Inorg. Chem. **1987**, *26*, 2733–2736 **2733**

Table I. Spectroscopic Data for $[Ir(\textit{trans}\text{-}CH_3CH{=}CHCHO)(CO)(PPh_3)_2]ClO_4$ (**1**) and $[Ir(\textit{trans}\text{-}C_6H_5CH{=}CHCHO)(CO)(PPh_3)_2]ClO_4$ (**2**)

compd	electronic abs,[a] nm
1	438 (630), 383 (2670), 329 (3760)
2	437 (610), 381 (2960), ca. 320[b]

compd	IR abs,[c] cm^{-1} $\nu(C{=}O)$	 $\nu(C{\equiv}O)$
trans-$CH_3CH{=}CHCHO$	1689, 1642	
1	1631, 1604	2003
trans-$C_6H_5CH{=}CHCHO$	1674, 1626	
2	1612, 1580	1981

compd	^1H NMR,[d] ppm
trans-$CH_3CH{=}CHCHO$	9.58 (d, CHO), 6.96 (m, CH_3CH), 6.14 (m, $CHCHO$), 2.02 (dd, CH_3)
1	8.31 (d, CHO), 7.50 (m, PC_6H_5), 6.76 (m, CH_3CH), 5.46 (m, $CHCHO$), 1.80 (dd, CH_3)
trans-$C_6H_5CH{=}CHCHO$	9.67 (d, CHO), 7.30 (m, C_6H_5CH, C_6H_5CH),[e] 6.52 (m, $CHCHO$)
2	8.64 (d, CHO), 7.50 (m, C_6H_5CH, C_6H_5CH, PC_6H_5),[f] 6.02 (m, $CHCHO$)

[a] Under nitrogen at 25 °C in CH_2Cl_2 solution. Extinction coefficients are given in parentheses. [b] Shoulder due to the strong band near 300 nm. [c] Nujol mull. [d] Under nitrogen at 25 °C at 60 MHz, $CDCl_3$ solution. Chemical shifts are relative to Me_4Si. [e] Multiplets centered at 7.30 ppm. [f] Multiplets centered at 7.50 ppm.

$(CO)(PPh_3)_2]^+$, whose spectral data were not reported,[7] there have been no reports on $[IrL(CO)(PPh_3)_2]^+$ in which L is coordinated through the π system of the olefinic group of L. The significant decreases in $\nu(C{=}O)$ of *trans*-$CH_3CH{=}CHCHO$ and *trans*-$C_6H_5CH{=}CHCHO$ upon coordination to $Ir(CO)(PPh_3)_2^+$ also suggest that the unsaturated aldehydes in **1** and **2** are coordinated through the oxygen atom but not through the olefinic group. The $\nu(C{=}C)$ bands of the unsaturated aldehydes are obscured by the very strong absorption bands of $\nu(C{=}O)$ in all spectra of the free unsaturated aldehydes and iridium complexes. A strong and broad absorption band observed at 1100 cm^{-1} for **1** and **2** (not listed in Table I) is attributable to the tetrahedral (Td) anion ClO_4^-,[5] and in agreement, **1** and **2** are 1:1 electrolytes as shown by the conductance measurements (see Experimental Section). The fact that the olefinic protons of *trans*-$CH_3CH{=}CHCHO$ and *trans*-$C_6H_5CH{=}CHCHO$ do not show significant changes in the chemical shifts upon coordination to $Ir(CO)(PPh_3)_2^+$ (see Table I) also suggests that the coordination of the unsaturated aldehydes in **1** and **2** does not occur through the π system of the olefinic group. It should be mentioned that the reactions of **3** with saturated aldehydes such as $CH_3CH_2CH_2CHO$ and CH_3CH_2CHO did not afford the products analogous to **1** and **2**. The isolated greenish products seem to be mixtures of **3** and a small amount of uncharacterized iridium complexes that do not contain the saturated aldehydes.

Catalytic Activities

It is known that the complexes $[IrL(CO)(PPh_3)_2]ClO_4$ (L = unsaturated nitriles coordinated through the nitrogen atom) react with H_2 to give dihydridoiridium(III) complexes $[Ir(H)_2L(CO)(PPh_3)_2]ClO_4$ and that they catalyze hydrogenation of the unsaturated nitrile (L) to the corresponding saturated nitrile at elevated temperature (100 °C).[1] Reactions of **1** and **2** with H_2 would provide valuable information for the catalytic hydrogenation of *trans*-$CH_3CH{=}CHCHO$ and *trans*-$C_6H_5CH{=}CHCHO$ with **1** and **2**, respectively. It has been found that $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$[8] is the only product of the reactions of **1** and **2** with H_2.

Complex **1** catalyzes the hydrogenation of *trans*-$CH_3CH{=}CHCHO$ to $CH_3CH_2CH_2CHO$ at 25 °C (see Figure 1). The same results as shown in Figure 1 have been obtained by using **3** in place of **1**. Complex **2** does not show catalytic activity for the hydrogenation of *trans*-$C_6H_5CH{=}CHCHO$ even at 100 °C. The olefinic group of *trans*-$C_6H_5CH{=}CHCHO$ may be too stable due to the extended conjugate system to undergo the hydrogenation reaction. It is interesting to see that complex **3** is active for the hydrogenation of $CH_2{=}CHCHO$ to give CH_3CH_2CHO at 25 °C (see Figure 1), although a $CH_2{=}CHCHO$ complex of iridium has not been isolated from the reaction of **3** and $CH_2{=}CHCHO$. Decarbonylation products (alkane and alkene) have not been detected in the reactions of $CH_2{=}CHCHO$ with **3** and *trans*-$CH_3CH{=}CHCHO$ with **1** under N_2 and H_2 at 25 °C for several days. The hydrogenation of $CH_2{=}CHCHO$ is much faster than that of *trans*-$CH_3CH{=}CHCHO$ and proceeds to completion without formation of oligomers whereas a considerable amount of nonvolatile oligomers is obtained during the hydrogenation of *trans*-$CH_3CH{=}CHCHO$ with **1** at 25 °C. Approximately the same number of moles of *trans*-$CH_3CH{=}CHCHO$ is converted into oligomers as is hydrogenated to $CH_3CH_2CH_2CHO$ in the presence of **1** at 25 °C. A small amount of oligomers is also produced in the absence of H_2: less than 1% of *trans*-$CH_3CH{=}CHCHO$ is converted into oligomers when 37 mmol of *trans*-$CH_3CH{=}CHCHO$ is stirred under N_2 at 25 °C for 48 h in the presence of 0.1 mmol of **1**. The hydrogenation of $CH_2{=}CHCHO$ with **3** is somewhat different from the results obtained with the rhodium complex, $[Rh(CH_2{=}CHCHO)(CO)(PPh_3)_2]ClO_4$, which converts more $CH_2{=}CHCHO$ into the oligomers than to the hydrogenation product, CH_3CH_2CHO.[5]

The fact that the hydrogenation with **3** and **1** occurs at the olefinic group of $CH_2{=}CHCHO$ and *trans*-$CH_3CH{=}CHCHO$ requires an interaction between the olefinic group of the unsaturated aldehydes and the iridium in some part of the catalytic cycle. It still remains uncertain whether the hydrogenation occurs by the well-established mechanism through the olefinic π-bonded complexes or by 1,4-addition of Ir–H to the unsaturated aldehydes.

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Registry No. **1**, 109150-66-5; **2**, 109124-71-2; **3**, 32356-67-5; $CH_2{=}CHCHO$, 107-02-8; *trans*-$CH_3CH{=}CHCHO$, 123-73-9.

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Iron(II) Aryldiazene Complexes as Precursors of New Derivatives of the Type $[FeL(CO)\{P(OEt)_3\}_4]^{2+}$: Synthesis and Characterization

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In previous reports[1] we described the synthesis of the first aryldiazene iron(II) derivatives of the type $[Fe(ArN{=}NH)(CO)P_4]^{2+}$ [P = $P(OEt)_3$], which showed the ArNNH ligand to be a good leaving group in the complexes. The facile substitution of this ligand should therefore make the diazene compound a suitable starting material for the synthesis of new mono derivatives of iron(II) with unusual ligands. In this paper, as part of our studies on the chemistry of Fe(II) phosphite complexes,[2] we report an extensive study on the reactivity of the $[Fe(ArN{=}NH)(CO)P_4]^{2+}$ cations with several ligands, which allowed the synthesis of aldehyde, sulfide, and arylhydrazine complexes containing the

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Scheme I

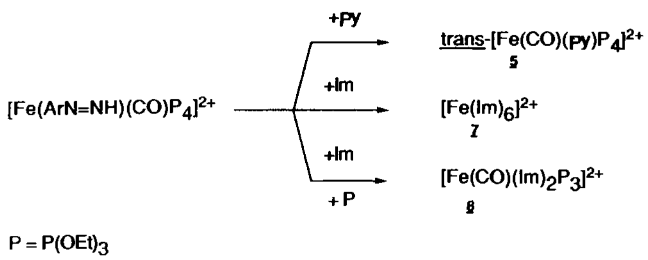


Table I. Selected IR and NMR (^1H and $^{31}P\{^1H\}$) Data for the Iron(II) Complexes

		IR,[c] cm^{-1}		^1H NMR[d]			$^{31}P\{^1H\}$ NMR[d,f]	
no.	compd[a,b]	$\nu(CO)$	other	solvent	δ	assign	spin syst	chem shift, δ, and coupl const, Hz
1a	*trans*-$[Fe(CH_3CHO)(CO)L_4]^{2+}$	2004 s (1999 s)	1668 m (OC) (1667 m)	CD_2Cl_2	2.09 d 9.37 q	$C\mathit{H}_3CHO$ $CH_3C\mathit{H}O$		131.7 s
1b	*trans*-$[Fe(C_2H_5CHO)(CO)L_4]^{2+}$	2007 s (1999 s)	1665 m (OC) (1664 m)	CD_2Cl_2	0.95 t, 2.40 m 9.41 br	$C_2\mathit{H}_5CHO$ $C_2H_5C\mathit{H}O$		131.6 s
1c	*trans*-$[Fe(C_6H_5CHO)(CO)L_4]^{2+}$	2006 s (1999 s)	1620 m (OC) (1623 m)	CD_2Cl_2	7.66 m 9.36 br	$C_6\mathit{H}_5CHO$ $C_6H_5C\mathit{H}O$		131.8 s
2a	*cis*-$[Fe(CO)L_4\{(CH_3)_2S\}]^{2+}$	2031 s (2024 s)		CD_2Cl_2	2.01 s	$(C\mathit{H}_3)S$	AB_2C	$\delta_A = 142.6$, $\delta_B = 133.9$, $\delta_C = 133.7$ $J_{AB} = 137.0$, $J_{AC} = 116.0$, $J_{BC} = 149.5$
2b	*cis*-$[Fe(CO)L_4\{CH_3(C_2H_5)S\}]^{2+}$	2031 s (2022 s)		CD_2Cl_2	2.14 s 2.58 q	$C\mathit{H}_3(CH_3CH_2)S$ $CH_3(CH_3C\mathit{H}_2)S$	AB_2C	$\delta_A = 142.3$, $\delta_B = 133.8$, $\delta_C = 133.7$ $J_{AB} = 138.0$, $J_{AC} = 115.4$, $J_{BC} = 150.0$
3a	*cis*-$[Fe(4-CH_3C_6H_4NHNH_2)(CO)L_4]^{2+}$	2029 s (2027 s)	 (3354 w, 3306 w) (NH)	$(CD_3)_2SO$	6.35 br 4.8 br	$4-CH_3C_6H_4N\mathit{H}NH_2$ $4-CH_3C_6H_4N\mathit{H}_2$	AB_2C	$\delta_A = 147.4$, $\delta_B = 136.0$, $\delta_C = 131.6$ $J_{AB} = 120.0$, $J_{AC} = 135.9$, $J_{BC} = 136.5$
3b	*cis*-$[Fe(4-CH_3OC_6H_4NHNH_2)(CO)L_4]^{2+}$	2031 s (2028 s)	 (3330 w, 3308 w) (NH)	$(CD_3)_2SO$	6.16 br 4.7 br	$4-CH_3OC_6H_4N\mathit{H}NH_2$ $4-CH_3OC_6H_4NHN\mathit{H}_2$	AB_2C	$\delta_A = 147.4$, $\delta_B = 136.2$, $\delta_C = 131.7$ $J_{AB} = 118.0$, $J_{AC} = 135.4$, $J_{BC} = 137.0$
3c	*cis*-$[Fe(4-NO_2C_6H_4NHNH_2)(CO)L_4]^{2+}$	2029 s (2023 s)	 (3362 w, 3290 w) (NH)	$(CD_3)_2SO$	7.82 br 5.2 br	$4-NO_2C_6H_4N\mathit{H}NH_2$ $4-NO_2C_6H_4NHN\mathit{H}_2$	AB_2C	$\delta_A = 146.7$, $\delta_B = 135.5$, $\delta_C = 130.7$ $J_{AB} = 123.0$, $J_{AC} = 135.3$, $J_{BC} = 138.0$
4	*cis*-$[Fe(4-CH_3OC_6H_4NH_2)(CO)L_4]^{2+}$	2034 s (2031 s)	 (3329 w, 3273 w) (NH)	CD_2Cl_2			AB_2C	$\delta_A = 148.6$, $\delta_B = 135.7$, $\delta_C = 131.7$ $J_{AB} = 120.5$, $J_{AC} = 128.9$, $J_{BC} = 141.0$
5	*trans*-$[Fe(CO)(py)L_4]^{2+}$	2018 s (2008 s)		$(CD_3)_2CO$	8.90 m, 8.57 m	$C_5\mathit{H}_5N$		130.5 s
6	*cis*-$[FeN_3(CO)L_4]^+$	2020 s (2018 s)	2056 s (N_3) (2058 s)	$(CD_3)_2CO$			AB_2C	$\delta_A = 150.3$, $\delta_B = 136.6$, $\delta_C = 135.7$ $J_{AB} = 132.0$, $J_{AC} = 102.5$, $J_{BC} = 155.0$
8	$[Fe(CO)(Im)_2L_3]^{2+}$	2004 s (1997 s)	 (3310 m) (NH)	$(CD_3)_2CO$	11.9 8.47 7.61 7.73	$N(1)\mathit{H}^e$ $C(2)\mathit{H}^e$ $C(4)\mathit{H}^e$ $C(5)\mathit{H}^e$	AB_2	$\delta_A = 143.6$, $\delta_B = 131.0$ $J_{AB} = 136.0$

[a] L = $P(OEt)_3$. [b] All complexes were obtained as BPh_4^- salts. [c] In CH_2Cl_2 solution and KBr pellets (in parentheses). [d] At room temperature. [e] For coordinated imidazole (Im). [f] Positive shift downfield from 85% H_3PO_4.

$Fe(CO)P_4$ moiety. Furthermore, imidazole was also tested for reactivity toward the diazene complex, and the preparation of the $[Fe(CO)(Im)_2P_3]^{2+}$ derivative is also reported.

Experimental Section

Solvents and Reagents. Organic solvents were purified and dried by standard methods and distilled under a stream of nitrogen just prior to use. Diazonium salts were obtained as described in the literature.[3] Aldehydes were purified by distillation under nitrogen. Other reagents were purchased from commercial sources in the highest available purity and used as received.

Physical Measurements. Solution ^1H NMR spectra were obtained with a Varian EM-390 or Varian FT-80A spectrometer, with tetramethylsilane as internal standard. Fourier-mode, proton-noise-decoupled $^{31}P\{^1H\}$ spectra were collected on a Varian FT-80A operating at 32.203 MHz. The chemical shifts are referred to 85% H_3PO_4, downfield shifts being considered positive. IR spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer. Conductivities of 10^{-3} M solutions of the complexes in nitromethane at 25 °C were measured with a "Halosis" bridge. Solution magnetic susceptibilities were determined by the Evans method.[4]

Synthesis of the Complexes. All preparative work was performed under an inert atmosphere using standard Schlenk techniques. Once isolated, the compounds were shown to be air-stable for a period of days. The hydride $[FeH(CO)\{P(OEt)_3\}_4]BPh_4$ species was prepared according to the procedure previously reported.[1b]

$[FeL(CO)\{P(OEt)_3\}_4](BPh_4)_2$ [L = CH_3CHO (1a), CH_3CH_2CHO (1b), C_6H_5CHO (1c), $(CH_3)_2S$ (2a), $CH_3(C_2H_5)S$ (2b), 4-$CH_3C_6H_4NHNH_2$ (3a), 4-$CH_3OC_6H_4NHNH_2$ (3b), 4-$NO_2C_6H_4NHNH_2$ (3c), 4-$CH_3OC_6H_4NH_2$ (4), C_5H_5N (py) (5)]. These complexes were originally prepared by treating the $[Fe(ArN{=}NH)(CO)\{P(OEt)_3\}_4](BPh_4)_2$ (Ar = 4-$CH_3C_6H_4$ or 4-ClC_6H_4) complexes with an excess of the appropriate ligand in dichloromethane. Since the diazene complex is quantitatively formed when the hydride $[FeH(CO)\{P(OEt)_3\}_4]^+$ is reacted with the aryldiazonium salt, the following method is more direct. For example, the synthesis of $[Fe(CH_3CHO)(CO)\{P(OEt)_3\}_4](BPh_4)_2$ (**1a**) is as follows. To a solution of $[FeH(CO)\{P(OEt)_3\}_4]BPh_4$ (1.07 g, 1 mmol) in 10 mL of CH_2Cl_2 was added a slight excess of $[4\text{-}CH_3C_6H_4N_2]BF_4$ (0.31 g, 1.5 mmol), and the reaction mixture was stirred at room temperature for 24 h. After filtration to remove the unreacted diazonium salt, an excess of acetaldehyde (0.17 mL, 3 mmol) in 10 mL of CH_2Cl_2 was slowly added to the diazene solution, which was stirred for ca. 20 h. The solvent was removed under reduced pressure to give a brown oil, which was triturated with ethanol (20 mL). The addition of $NaBPh_4$ (0.68 g, 2 mmol) afforded a yellow solid, which was filtered and twice crystallized from CH_2Cl_2/ethanol (3:20 mL); yield ≥60%. The other complexes were synthesized in parallel ways, giving yields ranging from 60 to 85%. Physical constants and elemental analyses for the complexes follow.

Anal. Calcd for **1a**: C, 62.95; H, 7.33. Found: C, 62.69; H, 7.36. Mp: 163 °C dec. Λ_M = 125.2 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (CD_2Cl_2): δ 7.30 m and 6.96 m (C_6H_5), 4.10 m (CH_2), 1.32 t (CH_3). Anal. Calcd for **1b**: C, 63.17; H, 7.39. Found: C, 63.00; H, 7.32. Mp: 134 °C dec. Λ_M = 118.1 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (CD_2Cl_2): δ 7.30 m and 6.96 m (C_6H_5), 4.09 m (CH_2), 1.31 t (CH_3). Anal. Calcd for **1c**: C, 64.35; H, 7.16. Found: C, 64.09; H, 7.16. Mp: 167 °C dec. Λ_M = 121.7 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (CD_2Cl_2): δ 7.30 m and 6.96 m (C_6H_5), 4.09 m (CH_2), 1.29 t (CH_3). Anal. Calcd for **2a**: C, 62.16; H, 7.37. Found: C, 61.86; H, 7.43. Mp: 149 °C dec. Λ_M = 114.6 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (CD_2Cl_2): δ 7.30 m and 6.96 m (C_6H_5), 4.07 m (CH_2), 1.31 t and 1.29 t (CH_3). Anal. Calcd for **2b**: C, 62.39; H, 7.44. Found: C, 61.95; H, 7.42. Mp: 159 °C dec. Λ_M = 121.9 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (CD_2Cl_2): δ 7.30 m and 6.97 m (C_6H_5), 4.10 m (CH_2), 1.28 t and 1.29 t (CH_3). Anal. Calcd for **3a**: C, 63.67; H, 7.35; N, 1.86. Found: C, 63.31; H, 7.43; N, 1.64. Mp: 140 °C dec. Λ_M = 122.6 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($Me_2SO\text{-}d_6$): δ 7.19 m and 6.88 m (C_6H_5 and C_6H_4), 4.19 m (CH_2), 2.22 s (CH_3 (arylhydrazine)), 1.37 t, 1.28 t, and 1.26 t (CH_3). Anal. Calcd for **3b**: C, 63.00; H, 7.27; N, 1.84. Found: C, 62.90; H, 7.29; N, 1.69. Mp: 130 °C dec. Λ_M = 122.6 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($Me_2SO\text{-}d_6$): δ 7.16 m and 6.88 m (C_6H_5 and C_6H_4), 4.22 m (CH_2), 3.69 s (CH_3 (arylhydrazine)), 1.33 t and 1.29 t (CH_3). Calcd for **3c**: C, 61.61; H, 7.00; N, 2.73. Found: C, 61.30; H, 6.99; N, 2.55. Mp: 131 °C dec. Λ_M = 113.3 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($Me_2SO\text{-}d_6$): δ 8.26 m, 7.19 m, and 6.88 m (C_6H_5 and C_6H_4), 4.19 m (CH_2), 1.37 t and 1.26 t (CH_3). Anal. Calcd for **4**: C, 63.63; H, 7.28; N, 0.93. Found: C, 63.41; H, 7.35; N, 0.85. Mp: 136 °C dec. Λ_M = 113.4 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (CD_2Cl_2): δ 7.30 m and 6.97 m (C_6H_5 and C_6H_4), 4.08 m (CH_2), 3.74 s (CH_3 (anisidine)), 1.33 t, 1.32 t, and 1.26 t (CH_3). Anal. Calcd for **5**: C, 63.90; H, 7.22; N, 0.96. Found: C, 63.71; H, 7.28; N, 0.81. Mp: 165 °C dec. Λ_M = 122.9 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($Me_2CO\text{-}d_6$): δ 7.35 m and 6.88 m (C_6H_5), 4.40 m (CH_2), 1.42 t (CH_3).

$[FeN_3(CO)\{P(OEt)_3\}_4]BPh_4$ (6). An excess of LiN_3 (0.17 g, 3.47 mmol) was added to a solution of $[Fe(ArN{=}NH)(CO)P_4](BPh_4)_2$ (0.6 g, 0.4 mmol) in 15 mL of CH_2Cl_2 and the reaction mixture stirred for 24 h. After filtration, the solution was evaporated to dryness, leaving a yellow oil, which was triturated with ethanol (10 mL). The yellow solid that slowly formed was crystallized by slow cooling to −30 °C of its saturated dichloromethane/ethanol (0.5:10 mL) solution; yield ≥85%.

Anal. Calcd: C, 53.03; H, 7.27; N, 3.79. Found: C, 53.20; H, 7.12; N, 3.61. Mp: 105 °C dec. Λ_M = 50.3 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($Me_2CO\text{-}d_6$): δ 7.35 m and 6.88 m (C_6H_5), 4.32 m (CH_2), 1.38 t, 1.35 t, and 1.31 t (CH_3).

$[Fe(Im)_6](BPh_4)_2$ (7) (Im = $C_3H_4N_2$, Imidazole). To a solution of $[Fe(ArN{=}NH)(CO)P_4](BPh_4)_2$ (0.6 g, 0.4 mmol) in 10 mL of CH_2Cl_2 was added an excess of solid imidazole (0.27 g, 4 mmol) and the solution stirred until the precipitation of the white solid that immediately began to form had been completed. The solid was filtered and crystallized from acetone (20 mL) and ethanol (10 mL); yield ≥90%.

Anal. Calcd: C, 71.88; H, 5.85; N, 15.25. Found: C, 71.63; H, 6.08; N, 15.31. Mp: 186 °C dec. $\Lambda_M(Me_2CO)$ = 187.2 Ω^{-1} cm^2 mol^{-1}. μ_{eff} = 5.4 μ_B (in Me_2CO).

$[Fe(CO)(Im)_2\{P(OEt)_3\}_3](BPh_4)_2$ (8). An excess of imidazole (0.27 g, 4 mmol) was added to a stirring solution of $[Fe(ArN{=}NH)(CO)P_4]^{2+}$ (0.6 g, 0.4 mmol) in 20 mL of dichloromethane, and after 15 min, an excess of triethylphosphite (2 mL, 12 mmol) was also added. The solution was refluxed for ca. 1 h, cooled at room temperature, and then filtered. The solvent was removed at reduced pressure to give a yellow oil, which was treated with ethanol (20 mL). The resulting solid obtained was repeatedly crystallized from CH_2Cl_2/ethanol (4:25 mL); yield ≥65%.

Anal. Calcd: C, 64.61; H, 6.91; N, 4.13. Found: C, 64.85; H, 6.75; N, 4.20. Mp: 146 °C dec. Λ_M = 126.7 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($Me_2CO\text{-}d_6$): δ 7.32 m and 6.89 m (C_6H_5), 4.08 m (CH_2), 1.33 t and 1.24 t (ratio 1:2; CH_3).

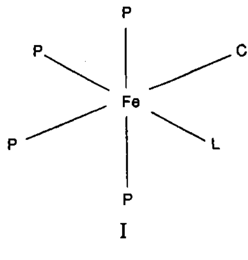
Results and Discussion

The synthesis of the new $[FeL(CO)\{P(OEt)_3\}_4](BPh_4)_2$ complexes containing aldehyde (**1**), sulfide (**2**), arylhydrazine (**3**), and anisidine (**4**) as ligands has been achieved by reacting the diazene derivatives $[Fe(ArN{=}NH)(CO)\{P(OEt)_3\}_4]^{2+}$ (Ar = 4-$CH_3C_6H_4$ or 4-ClC_6H_4) in CH_2Cl_2 with an excess of the appropriate ligand, as shown in (1).

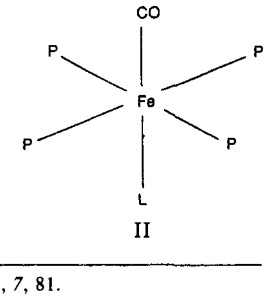
$$[Fe(ArN{=}NH)(CO)\{P(OEt)_3\}_4]^{2+} \xrightarrow[\text{excess}]{L} [FeL(CO)\{P(OEt)_3\}_4]^{2+} \qquad (1)$$

L: CH_3CHO, **1a**; CH_3CH_2CHO, **1b**;
C_6H_5CHO, **1c**; $(CH_3)_2S$, **2a**; $CH_3(C_2H_5)S$, **2b**;
4-$CH_3C_6H_4NHNH_2$, **3a**; 4-$CH_3OC_6H_4NHNH_2$, **3b**;
4-$NO_2C_6H_4NHNH_2$, **3c**; 4-$CH_3OC_6H_4NH_2$, **4**

Selected spectroscopic properties of the iron(II) complexes, which are diamagnetic and 2:1 electrolytes,[5] are reported in Table I. For all compounds the infrared spectra show only one ν(CO) band at 2034–2004 cm^{-1}, both in the solid state and in CH_2Cl_2 solution. Furthermore, except for the aldehyde compounds **1**, the $^{31}P\{^1H\}$ NMR spectra are AB_2C multiplets in the temperature range from −70 to +34 °C, which can be simulated with the parameters reported in Table I. Cis geometry (I) can therefore be proposed in solution for these compounds. On the contrary, a trans structure (II) seems to be attributable to aldehyde[6] com-



I



II

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(6) Any attempt at preparing the formaldehyde complex by reacting the diazene precursor with both paraformaldehyde and gaseous CH_2O was unsuccessful.

plexes **1**, whose $^{31}P\{^1H\}$ NMR spectra between −70 and +34 °C appear as sharp singlets at δ 131.8–131.6.

The infrared spectra of RCHO complexes **1** show the $\nu(CO)$ of the aldehydic carbonyl group at 1668–1620 cm^{-1} (CH_2Cl_2), reduced by about 55 cm^{-1} as compared to the free ligand value. Moreover, the ^1H NMR spectra show the peaks of both the aldehydic and nonaldehydic protons shifted to high field (ca. 0.4 and 0.1 ppm, respectively). These data support the coordination of the RCHO ligand, but do not allow the coordination mode for the aldehydic group to be assigned unambiguously. However, a comparison with the previously reported ketone and aldehyde complexes[1a,7] seems to exclude a π-bonded RCHO ligand on the basis of the presence[8] of its $\nu(CO)$ at 1668–1620 cm^{-1}. Moreover η^2-coordination would involve lowering of $\nu(CO)$ of much more than the observed 55 cm^{-1} in comparison to the free ligand.[9] Therefore a σ-bonded oxygen atom for our RCHO derivatives can be tentatively proposed.

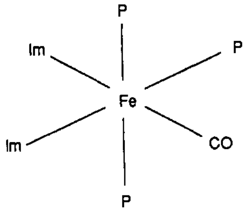
In complexes **1** the aldehydic ligand does not show any exchange with nitromethane at 34 °C within 2 h.

Sulfides of the type $(CH_3)_2S$ and $CH_3(C_2H_5)S$ can easily substitute the diazene group to give the first thioether iron(II) complexes (**2**) containing phosphite ligands.[10]

The infrared spectra of arylhydrazine complexes (**3**) show two bands of medium intensity in the 3362–3290-cm^{-1} region, assigned to the $\nu(NH)$ frequencies (Table I). In the ^1H NMR spectra two broad signals, which disappear on shaking with D_2O, are present at δ 4.7–5.2 and 6.16–7.82 and were attributed respectively to the NH_2 and NH protons of the hydrazine ligand.[11] Comparison with the ^1H NMR spectra of the free ligand show that, while the NH_2 protons are shifted to low field on coordination, the NH signal remains almost unaltered in the complexes, suggesting that the hydrazine ligand is unidentate in these derivatives.[12] In contrast with the diazene ligand in $[Fe(ArN{=}NH)(CO)\{P(OEt)_3\}_4]^{2+}$ compounds, the arylhydrazine group in **3** is rather inert to the substitution reaction, and starting complexes **3** can be recovered unchanged after 2–3 days of reaction with CO or CNR.

The diazene complex $[Fe(ArN{=}NH)(CO)P_4]^{2+}$ reacts in CH_2Cl_2 with an excess of azide ions to give only the mono derivative $[FeN_3(CO)P_4]^+$ (cation of **6**). The IR spectrum shows a strong band at 2056 cm^{-1} (CH_2Cl_2), attributed to stretching of the azide ligand, and the $^{31}P\{^1H\}$ NMR spectrum between −70 and +34 °C is an AB_2C multiplet—in agreement, in this case too, with cis geometry for the complex.

We also studied the reaction of the diazene complex toward pyridine (py) and imidazole (Im); the results are summarized in Scheme I. While the starting $[Fe(ArN{=}NH)(CO)P_4]^{2+}$ compound reacts with pyridine to give the *trans*-$[Fe(CO)(py)P_4]^{2+}$ derivative (singlet at δ 130.5 in the $^{31}P\{^1H\}$ NMR spectrum), with imidazole the white paramagnetic ($\mu_{eff} = 5.4\ \mu_B$) $[Fe(Im)_6]^{2+}$ (cation of **7**) complex[13] is obtained. Owing to its low solubility, the hexakis derivative separated out from the reaction mixture even when we operated with a low complex:imidazole ratio (1:1 or 1:2). The reaction with imidazole was also carried out in the presence of excess of phosphite ligand; in this case, we obtained the new complex $[Fe(CO)(Im)_2P_3]^{2+}$ (cation of **8**), which was isolated and characterized[14] (Table I). The $[Fe(CO)(Im)_2P_3]^{2+}$ compound is a stable yellow solid, is diamagnetic, and is a 1:2 electrolyte. Its $^{31}P\{^1H\}$ NMR spectrum is an AB_2 multiplet between −70 and +34 °C, which can be simulated with the values reported in Table I. The infrared spectra of **8** show the $\nu(CO)$ band at 2004 cm^{-1} (in CH_2Cl_2), and by comparison with the data reported in Table I for other analogous Fe(II) complexes,[15] this value seems to indicate that the CO ligand is trans to an imidazole group. On this basis, type III geometry may reasonably be proposed in solution for this compound. In the phosphite methyl region the ^1H NMR spectra of **8** show two triplets of intensity ratio 1:2, while a complicated multiplet appears in the methylene region. This may be explained on the basis of virtual coupling of the two mutually trans phosphites present in type III geometry. Last, the ^1H NMR spectra show a broad signal near δ 11.9, attributed to the nitrogen-bound proton on the imidazole group, and three resonances between δ 7.73 and δ 8.47, tentatively assigned to the other H–C protons of the Im ligand (Table I), in agreement with previously reported[16] imidazole complexes of cobalt(III).



III

Acknowledgment. The financial support of the MPI and CNR, Rome, is gratefully acknowledged. We thank Daniela Baldan and Giuseppe Inzerillo for technical assistance.

Registry No. (**1a**)$(BPh_4)_2$, 108945-53-5; (**1b**)$(BPh_4)_2$, 108945-55-7; (**1c**)$(BPh_4)_2$, 108945-57-9; (**2a**)$(BPh_4)_2$, 108968-96-3; (**2b**)$(BPh_4)_2$, 108968-98-5; (**3a**)$(BPh_4)_2$, 108945-59-1; (**3b**)$(BPh_4)_2$, 108945-61-5; (**3c**)$(BPh_4)_2$, 108945-63-7; (**4**)$(BPh_4)_2$, 108945-65-9; (**5**)$(BPh_4)_2$, 108945-67-1; (**6**)$(BPh_4)_2$, 108945-69-3; (**7**)$(BPh_4)_2$, 108945-72-8; (**8**)$(BPh_4)_2$, 108945-71-7; $[Fe(4\text{-}CH_3C_6H_4N{=}NH)(CO)\{P(OEt)_3\}_4](BPh_4)_2$, 95738-81-1; $[Fe(4\text{-}ClC_6H_4N{=}NH)(CO)\{P(OEt)_3\}_4](BPh_4)_2$, 100112-71-8; $[FeH(CO)\{P(OEt)_3\}_4]BPh_4$, 95738-79-7.

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(8) A π-bonded aldehydic ligand should show the disappearance of $\nu(CO)$ as well as an unaltered ^1H NMR spectrum of the ligand on complex formation, as previously reported for Pd and Pt derivatives: Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 982.

(9) η^2-Formaldehyde complexes show $\nu(CO)$ at 1220–1017 cm^{-1}: (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Berke, H.; Bankhardt, W.; Huttner, G.; Von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 2754. (c) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019.

(10) The use of more bulky sulfides such as $(C_2H_5)_2S$ or $CH_3(C_6H_5)S$ does not allow preparation of the corresponding complexes, probably owing to the steric requirements of the complex for sulfide coordination.

(11) The presence of a weak broad signal for the nitrogen-bound proton resonance of $ArNHNH_2$ complexes is a feature that has already been observed for the hydrazine derivatives of several metals and has been attributed to an exchange process with traces of water present in the solvent: Frisch, P. D.; Hunt, M. M.; Kita, W. G.; McCleverty, J. A.; Rae, A. E.; Seddon, D.; Swann, D.; Williams, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1819. Carroll, J. A.; Sutton, D.; Xiaoheng, Z. *J. Organomet. Chem.* **1982**, *244*, 73.

(12) Hydrazine complexes of iron(II) are generally of the type $[FeX_2(N_2H_4)_2]$ and $[Fe(N_2H_4)_3]^{2+}$ with bridge N_2H_4 ligand, prepared from iron(II) salts and hydrazine. In only two cases, i.e. $[\pi\text{-}C_5H_5Fe(CO)_2(N_2H_4)]^+$ and $[Fe(dpttd)(CH_3NHNH_2)]$ complexes,[12e,f] is the monodentate hydrazine ligand present: (a) Bottomley, F. *Q. Rev., Chem. Soc.* **1970**, *24*, 617 and references cited therein. (b) Anagnostopoulos, A.; Nicholls, D.; Reed, J. *Inorg. Chim. Acta* **1979**, *32*, L17. (c) Starodub, V. A.; Novakovskii, M. S.; Kirichenko, V. G.; Chekin, V. V.; Velikodnyi, A. I. *Koord. Khim.* **1975**, *1*, 1706. (d) Glavic, P.; Slivnik, J.; Bole, A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1781. (e) Sellmann, D.; Kleinschmidt, E. *J. Organomet. Chem.* **1977**, *140*, 211. (f) Sellmann, D.; Kleine-Kleffmann, U. *J. Organomet. Chem.* **1983**, *258*, 315.

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(14) It may be noted that attempts to prepare analogous compounds with different stoichiometry, i.e. mono- or triimidazole derivatives, failed, **7** being the only isolated product.

(15) The $\nu(CO)$ band does fall in the range 2034–2029 cm^{-1} for all cis complexes of geometry I whose ligand trans to the CO group is a good π-acceptor such as phosphite. On the other hand, $\nu(CO)$ frequencies of 2007–2002 cm^{-1} are observed for the starting diazene and the aldehyde complexes and of 2018 cm^{-1} for the pyridine derivative, all containing a σ-donor ligand trans to the carbonyl group.

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