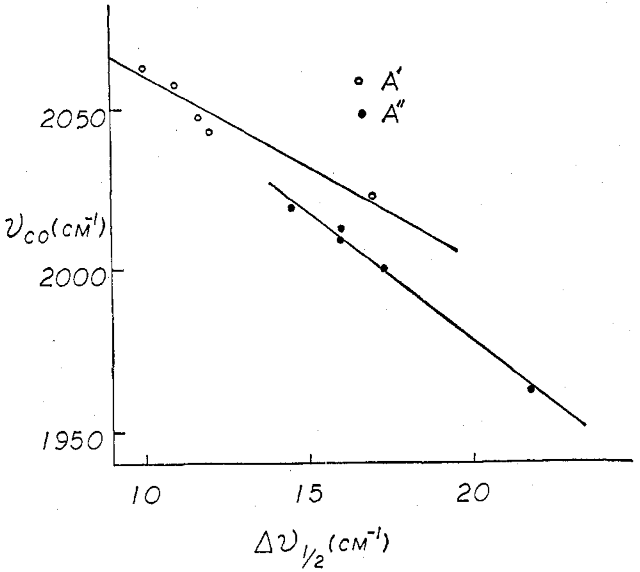

Figure 3.—Correlation between $\Delta\nu_{1/2}$ and ν_{CO} in $(C_5H_5)Fe(CO)_2X$ compounds.

$(C_5H_5)Fe(CO)_2X$ series.[33] Figure 3 contains plots of linear relationships between $\Delta\nu_{1/2}$ *vs.* ν_{CO} for both the A′ and A″ vibrational modes. The magnitude of $\Delta\nu_{1/2}$ is expected to be related to the degree of solvent interactions with the MCO dipoles.[34] This interaction is presumably dependent on the extent of polarization of the carbonyl groups in addition to steric factors about these groups. Since there are no significant deviations from linearity for such large ligands as trichlorotin, steric factors do not appear to be important in these cases. These observations are therefore in agreement with intensity studies, indicating an increase in the electric dipole of the MCO grouping as the CO stretching frequency decreases.

The interpretations of the intensities in the $(C_5H_5)Fe(CO)_2X$ derivatives are consistent with recent calculations of the infrared intensities in *fac*-$M(CO)_3L_3$ molecules, *e.g.*, $(C_5H_5)Mn(CO)_3$ or $(C_6H_6)Cr(CO)_3$, by Anderson and Brown[17] employing a molecular orbital model. These authors conclude that the asymmetric: symmetric intensity ratio should be a very sensitive measure of the importance of back-bonding in compounds of this type. Analogous arguments should apply to the A′ and A″ vibrational modes in the $(C_5H_5)Fe(CO)_2X$ species. Indeed, similar calculations by Anderson[35] on the $(C_6H_6)Cr(CO)_2L$ species clearly indicate this to be the case.

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[33] This trend also exists for the $(C_6H_5CH_2C_5H_5)Fe(CO)_2P(C_6H_5)_3$ complex.

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Reactions of Mono- and Bis(organo)phosphines with Iron Carbonyls

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Reactions of $Fe_2(CO)_9$ and various primary and secondary phosphines at 25° give the phosphine–iron tetracarbonyl species $Fe(CO)_4$phos (phos = CH_3PH_2, $C_6H_5PH_2$, $P(C_6H_5)_2H$, $P(p\text{-}CH_3C_6H_4)_2H$, $P(CH_3)_2H$, $P(C_2H_5)_2H$, $P(C_6H_5)(CH_3)H$) as major products. A small amount of the dinuclear complexes $Fe_2(CO)_6(PRR')_2$ usually accompanies the formation of the $Fe(CO)_4$phos compounds. In the secondary phosphine–$Fe_2(CO)_9$ reactions a third product $Fe_2(CO)_6(PRR')H$ is also observed; this complex, which has a hydride bridging two metals, is better obtained from $Fe(CO)_4(PR_2H)$ by deprotonation with butyllithium followed by addition of $Fe_2(CO)_9$. On heating or on irradiation $Fe(CO)_4$phos species are converted to the dinuclear complexes $Fe_2(CO)_6(PR_2)_2$. When reactions of $Fe(CO)_5$ and $C_6H_5PH_2$ are run at 190°, the only product is $Fe_3(CO)_9(PC_6H_5)_2$. Several derivatives of this complex were obtained, by substitution of trimethyl phosphite for one, two, or three carbonyls.

Introduction

Reactions of iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$) with tertiary phosphines have been studied in considerable detail.[2] More recently analogous reactions with phosphine[3] and with several secondary phosphines have also been reported.[4,5] These latter reactions, when run using moderate conditions (80°),[4a] yield products derived from simple substitution of one or two carbonyls by phosphines. Using higher reaction temperatures, dinuclear complexes are formed with loss of hydrogen from the phosphine. Two different stoichiometries are reported; $Fe_2(CO)_6[P(C_6H_5)_2]_2$ is obtained from $Fe_3(CO)_{12}$ and $P(C_6H_5)_2H$ in refluxing toluene,[4b] and the unusual $Fe_2(CO)_6[P(CF_3)_2]_2H_2$ is reported to be formed from $Fe(CO)_5$ and $P(CF_3)_2H$ in toluene.[5]

Actually the isolation of carbonyl complexes of phosphine and of secondary phosphines with other metals is not uncommon. The stability of such complexes to loss of hydrogen and to consequent formation of phos-

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phido-bridged complexes is quite apparent. Similarly, the retention of phosphorus–phosphorus bonds in diphosphine–metal carbonyl reactions at low temperatures is striking.[6] These observations contrast with results obtained in reactions of metal carbonyls with organosulfur reagents; neither S–H nor S–S are retained in most of these reactions.[7]

Although metal complexes of various phosphines containing P–H units have been prepared, very little has been done to study the reactivity of this functionality in these systems. So simple a reaction as the conversion of a (secondary phosphine)metal carbonyl to a phosphido-bridged species had not previously been attempted. Other obvious reactions such as metalation of the phosphine had only briefly been mentioned before. Thus, Stone and coworkers[8] observed the reaction of $M(CO)_5[P(C_6F_5)_2H]$ (M = Cr, Mo) with butyllithium to give an isolable lithio compound which appeared unpromising as a synthetic intermediate.

More recently preparations of phosphido-bridged mixed transition metal complexes have been accomplished by reaction of $Fe(CO)_4[P(C_6H_5)_2H]$ with several allylmetal complexes[9] and by dehydrohalogenations of a mixture of this phosphine–metal complex and various metal complexes.[10]

We began this work with the synthesis of a number of primary and secondary phosphine complexes of iron and other metals by more or less standard methods. With the availability of these reagents the opportunity of studying the chemistry of these complexes presented itself. We report in this paper some of our studies on iron complexes.

Experimental Section

The various phosphines used in this study were prepared by standard methods: CH_3PH_2, from $LiAlH_4$ reduction of CH_3PCl_2;[11] $C_6H_5PH_2$, by thermal disproportionation of $C_6H_5P(OH)_2$;[12] $(CH_3)_2PH$ and $C_6H_5P(CH_3)H$, by $LiAlH_4$ reduction of $[(CH_3)_2PS-]_2$ and $[(C_6H_5)(CH_3)PS-]_2$;[13] $(C_2H_5)_2PH$, from $LiAlH_4$ reduction of $(C_2H_5)_2PCl$, run by a method analogous to that above;[11] $(C_6H_5)_2PH$ and $(p\text{-}CH_3C_6H_4)_2PH$, by lithium cleavage of an aryl group from the appropriate $(aryl)_3P$ using tetrahydrofuran as solvent,[14] followed by protonation with methanol.

All of the phosphines are toxic and should be handled with care. The gaseous and low-boiling liquid phosphines CH_3PH_2 and $(CH_3)_2PH$ can conveniently be handled in a standard vacuum system. These compounds are highly pyrophoric and must be kept from contact with air. The others, as liquids, were stored in septum-capped vials and dispensed by syringe as needed. However, *phenylphosphine has a particularly unpleasant odor,* which can be detected at remarkably low concentrations. To work with this substance it is absolutely essential to exercise extreme care. It is not generally practical to work outside a hood for any manipulations, including filtrations and evaporations using a water aspirator. Glassware should not be washed in the open, until residues have been treated with a dilute solution of an oxidizing agent such as H_2O_2 or $KMnO_4$, to destroy traces of the phosphine which may be retained.

Diiron enneacarbonyl was prepared by the literature method.[15] General methods for working under nitrogen were employed in this work.

Infrared spectra were recorded on Beckman IR-10 and Perkin-Elmer 421 instruments. Proton nmr measurements were made with Varian A-60A and HR-100 instruments, and mass spectra were recorded on the AEI MS-902. Molecular weights were determined from mass spectra or with a Mechrolab osmometer using benzene solutions of approximately 0.01 *m* concentration. Analyses were performed by the Galbraith Laboratories. Infrared and proton nmr data are given in Table I.

Preparation of Secondary Phosphineiron Tetracarbonyl Complexes. General Procedure.—These compounds were prepared by stirring the phosphine with a 10% excess of $Fe_2(CO)_9$ in benzene, until all the carbonyl had dissolved (24 hr). The solvent and $Fe(CO)_5$ were then removed and the residue was chromatographed on alumina. The products, $Fe(CO)_4(PR_2H)$, eluted first with hexane; these were in each case followed by small amounts of $Fe_2(CO)_6(PR_2)_2$ (eluting with 1:1 hexane–chloroform) and $Fe_2(CO)_6(PR_2)H$ (eluting with chloroform).

$Fe(CO)_4[P(C_6H_5)_2H]$.—This compound was obtained in 68% yield (10.3 g) from 17.1 g of $Fe_2(CO)_9$ (47 mmol) and 8.62 g of $P(C_6H_5)_2H$ (42.6 mmol) on stirring 24 hr in 250 ml of benzene. The product, which was previouly known,[4a] was crystallized from heptane and was identified by comparison with the reported infrared spectrum. A trace of $Fe_2(CO)_6[P(C_6H_5)_2]_2$ and 1.5 g of $Fe_2(CO)_6[P(C_6H_5)_2]H$ (7.6%) were also obtained and identified by their infrared spectra.

We found this method of preparation of $Fe(CO)_4[P(C_6H_5)_2H]$ considerably more satisfactory than that in the literature.[3]

$Fe(CO)_4[P(p\text{-}CH_3C_6H_4)_2H]$.—This compound was obtained in 60.6% yield (36.4 g) from 62.8 g of $Fe_2(CO)_9$ (173 mmol) and 32.0 g of $P(p\text{-}CH_3C_6H_4)_2H$ (157 mmol) on stirring 24 hr in benzene. The product was obtained as yellow crystals by recrystallization from heptane. *Anal.* Calcd for $C_{18}H_{15}O_4PFe$: C, 56.6; H, 3.93; P, 8.12; mol wt 382. Found: C, 56.5; H, 3.94; P, 7.90; mol wt 388 (osmometric).

Only a trace of $Fe_2(CO)_6[P(CH_3C_6H_4)_2]_2$ was obtained, identified by its infrared spectrum. No $Fe_2(CO)_6[P(CH_3C_6H_4)_2]H$ was obtained.

$Fe(CO)_4[P(C_6H_5)(CH_3)H]$.—A solution of 17.5 g of $P(C_6H_5)(CH_3)H$ (141 mmol) in 400 ml of benzene was stirred with 56.1 g of $Fe_2(CO)_9$ (154 mmol). The product, a reddish yellow liquid, was purified by short-path distillation on a vacuum line, bath temperature 90°; 28.8 g (70%) was obtained. *Anal.* Calcd for $C_{11}H_9O_4PFe$: C, 45.2; H, 3.08; P, 10.6; mol wt 292. Found: C, 44.9; H, 3.19; P, 10.4; mol wt 292 (mass spectrometric).

The compounds $Fe_2(CO)_6[P(C_6H_5)CH_3]_2$ (trace) and $Fe_2(CO)_6[P(C_6H_5)CH_3]H$ (0.21 g, 0.4%) were also obtained. They were identified by their infrared spectra.

$Fe(CO)_4[P(CH_3)_2H]$.—This compound was obtained from the reaction of 19.0 g of $P(CH_3)_2H$ (207 mmol) and 123 g of $Fe_2(CO)_9$ (337 mmol) in 200 ml of benzene and 25 ml of toluene for 48 hr. The yellow liquid product was purified by short-path distillation on the vacuum line (bath temperature 30°); yield 47.7 g, 62%; mp 22–23°. Only traces of $Fe_2(CO)_6[P(CH_3)_2]_2$ and $Fe_2(CO)_6[P(CH_3)_2]H$ were also obtained, identified by their infrared spectra. *Anal.* Calcd for $C_6H_7O_4PFe$: C, 31.3; H, 3.04; P, 13.5; mol wt 230. Found: C, 31.3; H, 3.18; P, 13.2; mol wt 230 (mass spectrometric).

$Fe(CO)_4[P(C_2H_5)_2H]$.—The product, a yellow liquid, 7.45 g (41.3%), was obtained from 6.3 g of $P(C_2H_5)_2H$ and 28.4 g of $Fe_2(CO)_9$ in 250 ml of benzene. It was purified by short-path distillation in the vacuum system, bath temperature 45°. *Anal.* Calcd for $C_8H_{11}O_4PFe$: C, 37.2; H, 4.26; P, 12.0; mol wt 258. Found: C, 37.4; H, 4.31; P, 12.2; mol wt 258 (mass spectrometric).

Also obtained were 0.94 g (5.9%) of $Fe_2(CO)_6[P(C_2H_5)_2]_2$ and 0.82 g (3.2%) of $Fe_2(CO)_6[P(C_2H_5)_2]H$, identified by their infrared spectra.

Preparation of $Fe_2(CO)_6(PR_2)H$ Complexes. General Procedure.—The appropriate $Fe(CO)_4(PR_2H)$ complex was dissolved in tetrahydrofuran at 0° and treated first with an equimolar amount of *n*-butyllithium and then with an equimolar amount of $Fe_2(CO)_9$. The reaction mixture was allowed to warm to ambient temperature and stirred for 16 hr. Excess methanol was added, and after stirring an additional 0.5 hr, solvent was removed. The residue was extracted several times with 10% chloroform in hexane. The extracted material was chromatographed on alumina. A small amount of starting material generally eluted

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TABLE I

INFRARED AND NMR DATA FOR PHOSPHINEIRON CARBONYLS

Compd	ν_{CO}[a]	Other ir bands	Proton nmr[b]
$Fe(CO)_4(CH_3PH_2)$	2061 m, 2024 w, 1988 m, 1983 s, 1918 w	2360 m, 1420 m, 1300 m, 1100 s, 985 s, 810 s, 750 m, 725 s, 615 s, 515 m, 480 m, 415 w	(Neat liquid) 5.25, two quartets, $J_{P-H_2} = 36.4$ Hz, $J_{CH_3-H_2} = 6.2$ Hz (2) $P\mathit{H}_2$; 8.50, two overlapping triplets, $J_{P-CH_3} = 12.0$ Hz, $J_{H_2-CH_3} = 6.20$ Hz (3) $C\mathit{H}_3$
$Fe(CO)_4(C_6H_5PH_2)$	2063.5 s, 2028 m, 1989 s, 1955 vs, 1920 sh	2345 w, 2295 w, 1484 w, 1438 m, 1070 m, b, 890 s, 730 m, 685 m, 612 s	(Neat liquid) 2.50, multiplet (5) $C_6\mathit{H}_5$; 4.13, doublet, $J_{P-H} = 364$ Hz (2) $P\mathit{H}_2$
$Fe_2(CO)_6(CH_3PH)_2$ (sym)	2063 w, 2025 s, 1992 m, 1982 m	2320 w, 1110 w, 1010 w, 870 w, 601 m, 575 m	
$Fe_2(CO)_6(C_6H_5PH)_2$	2063 s, 2027 s, 2000 sh, 1996 s, 1984 s, 1974 m	2325 w, 1488 w, 1440 w, 1100 w, 940 m, 910 w, 675 w, 605 s, 580 s, 530 w	2.50, broad, $C_6\mathit{H}_5$
$Fe_3(CO)_7(PC_6H_5)_2(C_6H_5PH_2)_2$	2062 s, 2009 s, 1997 s, 1953 m	2300 w, 1485 m, 1438 m, 1505 w, 1095 m, 1070 sh, 1028 w, 922 m, 900 m	2.67, multiplet, $C_6\mathit{H}_5$
$Fe(CO)_4[(CH_3)_2PH]$	2059 s, 2116 w, 1983 s, 1945 vs, b	(Thin film) 2360 w, 1424 m, 1310 m, 1297 m, 995 s, 950 s, 856 m, 808 m, 747 m, 704 m, 615 s, b	(Neat liquid), 4.77, two septets, $J_{P-H} = 372$ Hz, $J_{CH_3-H} = 6.0$ Hz (1) P–*H;* 8.40, 1:1:1:1 quartet, $J_{CH_3-P} = 12$ Hz, $J_{CH_3-H} = 6.0$ Hz (6) $(C\mathit{H}_3)_2P$–
$Fe(CO)_4[(C_2H_5)_2PH]$	2057 s, 1991 s, 1942 vs, b	(Thin film) 2350 w, 1460 m, 1416 m, 1383 w, 1255 w, 1240 w, 1036 s, 867 s, 754 m, 730 m, 702 sh, 690 m, 610 s, b	(Neat liquid) 5.14, two triplets, $J_{P-H} = 351$ Hz, $J_{H-CH_2} = 5.1$ Hz (1) P–*H;* 8.08, $J_{P-CH_2} = 8.9$ Hz, $J_{CH_2-H} = 5.1$ Hz, $J_{CH_2-CH_3} = 7.5$ Hz (4) $P-C\mathit{H}_2$; 8.80, two triplets, $J_{P-C-CH_3} = 18.5$ Hz, $J_{CH_2-CH_3} = 7.5$ Hz (6) $P(CH_2C\mathit{H}_3)_2P$–
$Fe(CO)_4[(C_6H_5)(CH_3)PH]$	2059 s, 1984 s, 1950–1944 vs, b	(Thin film) 2350 w, 1486 s, 1437 s, 1415 s, 1135 m, 1308 m, sh, 1293 s, 1187 w, 1160 w, 1197 s, 1170 m, 1095 s, 915 vs, b, 775 s, 730 vs, b, 686 s, 613 vs, b	(Neat liquid) 2.67, multiplet (5) $C_6\mathit{H}_5$; 4.10, two quartets, $J_{P-H} = 359$ Hz, $J_{CH_3-H} = 6.2$ Hz (1) P–*H;* 8.47, 1:1:1:1 quartet, $J_{P-CH_3} = 11.1$ Hz, $J_{H-CH_3} = 6.2$ Hz (3) $P-C\mathit{H}_3$
$Fe(CO)_4[P(\mathit{p}\text{-}CH_3C_6H_4)_2H]$	2057 s, 1984 s, 1952 s, 1946 s	2340 w, 1600 m, 1497 m, 1397 m, 1309 m, 1183 w, 1100 s, 1036 w, 1017 w, 929 s, 875 s, 800 sh, 792 s, 707 m, 620 s	($CDCl_3$ soln) 2.68, multiplet (8) $C_6\mathit{H}_4$; 3.17, two singlets, $J_{P-H} = 372$ Hz (1) P–*H;* 7.67, singlet, $C\mathit{H}_3$
$Fe_2(CO)_6[(C_6H_5)_2P]H$	2076 m, 2070 w, 2035.5 s, 2004.5 m, 1993 w, 1983.5 w, sh, 1976.5 m	ν_{FeH} 3555 w; 1435 m, 1092 w, 998 w, 750 m, 720 w, 696 m, 610 m	2.62, multiplet (10) $C_6\mathit{H}_5$; 12.58, doublet, $J_{P-H} = 11.0$ Hz (1) Fe–*H*–Fe
$Fe_2(CO)_6[C_6H_5PCH_3]H$	2077.5 w, 2071 w, 2055 s, 2005 m, 1994 m, 1990 w, sh, 1975 s	ν_{FeH} 3550 w; 1435 w, 1293 w, 895 w, 730 m, 695 w	2.77, multiplet (5) $C_6\mathit{H}_5$; 7.85, doublet, $J_{P-CH_3} = 9.5$ Hz (2.4) $C\mathit{H}_3$; 8.35, doublet, $J_{P-CH_3} = 13.5$ Hz (0.6) $C\mathit{H}_3$; 12.56, doublet, $J_{P-H} = 11.0$ Hz (1) Fe–*H*–Fe
$Fe_2(CO)_6[(CH_3)_2P]H$	2065 m, 2026 s, 1992 s, 1974 s	ν_{FeH} 3605 w; 1410 vs, 949 m, 880 m, 840 w, 640 w, 620 w, 604 w, 610 m	8.08, doublet, $J_{P-CH_3{}^1} = 12.6$ Hz (3) $C\mathit{H}_3{}^1$; 9.56, doublet, $J_{P-CH_3{}^2} = 14.4$ Hz (3) $C\mathit{H}_3{}^2$; 12.20, doublet, $J_{P-H} = 13.0$ Hz (1) Fe–*H*–Fe
$Fe_2(CO)_6[(C_2H_5)_2P]H$	2067 m, 2027 s, 1992 s, 1975 s	ν_{FeH} 3610 w; 1457 w, 1230 w, 1037 m, 1020 w, 915 w, 761 m, 729 m, 692 w, 650 w, 620 w, sh, 610 s	12.20, doublet, $J_{P-H} = 12.0$ Hz (1) Fe–*H*–Fe; CH_3 and CH_2 groups occur as a complex multiplet, τ 7.40–9.30
$Fe_3(CO)_9(PC_6H_5)_2$	2046 s, 2025 s, 2009 m, 1997 w	1433 w, 1091 w, 998 w, 891 w, 616 w, 608 m, 590 m	
$Fe_3(CO)_8(PC_6H_5)_2P(OCH_3)_3$	2059 m, 2019 s, 1998 s, 1970 m	1480 w, 1435 w, 1180 w, 1090 m, 1050 sh, 1020 s, 995 m, 980 m, 608 s, 590 s, 530 m	2.55 (10) $C_6\mathit{H}_5$; 6.55, doublet, $J_{P-OCH_3} = 12$ Hz (9) $C\mathit{H}_3$; CH_3 and CH_2 groups occur as a complex multiplet, τ 7.40–9.30
$Fe_3(CO)_7(PC_6H_5)_2[P(OCH_3)_3]_2$	2040 m, 1997 s, 1973 s, b	1435 w, 1180 w, 1050 s, 1025 s, 610 m, 585 s, 550 m, 530 m	2.33, 2.70 (10) $C_6\mathit{H}_5$; 6.36, 6.51, 6.71 (18) $C\mathit{H}_3$; CH_3 and CH_2 groups occur as a complex multiplet, τ 7.40–9.30
$Fe_3(CO)_6(PC_6H_5)_2[P(OCH_3)_3]_3$	2006 m, 1978 s, 1971 m, 1936 m	1435 vw, 1180 w, 1020 s, 790 m, 608 w, 590 m, 530 w	2.21, 2.71 (10); 6.32, 6.47, 6.65, $C\mathit{H}_3$; CH_3 and CH_2 groups occur as a complex multiplet, τ 7.40–9.30

[a] Heptane solution; Perkin-Elmer 421. Values accurate to ± 1 cm^{-1}. [b] Values given in τ units (TMS internal standard, τ 10.00). Relative intensities are given in parentheses. Samples were dissolved in $CDCl_3$ except where noted.

first, followed by the product, eluting as a bright orange band with 1:1 chloroform–hexane. After evaporation the product was purified by repeated crystallization from octane.

$Fe_2(CO)_6[P(C_6H_5)_2]H$.—This orange crystalline product, mp 122–123°, was obtained in 38% yield (0.77 g) from 1.55 g of $Fe(CO)_4[P(C_6H_5)_2H]$ (4.36 mmol), 2.07 ml of 2.11 *M* *n*-butyllithium, and 1.62 g of $Fe_2(CO)_9$ (4.45 mmol) in 200 ml of solvent. *Anal.* Calcd for $C_{18}H_{11}O_6PFe_2$: C, 46.5; H, 2.37; P, 6.68; mol wt 466. Found: C, 45.9; H, 2.67; P, 6.19; mol wt 463 (osmometric).

$Fe_2(CO)_6[P(CH_3)_2]H$.—This red-brown crystalline compound was synthesized as above from 2.15 g of $Fe(CO)_4[P(CH_3)_2H]$ (9.34 mmol), 4.43 ml of 2.11 *M* *n*-butyllithium, and 3.40 g of $Fe_2(CO)_9$ (9.34 mmol) in 150 ml of tetrahydrofuran. The product was recrystallized five times from octane with considerable loss; yield 0.56 g (17.6%); mp 70–72°. *Anal.* Calcd for $C_8H_7O_6PFe_2$: C, 28.1; H, 2.05; P, 9.06; mol wt 342. Found: C, 25.5; H, 2.59; P, 8.60; mol wt 350 (osmometric).

$Fe_2(CO)_6[P(C_2H_5)_2]H$.—This was prepared from 2.17 g of $Fe(CO)_4[P(C_2H_5)_2H]$ (8.40 mmol), 3.98 ml of 2.11 *M* *n*-butyllithium, and 3.06 g of $Fe_2(CO)_9$ (8.40 mmol) in 150 ml of tetrahydrofuran. The product was obtained as red-brown crystals; yield 0.93 g (30%); mp 58–60°. *Anal.* Calcd for $C_{12}H_{11}O_6PFe_2$: C, 32.1; H, 3.13; P, 8.15; mol wt 370. Found: C, 32.5; H, 2.97; P, 8.38; mol wt 395 (osmometric).

$Fe_2(CO)_6[P(C_6H_5)(CH_3)]H$.—Synthesis was accomplished from 4.28 g of $Fe(CO)_4[P(C_6H_5)(CH_3)H]$ (1.47 mmol), 6.95 ml of 2.11 *M* *n*-butyllithium, and 5.33 g of $Fe_2(CO)_9$ (14.8 mmol) in 200 ml of solvent. The product was red-brown crystals; 2.09 g (35%); mp 119–123°. Its nmr spectrum showed two isomers (Table I). *Anal.* Calcd for $C_{13}H_9O_6PFe_2$: C, 38.3; H, 2.53; P, 7.88; mol wt 404. Found: C, 38.6; H, 2.23; P, 7.67; mol wt 412 (osmometric).

Irradiation of $Fe(CO)_4(PR_2H)$ Complexes. $Fe(CO)_4[P(C_6H_5)_2H]$.—A sample of this compound (2.0 g, 5.64 mmol) was dissolved in 200 ml of tetrahydrofuran and irradiated with a GE H-100-PSP44-4 ultraviolet lamp for 24 hr. Solvent was then removed and the residue chromatographed on alumina. One band was observed; this was eluted by a 1:1 v/v chloroform–hexane solvent mixture. The product $Fe_2(CO)_6[P(C_6H_5)_2]_2$ was crystallized from heptane; yield 1.48 g, 81%; mp 160–161° (lit.[16] mp 163–165°).

$Fe(CO)_4[P(CH_3)_2H]$.—Using the same procedure, this complex (1.90 g, 8.26 mmol) was converted to $Fe_2(CO)_6[P(CH_3)_2]_2$, 1.15 g, 69%; mp 216–217° (lit.[6] mp 221–222°).

Reactions of CH_3PH_2 and $C_6H_5PH_2$ and Iron Carbonyls. Preparation of $Fe(CO)_4(CH_3PH_2)$.—Diiron enneacarbonyl (3.0 g, 8.25 mmol) was placed in a heavy-walled glass tube of approximately 25-ml capacity. This tube was then attached to a vacuum system and evacuated and methylphosphine (0.75 g, 15.6 mmol) was distilled into it. The tube was sealed and allowed to remain at room temperature. A slow reaction occurred with a red liquid and a blackish solid appearing after 1 day. After 3 days the tube was cooled to −196° and reopened to the vacuum system. Some noncondensable gas (not measured) was observed and on warming methylphosphine (0.27 g, 5.6 mmol) and iron pentacarbonyl (1.5 g, 7.7 mmol) distilled over quickly, the last two components passing −24° and collecting at −196 and −78°, respectively. The product $Fe(CO)_4(CH_3PH_2)$ was distilled slowly from the tube over about a 24 hr period into a −78° trap. It was purified by slow fractionation through 0, −24 (collecting the product), and −78° traps to give a total yield of 1.35 g (76% yield based on $Fe_2(CO)_9$). The product, a yellow liquid, was quite air sensitive but could be handled outside the vacuum system if care was exercised to exclude oxygen. *Anal.* Calcd for $C_5H_5FePO_4$: C, 47.8; H, 3.98; P, 14.4; mol wt 216. Found: C, 48.1; H, 3.74; P, 14.3; mol wt 216 (mass spectrometric).

The reaction tube retained black and red solids which had a resin-like appearance. These solids were insoluble in hydrocarbon solvents but soluble in acetone. Attempted chromatography showed that neither $Fe_2(CO)_6(CH_3PH)_2$ nor $Fe_3(CO)_9(PCH_3)_2$ was contained in appreciable quantity.

Conversion of $Fe(CO)_4(CH_3PH_2)$ to $Fe_2(CO)_6(CH_3PH)_2$.—A 1.30-g sample of $Fe(CO)_4(CH_3PH_2)$ (6.0 mmol) was transferred to a 250-ml reaction bulb, using the vacuum system, and sealed under vacuum. Pyrolysis at 78° for 48 hr *in vacuo* gave no reaction, with complete recovery of starting material. At 110° for 48 hr, a small amount of decomposition occurred. From 1.30 g of $Fe(CO)_4(CH_3PH_2)$, there was recovered 1.05 g of $Fe(CO)_4(CH_3PH_2)$ (81% recovery) and 0.15 g of $Fe_2(CO)_6(CH_3PH)_2$; a small amount of black solid remained. At 145° for 1 hr there occurred considerable decomposition. From 1.05 g of $Fe(CO)_4(CH_3PH_2)$, 0.50 g (48%) of this starting material was recovered, with considerable CO (~4 mmol measured roughly by volume) but only traces of the dinuclear complex.

The conversion of $Fe(CO)_4(CH_3PH_2)$ to $Fe_2(CO)_6(CH_3PH)_2$ could be accomplished photolytically. A sample of $Fe(CO)_4(CH_3PH_2)$ (0.50 g, 2.31 mmol) was sealed in a 250-cm^{-3} pyrex reaction bulb *in vacuo* and the vessel was placed in the sunlight. After about 1 week substantial decomposition had occurred to give unattractive glassy red and black solid materials. The bulb was allowed to stand about 4 weeks at which time no more starting material could be seen in the bulb.

The bulb was opened to the vacuum system and a large amount of noncondensable gas was observed. No starting material or iron carbonyl was found however. The bulb was then separated from the vacuum system and under nitrogen the gummy residues were extracted into benzene, in which they were completely soluble. This red benzene solution was evaporated and the residue was chromatographed on alumina, eluting with benzene. Only one band, yellow in color, was eluted; the red color did not move on the column and decomposed rapidly. The yellow band, on evaporation, gave the yellow crystalline compound $Fe_2(CO)_6(CH_3PH)_2$ (0.30 g, 69% yield), mp 159–165°. *Anal.* Calcd for $C_8H_8Fe_2P_2O_6$: C, 25.7; H, 2.14; P, 16.6; Fe, 30.0; mol wt 374. Found: C, 25.8; H, 2.19; P, 16.3; Fe, 30.46; mol wt 374 (mass spectrometric).

Preparation of $Fe(CO)_4(C_6H_5PH_2)$ and $Fe_2(CO)_6(C_6H_5PH)_2$.—The reaction of 7.3 g of $Fe_2(CO)_9$ (20.0 mmol) and 1.80 g of $C_6H_5PH_2$ (16.3 mmol) was attempted in a sealed tube in the same manner as previously described, except that $C_6H_5PH_2$, being quite involatile in the vacuum system, was syringed into the vessel. Approximately 0.50 g of $Fe(CO)_4(C_6H_5PH_2)$ (1.80 mmol, 11% yield) was obtained. The work-up was hampered considerably because this product was not sufficiently volatile to transfer quickly and the geometry of the tube restricted heating to accomplish the transfer; as a result partial decomposition was observed by evolution of noncondensable gas. In this process $Fe_2(CO)_6(C_6H_5PH)_2$ was formed as one product. This could be isolated on chromatography of the solid residue using alumina and eluting with benzene. The yield of this product in this run was 1.78 g (44%). A second solid product was also formed, which eluted as an orange band overlapping with this yellow band. This product was eventually isolated in sufficient quantity in a large-scale reaction to allow its tentative characterization as $Fe_3(CO)_7(PC_6H_5)_2(C_6H_5PH_2)_2$.

Satisfactory analyses for $Fe(CO)_4(C_6H_5PH_2)$ were not obtained due to the difficulty in its purification. However its identity was clearly established by infrared and nmr data (Table I).

Yellow $Fe_2(CO)_6(C_6H_5PH)_2$ could be crystallized from acetonitrile–water to give a yellow powder or from heptane (in which it was very soluble) to give yellow-orange crystals, mp 112–113°. *Anal.* Calcd for $C_{18}H_{12}Fe_2P_2O_6$: C, 43.3; H, 2.41; Fe, 22.4; P, 12.4; mol wt 498. Found: C, 43.4; H, 2.24; Fe, 22.6; P, 12.6; mol wt 498 (mass spectrometric).

Orange $Fe_3(CO)_7(PC_6H_5)_2(C_6H_5PH_2)_2$ could be crystallized from heptane at −25°; mp 175° dec. *Anal.* Calcd for $C_{31}H_{24}Fe_3P_4O_7$: C, 46.8; H, 2.98; P, 15.4; mol wt 804. Found: C, 46.9; H, 3.10; P, 15.4; mol wt 804 (mass spectrometric).

The reaction of $C_6H_5PH_2$ and $Fe_2(CO)_9$ could be run in an open flask more conveniently, and, furthermore, larger quantities could be employed. For example, 7.4 g of $Fe_2(CO)_9$ (20.8 mmol) and 2.0 g of $C_6H_5PH_2$ (18.2 mmol) were stirred in 50 ml of benzene. After about 2 days no $Fe_2(CO)_9$ was observed and the solution had a deep red color. Evaporation, followed by chromatography on alumina using heptane, gave first a pale yellow band ($Fe(CO)_5$) and then an intense yellow band. This was collected under nitrogen and evaporated to give $Fe(CO)_4(C_6H_5PH_2)$ (4.0 g (crude weight), ~80% yield). Further elution of the column using benzene gave an additional band which yielded only a trace of $Fe_2(CO)_6(C_6H_5PH)_2$, identified by its infrared spectrum.

Preparation of $Fe_3(CO)_9(PC_6H_5)_2$.—Iron pentacarbonyl (3.0 ml, 20 mmol) and phenylphosphine (1.5 ml, 14 mmol) were heated at 100° in 50 ml of decalin for 10 hr. The mixture was then raised to reflux, 189°, for 6 hr. After cooling, the solvent was removed under vacuum at 80° (0.1 mm). The residue was extracted into chloroform, which on evaporation gave a dark red solid. This was dissolved in 1:1 hexane–benzene and chromatographed on Florisil. The dark red solution was evaporated and the product was crystallized from acetone–water. The product was obtained as red crystals (1.8 g, 43%; mp 130–135°). *Anal.* Calcd for $C_{21}H_{10}Fe_3O_9P_2$: C, 39.7; H, 1.57; P, 9.75; Fe, 26.4; mol wt 636. Found: C, 41.5; H, 1.82; P, 9.70; Fe, 26.6; mol wt 636 (mass spectrometric).

Reaction of $Fe_3(CO)_9(PC_6H_5)_2$ and Trimethyl Phosphite.—Trimethyl phosphite (3.0 ml, 25.2 mmol) and $Fe_3(CO)_9(PC_6H_5)_2$

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[16] B. E. Job, R. A. N. McLean, and D. T. Thompson, *Chem. Commun.*, 895 (1966).

(3.0 g, 4.27 mmol) were refluxed in 50 ml of xylene for 5.5 hr. After cooling, the solvent and excess phosphite were evaporated under vacuum (0.1 mm). The solid residue was dissolved in 1:1 hexane–benzene and chromatographed on alumina. Three red bands developed in this chromatography.

Band A.—Elution of the first band with 1:1 hexane–benzene gave a red solution, which on evaporation left a red solid. This was recrystallized at −78° from dichloromethane–hexane to give 0.13 g of red crystals, mp 136–138°, identified as $Fe_3(CO)_8(PC_6H_5)_2P(OCH_3)_3$. *Anal.* Calcd for $C_{23}H_{19}O_{11}P_3Fe_3$: C, 37.7; H, 2.59; P, 12.7; mol wt 732. Found: C, 37.9; H, 2.68; P, 12.7; mol wt 732 (mass spectrometric).

Band B.—This band eluted with 1:1 hexane–benzene; the product was recrystallized from dichloromethane at −40° to give 0.15 g of dark red crystalline $Fe_3(CO)_7(PC_6H_5)_2[P(OCH_3)_3]_2$, which decomposed at 230° without melting. *Anal.* Calcd for $C_{22}H_{28}O_{13}P_4Fe_3$: C, 36.3; H, 2.18; P, 14.9; mol wt 828. Found: C, 36.6; H, 3.29; P, 14.8; mol wt 828 (mass spectrometric).

Band C.—The third band eluted with benzene. The product $Fe_3(CO)_6(PC_6H_5)_2[P(OCH_3)_3]_3$ was obtained at −40° from dichloromethane, as dark red crystals (0.15 g), which decomposed at 180° without melting. *Anal.* Calcd for $C_{27}H_{37}O_{15}P_5Fe_3$: C, 35.1; H, 4.00; P, 16.8; mol wt 924. Found: C, 35.3; H, 4.05; P, 17.0; mol wt 924 (mass spectrometric).

Results and Discussion

When equimolar quantities of various secondary phosphines and diiron enneacarbonyl are allowed to react, the appropriate phosphineiron tetracarbonyl may be obtained in high yield along with iron pentacarbonyl

$$\text{phos} + Fe_2(CO)_9 \longrightarrow Fe(CO)_4\text{phos} + Fe(CO)_5$$

$$(\text{phos} = (CH_3)_2PH,\ (C_2H_5)_2PH,\ (C_6H_5)_2PH,\ (p\text{-}CH_3C_6H_4)_2PH,\ C_6H_5P(CH_3)H)$$

These reactions can be run in an open system or, when the phosphines are gaseous, in a sealed tube or bomb. The products were separated from other materials present by column chromatography. Final purification was accomplished by crystallization of solids or vacuum distillation of liquids.

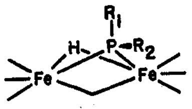
The products were yellow to gold solids or liquids. The liquids were air sensitive, but the two solids $Fe(CO)_4[P(C_6H_5)_2H]$ and $Fe(CO)_4[P(p\text{-}CH_3C_6H_4)_2H]$ were not particularly so and could be handled in air. The complexes were thermally stable at room temperature.

These reactions are not strictly analogous to the preparation of $Fe(CO)_4[P(C_6H_5)_2H]$ reported earlier,[3] in that the preparation utilized $Fe(CO)_5$ in refluxing butanol in an autoclave. In refluxing benzene $Fe_2(CO)_9$ and $P(C_6H_5)_2H$ were reported to give $Fe(CO)_3[P(C_6H_5)_2H]_2$. We did not observe any $Fe(CO)_3(PR_2H)_2$ species in the reactions run here in contrast to the cited work.[3]

A crystal structure study has established the structure of $Fe(CO)_4[P(C_6H_5)_2H]$;[17] the phosphine group is substituted on the axial position of a trigonal bipyramid. The complexes described here appear to have the same structure since the carbonyl stretching frequencies of all $Fe(CO)_4$phos complexes are all very similar.

The proton nmr spectra for the $Fe(CO)_4(PR_2H)$ complexes were straightforward showing an appropriate pattern for the alkyl or aryl protons and a widely spaced pattern for the hydrogen bonded to phosphorus ($J_{P-H} \approx 360$ Hz). These data are presented in Table I.

In each secondary phosphine–$Fe_2(CO)_9$ reaction, two additional classes of products separated on chromatography and were isolated in small yield. One of these was the expected phosphido-bridged species $Fe_2(CO)_6(PR_2)_2$, members of a class of compounds which were previously known, having been synthesized earlier from iron carbonyl and either diphosphines[6] or secondary phosphines.[4,5] The second group of compounds had the molecular formula $Fe_2(CO)_6(PR_2)H$; we characterize these compounds as having the same general geometry as $Fe_2(CO)_6(PR_2)_2$ except that a bridging hydride has replaced one of the bridging phosphido groups (I) (Figure 1).



I

Figure 1.—Structure of $Fe_2(CO)_6(PRR')H$.

The latter complexes can be prepared in better yield by an alternate route. The reaction of the appropriate complex $Fe(CO)_4[PR_2H]$ with butyllithium will metalate the phosphine,[18] and the resulting lithio complex $Fe(CO)_4[PR_2]Li$ *in situ* is a useful intermediate for further syntheses. When this complex is treated with $Fe_2(CO)_9$, stirred at 25°, and then worked up in the usual manner, the appropriate $Fe_2(CO)_6(PR_2)H$ is obtained in acceptable quantities. We expect that the formation of these complexes in the phosphine–$Fe_2(CO)_9$ reaction may occur by an analogous reaction. $Fe(CO)_4(PR_2H)$ and excess phosphine yield $Fe(CO)_4PR_2^-PR_2H_2^+$, and the anion reacts with additional $Fe_2(CO)_9$.

The reaction of $Fe(CO)_4[PR_2]Li$ and $Fe_2(CO)_9$ seems a reasonable one to lead to the observed product $Fe_2(CO)_6(PR_2)H$. The lithio complex may be considered to behave somewhat like a phosphine in its reactions; having a free lone pair it could displace $Fe(CO)_5$ from $Fe_2(CO)_9$ to give $[(CO)_4FePR_2Fe(CO)_4]Li$. This sort of reaction has been observed before.[19] The product could rearrange with carbon monoxide loss and abstract a hydrogen to give the product

$$\begin{tikzcd} Fe(CO)_4[PR_2]Li + Fe_2(CO)_9 \arrow[r] & {[(CO)_4FePR_2Fe(CO)_4]Li]} \arrow[d, "-2CO,\ +H^+"] \\ & Fe_2(CO)_6(PR_2)H \end{tikzcd}$$

The carbonyl stretching frequencies for the $Fe_2(CO)_6(PR_2)H$ complexes are not too dissimilar from those for $Fe_2(CO)_6(PR_2)_2$, as expected from the similarity in overall geometry of the two species. The bridging hydride shows up at high field in the nmr spectra, as expected, split into a doublet due to J_{P-H}. Evidence for the bent HFe_2P framework comes from the observation of two different methyl group resonances in the nmr spectrum of $Fe_2(CO)_6[P(CH_3)_2]H$ and from the existence of two isomers of $Fe_2(CO)_6[P(C_6H_5)CH_3]H$, differing with respect to the orientations of CH_3 and C_6H_5 groups.

We also observed that ultraviolet irradiation of the $Fe(CO)_4[PR_2H]$ complexes would effect their conversion to the dinuclear species $Fe_2(CO)_6(PR_2)_2$. These

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[17] B. T. Kilbourn, V. A. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969).

[18] See P. M. Treichel, W. M. Douglas, and W. K. Dean, *Inorg. Chem.*, **11**, 1615 (1972).

[19] R. J. Haines, C. R. Nolte, R. Greatrex, and N. N. Greenwood, *J. Organometal. Chem.*, **26**, C45 (1971).

reactions are clean and proceed in high yield to the desired products.

The primary phosphines CH_3PH_2 and $C_6H_5PH_2$ and diiron enneacarbonyl react similarly to give $Fe(CO)_4[CH_3PH_2]$ and $Fe(CO)_4[C_6H_5PH_2]$ along with iron pentacarbonyl. Traces of the dinuclear complexes $Fe_2(CO)_6(PRH)_2$ are also obtained. Both methyl- and phenylphosphineiron tetracarbonyls are volatile, very air-sensitive golden liquids. The methylphosphine complex is sufficiently volatile to allow it to be easily handled in a conventional vacuum system, but the less volatile phenylphosphine complex cannot be handled in this manner. This product could be vacuum distilled at about 70°, but decomposition occurred with concurrent lower yield, giving also $Fe_2(CO)_6(C_6H_5PH)_2$ and glassy red-black solids.

Both primary phosphineiron carbonyl complexes are thermally stable at room temperature. The methylphosphine complex was stable under vacuum at 80° but decomposed very slowly at 110° and underwent appreciable decomposition at 145°. The decomposition reaction was complex and although the expected dinuclear compound $Fe_2(CO)_6(CH_3PH)_2$ was formed, the usual glassy red-black solids were also observed. As noted earlier, $Fe(CO)_4[C_6H_5PH_2]$ partially decomposed on distillation at 80°. There were two isolable products—$Fe_2(CO)_6(C_6H_5PH)_2$ and traces of an orange compound tentatively characterized as $Fe_3(CO)_7(PC_6H_5)_2[C_6H_5PH_2]_2$.

A higher temperature both the mononuclear and dinuclear complexes are products of these phosphine–iron carbonyl reactions with the yield of the latter product increasing at higher temperature. With phenylphosphine, the dinuclear species can be obtained as the primary product, mostly free from $Fe(CO)_4(C_6H_5PH_2)$, at temperatures around 140°. The complex $Fe_3(CO)_9(PC_6H_5)_2$ was seen in these reactions when the temperature exceeded 140°; it was the predominant product at 190°. This compound is predicted to have the same framework geometry (*i.e.*, Fe_3X_2, $X = PC_6H_5$) as other known $Fe_3(CO)_9X_2$ species for which structural data are available, including $Fe_3(CO)_9S_2$,[20] $Fe_3(CO)_9Se_2$,[21] $Fe_3(CO)_9(NCH_3)_2$,[22] and $Fe_3(CO)_9[NN{=}C(C_6H_5)_2]_2$;[23] preliminary crystallographic data now confirm this.[24]

The red-black glassy solids were characteristic of most reactions of primary phosphines and of primary phosphine–iron carbonyl complexes. The amount of this material is usually small, since the yields of isolated products are generally good. We suspect that these intractable materials arise by reduction of the iron carbonyl or of a complex of iron carbonyl by the phosphine. If this is so, the lack of such reactions with secondary phosphines is not surprising since these reagents are poorer reducing agents. More work has yet to be done on this problem.

Infrared data on $Fe(CO)_4(C_6H_5PH_2)$ and $Fe(CO)_4(CH_3PH_2)$ confirm that their structures are identical with those of the other $Fe(CO)_4$phos complexes reported here. The proton nmr of these complexes is also straightforward. For the former compound, a phenyl ring proton multiplet and a doublet for the PH_2 group ($J_{P-H_2} = 364$ Hz) are observed. The spectrum of $Fe(CO)_4(CH_3PH_2)$, run at 100 MHz, showed the methyl group resonance as two overlapping triplets ($J_{P-CH_3} = 12$ Hz, $J_{H_2-PCH_3} = 6.2$ Hz) and the PH_2 resonance as two widely spaced quartets ($J_{P-H_2} = 364$ Hz, $J_{CH_3-PH_2} = 6.2$ Hz). Interestingly, at 60 MHz, the upfield half of the PH_2 resonance accidently coincided with the downfield half of the methyl resonance giving a complex unrefinable pattern.

The framework geometries of $Fe_2(CO)_6(RPH)_2$ and $Fe_2(CO)_6(PR_2)_2$ should be identical and also similar to that of $Fe_2(CO)_6(SR)_2$[25] in that the Fe_2A_2 unit is not planar. Indeed there exists a strong similarity in the ν_{CO} infrared absorptions in all these compounds. In each complex four major ν_{CO} peaks are observed; in the case of $Fe_2(CO)_6(RPH)_2$ complexes these occur at 2060, 2020, 1990, and 1970 cm^{-1}.

For the $Fe_2(CO)_6(RPH)_2$ complexes three isomers are possible, a result of the different orientations that R and H can assume (Figure 2). Two of these isomers have C_{2v} symmetry; the other has C_s symmetry. We had hoped to observe the existence of isomers and possibly to separate them. However the problem proved rather more complex than was expected.

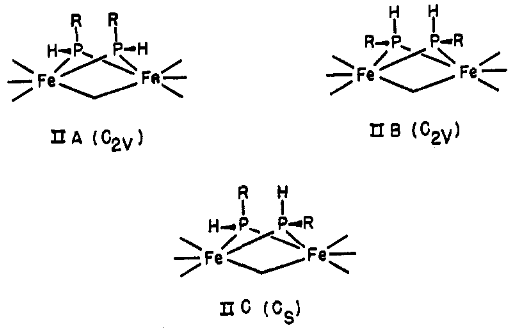

Figure 2.—The three possible isomeric structures for $Fe_2(CO)_6(RPH)_2$.

As far as could be determined there was only one isomer of $Fe_2(CO)_6(C_6H_5PH)_2$ present. The infrared spectrum gave no evidence of isomers, and in the proton nmr the phenyl ring proton absorption occurred as a broad symmetrical singlet, quite untypical for this group. (In both isomers of $Fe_2(CO)_6(C_6H_5PCH_3)_2$, for example, the phenyl resonance is distinctly a narrow multiplet pattern.) Somewhat more puzzling, however, was the lack of a resonance for the hydrogen bonded to phosphorus. The same observation was made using $Fe_2(CO)_6(CH_3PH)_2$. This phenomenon has not yet been satisfactorily explained. The possibility that these protons are undergoing rapid exchange with traces of water is precluded by the observation that $Fe_2(CO)_6(C_6H_5PH)_2$ fails to undergo isotopic exchange with deuterium oxide. In view of the straightforward nmr spectra for the $Fe(CO)_4$phos complexes, this observation merits further study.

There was clear evidence for the existence of two isomers for $Fe_2(CO)_6(CH_3PH)_2$. The nmr spectrum (CH_3 protons) of crude samples showed a primary

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(20) W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, **296**, 91 (1958); C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 493 (1965).

(21) L. F. Dahl and P. W. Sutton, *ibid.*, **2**, 1067 (1963).

(22) R. J. Doedens, *ibid.*, **8**, 570 (1969).

(23) P. R. Baikie and O. S. Mills, *Chem. Commun.*, 1228 (1967).

(24) L. F. Dahl and J. J. Huntsman, submitted for publication.

(25) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963).

pattern of eight lines and a secondary pattern of two distinct multiplets. The former could be obtained free of the second isomer on crystallization using heptane. The pure isomer of $Fe_2(CO)_6(CH_3PH)_2$ has no P–H resonance in the nmr, and it has one type of methyl group; hence it must be one of the C_{2v} isomers. The explanation of the eight-line pattern from this latter resonance is unclear.

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Deprotonation and Subsequent Alkylation of Phosphine–Metal Carbonyl Complexes

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Deprotonations of several (secondary phosphine)metal carbonyls ($CH_3C_5H_4Mn(CO)_2L$, $Cr(CO)_5L$, $Mo(CO)_5L$, $W(CO)_5L$, $Mo(CO)_4L_2$, $Fe(CO)_4L$ ($L = P(C_6H_5)_2H$); $Fe(CO)_4P(C_6H_5)(CH_3)H$) with *n*-butyllithium have been carried out; the resulting lithio compounds react *in situ* with methyl iodide to yield appropriate methylphenylphosphinemetal complexes. The complex $Fe_2(CO)_6(C_6H_5PH)_2$ also deprotonates under the same conditions to give a dilithio species, which reacts as expected with methyl iodide and 1,3-dibromopropane.

Introduction

We have described reactions of several primary and secondary phosphines with carbonyls of iron[2] and of other metals.[3] A number of complexes were prepared in these studies, including simple products of substitution of a phosphine for a carbonyl. As a major part of this study we hoped to investigate the reactivity accorded such species through the presence of the P–H bond in the complex.

One particular reaction appeared rather promising. We reasoned that since hydrogen in the free ligand was reasonably acidic, it should retain this acid character when complexed to a metal; presumably with an appropriate base the proton could be removed. The data presented here indicate that this is so.

In one previous instance, an analogous deprotonation reaction sequence was carried out. Stone and coworkers,[4] investigating various pentafluorophenylphosphinemetal complexes, prepared $Cr(CO)_5[P(C_6F_5)_2H]$ and the molybdenum analog of this complex. Addition of *n*-butyllithium gave the isolable species $M(CO)_5[P(C_6F_5)_2]Li$ ($M = Cr, Mo$). Reactions with hydrogen chloride in dichloromethane, with methyl iodide, and with $(C_6F_5)_2PCl$ gave only small quantities of the expected products, however, and these authors felt that this was not a synthetic method of any particular promise so the studies were not extended further.

Experimental Section

The preparations of $Cr(CO)_5[P(C_6H_5)_2H]$, $Mo(CO)_5[P(C_6H_5)_2H]$, $W(CO)_5[P(C_6H_5)_2H]$, and $Mo(CO)_4[P(C_6H_5)_2H]_2$ are described in the literature.[5] We described the preparations of $Fe(CO)_4[P(C_6H_5)_2H]$,[2] $Fe(CO)_4[P(C_6H_5)(CH_3)H]$,[2] $Fe_2(CO)_6(C_6H_5PH)_2$,[2] and $CH_3C_5H_4Mn(CO)_2[P(C_6H_5)_2H]$[2] earlier. *n*-Butyllithium was a commercial sample and was standardized by established methods.[6] Other reagents were commercial samples.

All reactions were carried out under a nitrogen atmosphere.

Infrared spectra were obtained on a Beckman IR-10 spectrometer; nmr data were obtained on Varian A-60A and T-60 instruments. These data are presented in Table III.

Deprotonation and Alkylation of Secondary Phosphine–Metal Carbonyl Complexes. General Procedure.—The indicated quantity of the phosphine–metal complex was dissolved in 50 ml of tetrahydrofuran at room temperature and deprotonated using an equimolar quantity of standardized *n*-butyllithium in hexane. After *ca.* 10 min, a large excess (5 ml) of methyl iodide was added. Stirring was continued for 30 min; then the solvent was removed and the residue extracted with 1:1 hexane–chloroform. The resulting solution was chromatographed on alumina using the same solvent mixture. In each case one band eluted. The residue left on evaporation of the solvent was recrystallized from heptane.

Data for these reactions and for the products obtained are given in Table I. Routine infrared and nmr data on the products of these reactions are recorded in Table III.

Infrared Study on the Deprotonation Reactions.—A sample of the starting material was dissolved in tetrahydrofuran and the infrared spectrum (ν_{CO}) recorded under high resolution. The equivalent amount of standard butyllithium was added and the spectrum of the lithium complex recorded. Data are given below (Table II).

It might be noted that addition of chloroform to this solution apparently destroyed the lithio complex almost instantly. The bands appropriate to this complex were lost, and new ν_{CO} bands were observed. The latter did not appear to correspond with the starting material, $M(CO)_x(PR_2H)$. Extensive decomposition was noted visually. This reaction is under study at this time.

Proton-Exchange Reactions as an Indication of Acid Strengths.—(1) A sample of $P(C_6H_5)_2H$ (0.383 g, 206 mmol) in 100 ml of tetrahydrofuran was deprotonated with 1.53 ml of 1.355 *M* *n*-butyllithium. Then 0.7265 g of $Fe(CO)_4[P(C_6H_5)_2H]$ (2.06 mmol) was added. The infrared spectrum showed peaks at 2000 and 1893 cm^{-1}, indicating that only $Fe(CO)_4[P(C_6H_5)_2]Li$ was present.

(2) A 0.7309-g sample of $Fe(CO)_4[P(C_6H_5)_2H]$ (2.06 mmol) in 100 ml of tetrahydrofuran was deprotonated with 1.52 ml of 1.355 *M* *n*-butyllithium. Then 0.383 g (2.06 mmol) of $P(C_6H_5)_2H$ was added. An infrared spectrum showed peaks at 2000 and 1893 cm^{-1}, characteristic of $Fe(CO)_4[P(C_6H_5)_2]Li$.

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