GaI_3]$[10] up to 2.683(5) Å in $[Ph_2(H)P\text{-}Ga\{CH_2(t\text{Bu})\}_3]$.[11][12]

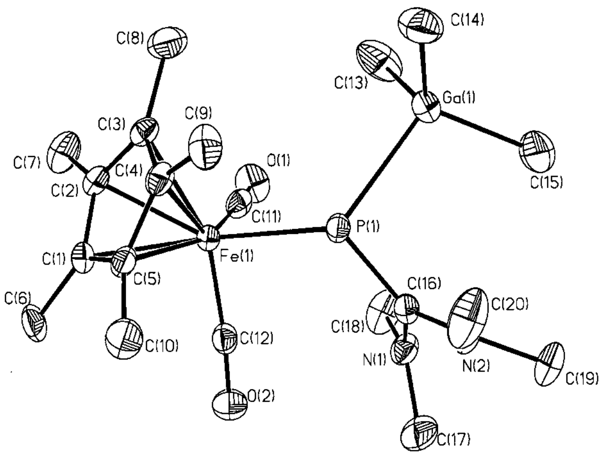


Figure 3. Molecular structure of **3a** in the crystal. Selected bond lengths [Å] and angles [deg]: Ga(1)−C(13) 1.976(6), Ga(1)−C(14) 1.990(5), Ga(1)−C(15) 1.996(5), Ga(1)−P(1) 2.5027(16), Fe(1)−C(12) 1.754(5), Fe(1)−C(11) 1.756(5), Fe(1)−P(1) 2.3233(17), P(1)−C(16) 1.780(4), O(1)−C(11) 1.147(5), O(2)−C(12) 1.151(5), N(1)−C(16) 1.363(5), N(1)−C(18) 1.459(6), N(1)−C(17) 1.462(6), N(2)−C(16) 1.354(5), N(2)−C(20) 1.455(6), N(2)−C(19) 1.473(5); C(13)−Ga(1)−C(14) 112.2(2), C(13)−Ga(1)−C(15) 114.1(3), C(14)−Ga(1)−C(15) 112.6(3), C(13)−Ga(1)−P(1) 107.68(16), C(14)−Ga(1)−P(1) 103.75(17), C(15)−Ga(1)−P(1) 105.67(17), C(12)−Fe(1)−C(11) 97.5(2), C(12)−Fe(1)−P(1) 90.07(15), C(11)−Fe(1)−P(1) 93.83(15), C(16)−P(1)−Fe(1) 117.14(16), C(16)−P(1)−Ga(1) 100.63(15), Fe(1)−P(1)−Ga(1) 122.55(7), C(16)−N(1)−C(18) 122.5(4), C(16)−N(1)−C(17) 122.4(4), C(18)−N(1)−C(17) 115.0(4), C(16)−N(2)−C(20) 123.1(4), C(16)−N(2)−C(19) 122.2(4), C(20)−N(2)−C(19) 113.4(4), O(1)−C(11)−Fe(1) 175.4(4), O(2)−C(12)−Fe(1) 174.7(4), N(2)−C(16)−N(1) 115.0(4), N(2)−C(16)−P(1) 117.9(3), N(1)−C(16)−P(1) 127.1(3)

Experimental Section

All operations were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under argon prior to use. − Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer. − ^1H, ^{13}C, and ^{31}P-NMR spectra were recorded at 22 °C by using a Bruker AC 100 (^1H, 100.13 MHz, ^{31}P, 40.53 MHz), Bruker Avance DRX 500 (^1H, 500.13 MHz, ^{13}C, 125.75 MHz, ^{31}P, 202.46 MHz); references: $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). − Elemental analyses were performed in the microanalytical laboratory of the University of Bielefeld. − The metallophosphaalkene $[\eta^5\text{-Cp*(CO)}_2\text{Fe}{-}\text{P}{=}\text{C(NMe}_2)_2]$ (**1a**)[1] and the metalloarsaalkene $[\eta^5\text{-Cp*(CO)}_2\text{Fe}{-}\text{As}{=}\text{C(NMe}_2)_2]$ (**1b**)[2] were synthesized according to the literature. $AlMe_3$, $GaMe_3$ and $InMe_3$ were purchased commercially (Strem).

$[(\eta^5\text{-}C_5Me_5)(CO)_2FeP\{AlMe_3\}C(NMe_2)_2]$ (2a): A chilled solution (−78 °C) of **1a** (0.39 g, 1.03 mmol) in 50 mL of *n*-pentane was combined with 0.42 mL of a 2.39 M solution of $AlMe_3$ in toluene. Stirring was continued for a period of 1.5 h, during which the mixture was allowed to warm-up to room temp. It was filtered, and the filtrate was diluted with 100 mL of *n*-pentane. Storing at −28 °C for 20 h afforded **2a** (0.19 g, 43%) as a dark brown, air and moisture sensitive solid. − IR (KBr): $\tilde{\nu}$ = 2000 (s, CO), 1951 (s, CO). − ^1H NMR (C_6D_6): δ = −0.14 (s, 9 H, $AlMe_3$), 1.51 (s, 15 H, C_5Me_5), 2.70 (s, br, 12 H, NMe_2). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −2.98 (s, $AlCH_3$), 9.31 [s, $C_5(CH_3)_5$], 43.45 (s, NCH_3), 96.25 [s, $C_5(CH_3)_5$], 202.95 (d, $^1J_{PC}$ = 75.8 Hz, PC), 219.38 (s, CO). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −12.12 s. − $C_{20}H_{36}AlFeN_2O_2P$ (419.35): calcd. C 53.34, H 8.06, N 6.22; found C 50.89, H 7.91, N 6.03. The C,H,N elemental analysis was repeated several times with crystalline samples, however, no better C-values were obtained.

$[(\eta^5\text{-}C_5Me_5)(CO)_2FeAs\{AlMe_3\}C(NMe_2)_2]$ (2b): To a chilled solution (−78 °C) of **1b** (0.32 g, 0.76 mmol) in *n*-pentane (50 mL) was added 0.33 mL of a 2.39 M solution of $AlMe_3$ (0.79 mmol) in toluene. An orange precipitate spontaneously occurred, which was redissolved upon warming up the mixture to 20 °C. Stirring was continued for 1 h, and then it was filtered. The filtrate was diluted with 50 mL of *n*-pentane and stored at −28 °C to afford 0.15 g (41%) of thermolabile orange-red crystalline **2b**. Solutions in benzene completely decomposed at 20 °C within a few hours which prevented the registration of a reliable $^{13}C\{^1H\}$ NMR spectrum. − ^1H NMR (C_6D_6): δ = −0.09 (s, 9 H, $AlMe_3$), 1.57 (s, 15 H, C_5Me_5), 2.73 (s, br, 12 H, NMe_2). − $C_{20}H_{36}AlAsFeN_2O_2$ (494.26): calcd. C 48.60, H 7.34, N 5.67; found C 48.31, H 6.94, N 5.60.

$[(\eta^5\text{-}C_5Me_5)(CO)_2FeP\{GaMe_3\}C(NMe_2)_2]$ (3a): A *n*-pentane solution (50 mL) of **1a** (0.47 g, 1.24 mmol) was combined at −78 °C with 0.54 g (1.24 mmol) of a 2.3 M solution of $GaMe_3$ in *n*-hexane.

Table 1. Crystallographic data for **2a** and **3a**

	2a	**3a**
empirical formula	$C_{20}H_{36}AlFeN_2O_2P$	$C_{20}H_{36}FeGaN_2O_2P$
mol. mass (g mol^{-1})	450.31	493.05
temp. (K)	173	173
cryst. size (mm)	0.5 × 0.5 × 0.4	0.6 × 0.5 × 0.3
cryst. syst.	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	15.300(4)	12.392(10)
b (Å)	8.057(2)	15.118(6)
c (Å)	20.221(3)	13.419(8)
α (deg)	90	90
β (deg)	102.36(2)	102.69(5)
γ (deg)	90	90
V (Å^3)	2434.9(9)	2453(3)
Z	4	4
cryst. color	dark-brown	dark-brown
habit	irregular	irregular
d_{calcd} (g cm^{-3})	1.228	1.335
μ Mo K_α (mm^{-1})	0.737	1.771
F(000)	960	1032
θ range (deg)	2.06 to 30.00	2.03 to 27.50
limiting indices	$0 \leq h \leq 21$	$0 \leq h \leq 16$
	$0 \leq k \leq 11$	$0 \leq k \leq 19$
.	$-28 \leq l \leq 27$	$-17 \leq l \leq 17$
no. of reflns. collected	7353	5875
no. of indep. reflns	7113 [$R_{(int)}$ = 0.0587]	5625 [$R_{(int)}$ = 0.0445]
no. of parameters	256	256
absorptions correction	none	semi-empirical from ψ-scans
ρ_{max}, ρ_{min} (e Å^{-3})	0.643, −0.655	0.425, −0.426
goodness of fit on F^2	1.034	1.008
R_F [$I > 2\sigma(I)$]	0.0593 [4650]	0.0576 [3444]
$wR_F{}^2$ [$I > 2\sigma(I)$]	0.1236	0.0951
treatment of hydrogen atoms	riding model	riding model

The stirred mixture was allowed to warm to 20 °C within a period of 2 h. Filtration, addition of *n*-pentane (50 mL) to the filtrate and storage at −28 °C for 20 h afforded 0.36 g (59%) of black crystalline **3a**. − IR (KBr): ṽ = 2000 (s, CO), 1947 (s, CO). − ^{1}H NMR (C_6D_6): δ = 0.20 (s, 9 H, $GaMe_3$), 1.51 (s, 15 H, C_5Me_5), 2.71 (s, 12 H, NMe_2). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 0.32 (s, $GaCH_3$), 9.24 [s, $C_5(CH_3)_5$], 43.33 (s, NCH_3), 96.23 [s, $C_5(CH_3)_5$], 203.76 (d, $^1J_{PC}$ = 80.6 Hz, PC), 219.62 (s, CO). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 14.52 s, br. − $C_{20}H_{36}FeGaN_2O_2P$ (493.06): calcd. C 48.72, H 7.36, N 5.68; found C 47.88, H 6.91, N 5.56.

[(η^5-C_5Me_5)(CO)$_2$FeAs{GaMe$_3$}C(NMe$_2$)$_2$] (3b): Analogously, the reaction of equimolar amounts of **1b** (0.15 g, 0.36 mmol) and $GaMe_3$ (0.16 g of a 2.3 M solution in *n*-hexane) in *n*-pentane gave 0.10 g (51%) of **3b** as red-black needles. − IR (KBr): ṽ = 1991 (s, CO), 1932 (s, CO). − ^{1}H NMR (C_6D_6): δ = 0.24 (s, 9 H, $GaMe_3$), 1.57 (s, 15 H, C_5Me_5), 2.68 (s, 12 H, NMe_2). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −0.46 (s, $GaCH_3$), 9.31 [s, $C_5(CH_3)_5$], 44.50 (s, NCH_3), 95.00 [s, $C_5(CH_3)_5$], 211.7 (s, AsC), 220.8 (s, CO). − $C_{20}H_{36}AsFeGaN_2O_2$ (537.00): calcd. C 44.73, H 6.76, N 5.22; found C 44.30, H 6.50.

[(η^5-C_5Me_5)(CO)$_2$FeP{InMe$_3$}C(NMe$_2$)$_2$] (4a): A chilled solution (−78 °C) of **1a** (0.53 g, 1.40 mmol) in *n*-pentane (50 mL) was treated with 0.7 mL of a 2 M solution of $InMe_3$ (1.40 mmol) in *n*-pentane. After the usual work up black crystalline **4a** (0.44 g, 58%) was isolated. − IR (KBr): ṽ = 1999 (s, CO), 1946 (s, CO). − ^{1}H NMR (C_6D_6): δ = 0.18 (s, 9 H, $InMe_3$), 1.50 (s, 15 H, C_5Me_5), 2.70 (s, 12 H, NMe_2). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −4.56 (s, $InCH_3$), 9.13 [s, $C_5(CH_3)_5$], 43.28 (s, NCH_3), 96.14 [s, $C_5(CH_3)_5$], 204.5 (d, $^1J_{PC}$ = 80.5 Hz, PC), 219.53 (s, CO). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 22.2 s, br. − $C_{20}H_{36}FeInN_2O_2P$ (538.16): calcd. C 44.64, H 6.74, N, 5.21; found C 44.64, H 6.80, N 5.12.

[(η^5-C_5Me_5)(CO)$_2$FeAs{InMe$_3$}C(NMe$_2$)$_2$] (4b): Black crystalline **4b** (0.37 g, 59%) was synthesized analogously from **1b** (0.46 g, 1.09 mmol) and 1.10 mmol (0.55 mL of a 2 M solution in *n*-pentane) of $InMe_3$. − IR (KBr): ṽ = 1993 (s, CO), 1931 (s, CO). − ^{1}H NMR (C_6D_6): δ = 0.21 (s, 9 H, $InMe_3$), 1.54 (s, 15 H, C_5Me_5), 2.66 (s, 12 H, NMe_2). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = −4.82 (s, $InCH_3$), 9.20 [s, $C_5(CH_3)_5$], 44.20 (s, NCH_3), 95.1 [s, $C_5(CH_3)_5$], 211.9 (s, AsC), 220.5 (s, CO). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 14.52 s, br. − $C_{20}H_{36}AsFeInN_2O_2$ (582.10): calcd. C 41.27, H 6.23, N 4.81; found C 41.10, H 6.06, N 4.62.

X-ray Structural Solution and Refinement: The same general procedures were employed to collect the X-ray diffraction data for complexes **2a** and **3a**. Crystal data collection and refinement parameters are given in Table 1. ORTEP drawing of the solid state structure of **2a** and **3a** are shown in Figures 1,2 and 3, respectively.[13] For **2a** and **3a** the data were collected with a Siemens P2$_1$ four-circle diffractometer (Mo-K_α radiation λ = 0.71073 Å). Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS and SHELXL-97. The structure was solved by using Direct Methods and was refined by using full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms.

Acknowledgments

This work was generously supported by the Deutsche Forschungsgemeinschaft, Bonn, Germany and the Fonds der Chemischen Industrie, Frankfurt, Germany, which are gratefully acknowledged.

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[13] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118723 (**2a**) and CCDC-118724 (**3a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk).

Received February 5, 1999
[I99039]