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REACTIONS OF METAL CARBONYL DERIVATIVES
II*. DITERTIARY PHOSPHINE AND ARSINE DERIVATIVES OF TETRACARBONYLDI-π-CYCLOPENTADIENYLDIIRON**,***

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SUMMARY

The ditertiary phosphine and arsine ligands $L=(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n=1, 2, 3$), *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$, $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ and $(C_6H_5)_2As(CH)_{2n}As(C_6H_5)_2$ ($n=1, 2$) have been shown to react with tetracarbonyldi-π-cyclopentadienyldiiron in benzene when the solution is refluxed or irradiated with ultraviolet light at room temperature to afford derivatives of the type $[\pi\text{-}C_5H_5Fe(CO)]_2L$. Analogous products are similarly obtained from the reactions of $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n=1, 2$), *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ with $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$. On the basis of infrared spectroscopic evidence it is shown that the two terminal carbonyl groups in $[\pi\text{-}RC_5H_4Fe(CO)_2]_2$ ($R=H, CH_3$) have been replaced by these donor ligands and a structure for the new products is proposed. The infrared and nuclear magnetic resonance spectra are discussed.

INTRODUCTION

Although the substitution reactions of metal carbonyl derivatives have been extensively studied, interest has been directed towards those involving mononuclear carbonyls. Reactions of neutral dinuclear carbonyl compounds with in particular ditertiary phosphine and arsine ligands have received much less attention[1]. Derivatives in which the "diphosphine" or "diarsine" ligand behaves as a monodentate have been isolated from these latter reactions. However, for the majority of products obtained from the dinuclear carbonyls the ligand acts as a bidentate and these products may

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* For Part 1 see ref. 13.

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in general be classified into four types, *viz.*:

(*i*) neutral dinuclear
(*ii*) neutral mononuclear
(*iii*) ionic
(*iv*) bridged polynuclear compounds.

Replacement of carbonyl groups bonded to the same metal atom by the chelating ligand leads to products of type (*i*). These compounds are symmetric or asymmetric depending on the degree of substitution. Pertinent examples of this type include $\mathrm{(CO)_3Fe(MR_x)_2Fe(CO)Diphos}$* [$\mathrm{M{=}P}$, $\mathrm{R{=}CH_3}$, $x=2$ (ref. 2); $\mathrm{M{=}S}$, $\mathrm{R{=}C_2H_5}$, $\mathrm{C_6H_5}$, $x=1$ (ref. 3)], $\mathrm{(CO)_4Mo[P(CH_3)_2]_2Mo(CO)_2Diphos}$[2,4], $\mathrm{(CO)_4Mn(SeC_6H_5)_2Mn(CO)_2Diphos}$[5] and $\mathrm{[Re(CO)_3Diphos]_2}$[6] obtained from the reaction of $\mathrm{(C_6H_5)_2PC_2H_4P(C_6H_5)_2}$ with $\mathrm{[Fe(CO)_3MR_x]_2}$, $\mathrm{[Mo(CO)_4P(CH_3)_2]_2}$, $\mathrm{[Mn(CO)_4SeC_6H_5]_2}$ and $\mathrm{Re_2(CO)_{10}}$ respectively. The second type of product is formed as a result of symmetric cleavage of the metal–metal bond in the parent compound on substitution of the carbonyl groups by the ligand. The paramagnetic compounds $\mathrm{Re(CO)_3Diphos}$, $\mathrm{Re(CO)_2Diphos_2}$, $\mathrm{Re(CO)Diphos_2}$[6], $\mathrm{Mn(CO)_3Diphos}$, $\mathrm{Mn(CO)Diphos_2}$[7] and $\mathrm{Mn(CO)_3Diars}$[8,]**, isolated from the reactions of $\mathrm{Re_2(CO)_{10}}$ and $\mathrm{Mn_2(CO)_{10}}$ with the appropriate ligand, fall into this category. Several dinuclear carbonyl compounds have been shown to disproportionate on reaction with ditertiary phosphine ligands and to afford ionic derivatives consisting of a substituted cation and an unsubstituted anion [type (*iii*) product]. For instance it has been established that the reactions of $[\pi\text{-}\mathrm{C_5H_5Fe(CO)_2]_2}$ with $\mathrm{(CH_3)_2PC_2H_4P(CH_3)_2}$[9] and $[\pi\text{-}\mathrm{C_5H_5Mo(CO)_3]_2}$ with $\mathrm{R_2PC_2H_nPR_2}$ [$\mathrm{R{=}CH_3}$, $n=4$ (ref. 9); $\mathrm{R{=}C_6H_5}$, $n=2$ (ref. 9), 4 (ref. 9, 10)] yield $[\pi\text{-}\mathrm{C_5H_5Fe(CO)(CH_3)_2PC_2H_4P(CH_3)_2}][\pi\text{-}\mathrm{C_5H_5Fe(CO)_2}]$ and $[\pi\text{-}\mathrm{C_5H_5Mo(CO)_2R_2PC_2H_nPR_2}][\pi\text{-}\mathrm{C_5H_5Mo(CO)_3}]$ respectively. Products in which the ligand bridges two molecules have also been isolated from the reactions of several dinuclear carbonyls with ditertiary phosphines. These type (*iv*) compounds are formed as a result of the substitution of carbonyl groups on different metal atoms in different molecules by the ligand. The compounds $\{\mathrm{Fe_2(CO)_5[P(CH_3)_2]_2}\}_2\mathrm{(C_6H_5)_2PC_2H_4P(C_6H_5)_2}$[2], $\{\mathrm{[Mo(CO)_3P(CH_3)_2]_2(C_6H_5)_2PC_4H_8P(C_6H_5)_2}\}_m$ ($m \geqslant 2$)[4] and $\{\mathrm{Co_2(CO)_4[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_3}\}\mathrm{[Co(CO)_4]_2}$[7] obtained respectively from the reactions of $\mathrm{[Fe(CO)_3P(CH_3)_2]_2}$, $\mathrm{[Mo(CO)_4P(CH_3)_2]_2}$ and $\mathrm{Co_2(CO)_8}$ with $\mathrm{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2}$ ($n=2$ or 4), may be classified as this type.

As an extension to our studies on the chemical reactivity of $[\pi\text{-}\mathrm{C_5H_5Fe(CO)_2]_2}$ we have studied its reactions, together with those of $[\pi\text{-}\mathrm{CH_3C_5H_4Fe(CO)_2]_2}$ with various ditertiary phosphine and arsine ligands and have obtained a new type product.

RESULTS AND DISCUSSION

A previous study has shown that under extreme conditions *i.e.* at temperatures greater than 160°, $\mathrm{(C_6H_5)_2PC_2H_4P(C_6H_5)_2}$ reacts with $[\pi\text{-}\mathrm{C_5H_5Fe(CO)_2]_2}$ to replace the cyclopentadienyl group and to afford $\mathrm{Fe(CO)_3(C_6H_5)_2PC_2H_4P(C_6H_5)_2}$ in low yield[11]. It is now established that under milder conditions carbonyl and not cyclopentadienyl substitution is effected by $\mathrm{(C_6H_5)_2PC_2H_4P(C_6H_5)_2}$ and related ligands. In particular it was noted that by refluxing benzene solutions of $[\pi\text{-}\mathrm{C_5H_5Fe(CO)_2]_2}$

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* Diphos=$\mathrm{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2}$.

** Diars=$o\text{-}\mathrm{C_6H_4[As(CH_3)_2]_2}$.

and the ditertiary phosphines L = $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 1, 2, 3), *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ or by irradiating solutions of these reagents with ultraviolet light at room temperature, products of the type $[\pi\text{-}C_5H_5Fe(CO)]_2L$ are obtained. Analogous derivatives containing the ditertiary arsine ligands $(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$ (n = 1, 2) were also isolated but these could only be synthesised photochemically. Further it was observed that similar products could be obtained by reacting $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ with the ligands $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 1, 2), *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ in refluxing benzene. These latter reactions are considerably slower than those involving $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ however.

These substituted derivatives of $[\pi\text{-}RC_5H_4Fe(CO)_2]_2$ (R = H, CH_3) are soluble in benzene and dichloromethane but insoluble or very slightly soluble in acetone, ethanol, cyclohexane and petroleum ether. Apart from $[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$ (n = 1, 2) they are stable in solution under an atmosphere of nitrogen but not air. The two "diarsine" derivatives are particularly unstable in solution at higher temperatures and this would explain the inability to obtain products from the reactions of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ with the two "diarsine" ligands in benzene under reflux conditions or to isolate $[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$ in pure form. All of the derivatives which were isolated pure were found to be air stable in the crystalline state.

The chemical composition of the new compounds was established by elemental analysis and from a comparison of the integrated intensities of the cyclopentadienyl and ligand proton peaks in the NMR spectra. The compounds are diamagnetic as demonstrated by the sharpness of the NMR spectral peaks while conductance measurements show them to be neutral. Powder X-ray diffraction studies on $[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 1, 2, 3) indicate them to be isomorphous.

The infrared spectra of the compounds of the type $[\pi\text{-}RC_5H_4Fe(CO)]_2L^\star$ (R = H, CH_3) contain bands in the C–O stretching region corresponding to bridging carbonyls only; there are no peaks that can be associated with terminal carbonyls. Further a single cyclopentadienyl proton resonance is observed in the NMR spectra of the substituted derivatives of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. Based on the spectroscopic evidence and the physical data presented above it is evident that the ditertiary phosphine and arsine ligands replace the two terminal carbonyl groups in $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and afford a novel type of product in which the ligand is bonded to two different metal atoms of the parent molecule. The structure proposed for these type of compounds is represented in the figure; the cyclopentadienyl groups must necessarily assume "*cis*" positions because of the stereochemistry of the ligand. A similar type structure is also proposed for the bis-substituted derivatives of $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$. The NMR spectra of these compounds $[\pi\text{-}CH_3C_5H_4Fe(CO)]_2L$ are anomalous but are nevertheless consistent with the major isomers in solution existing in this form. These spectra will be discussed later in the text. An alternative structure involving the tetranuclear species $[\pi\text{-}RC_5H_4Fe(CO)]_4L_2$ in which the two ligands bridge the two $[\pi\text{-}RC_5H_4Fe(CO)]_2$ moieties was eliminated from consideration of the molecular weight measurements. Interestingly this type of structure has been observed for $[Mo(CO)_3P(CH_3)_2]_4[(C_6H_5)_2PC_4H_8P(C_6H_5)_2]_2$[4].

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* L = ditertiary phosphine or arsine ligand.

TABLE I

CONDUCTIVITY, ANALYTICAL DATA AND MOLECULAR WEIGHTS

Compound[a]	Conductivity[b] (Ohm^{-1}·cm^2·mole^{-1})	Analyses (%)								Mol. wt.[c]	
		Found				Calcd.				Found	Calcd.
		C	H	Fe	P	C	H	Fe	P		
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PCH_2P(C_6H_5)_2$	2.0	65.0	4.8		9.3	65.1	4.7		9.1	681	682
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	3.0	65.7	5.0		9.1	65.6	4.9		8.9	700	696
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PC_3H_6P(C_6H_5)_2$	1.5	65.8	5.2		8.8	65.9	5.1		8.7		
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2$	10.7	65.9	4.7	15.9		65.7	4.7	16.1		687	694
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	10.5	64.2	4.9	15.6		64.2	5.0	15.7		673	711
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2AsCH_2As(C_6H_5)_2$	12.4			14.2				14.5		703	770
$[\pi\text{-}CH_3C_5H_4Fe(CO)]_2(C_6H_5)_2PCH_2P(C_6H_5)_2$	7.1	65.7	5.2	15.7	8.6	65.9	5.1	15.7	8.7	687	710
$[\pi\text{-}CH_3C_5H_4Fe(CO)]_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	2.3	66.1	5.5	15.2	8.4	66.3	5.3	15.4	8.6	763	724
$[\pi\text{-}CH_3C_5H_4Fe(CO)]_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	11.1	64.8	5.4	15.4	8.2	65.0	5.3	15.1	8.4	698	739

[a] All compounds are green and diamagnetic; decomposition temperatures are poorly defined. [b] 1–10× 10^{-4} *M* solutions in acetone. [c] Measured in benzene.

Crystallographic studies have shown that the two iron atoms and the two bridging carbonyl groups in $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ are coplanar[12]. Assuming that a similar coplanarity exists for these groups in $[\pi\text{-}RC_5H_4Fe(CO)]_2L$ ($R = H, CH_3$) and further that the ditertiary phosphine and arsine ligands as well as the cyclopentadienyl rings may be treated as point groups, compounds of the type $[\pi\text{-}RC_5H_4Fe(CO)]_2L$ with structure as shown in the figure will belong to the point group C_{2v}.

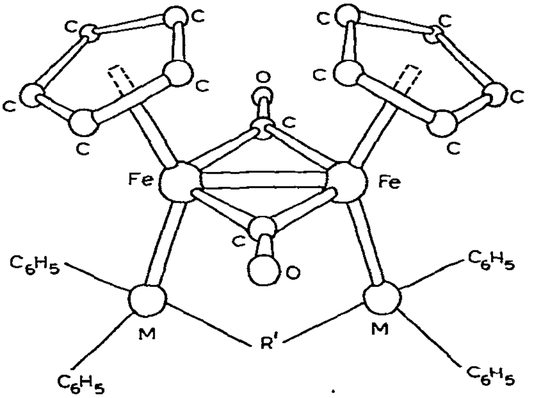
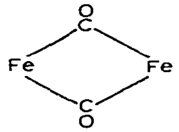


Fig. 1. Proposed structure for the compounds of the type $[\pi\text{-}RC_5H_4Fe(CO)]_2(C_6H_5)_2MR'M(C_6H_5)_2$ ($R = H, CH_3$; $M = P, As$) showing the stereochemistry of the iron atoms only.

Two infrared-active bridging carbonyl stretching modes ($A_1 + B_1$) are predicted for this point group. The A_1 mode will be expected to be of zero intensity for a structure containing planar carbonyl groups, however. The infrared spectra of the derivatives $[\pi\text{-}RC_5H_4Fe(CO)]_2L$ in solution exhibit two peaks in the bridging carbonyl region but the peak at higher frequency is extremely weak compared with the low energy band. It is thus apparent that in solution these bis-substituted compounds contain the group



in a planar or very near planar configuration. The intensity of the A_1 mode is considerably enhanced in the solid state spectra of these derivatives, however. This is particularly true of the products $[\pi\text{-}C_5H_5Fe(CO)]_2L$ where $L = (C_6H_5)_2PCH_2P(C_6H_5)_2$, $(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2AsCH_2As(C_6H_5)_2$. The relative intensities of the A_1 and B_1 modes vary considerably with change in ligand and it is thus suggested that the activation of the A_1 mode results from a deviation of the carbonyl groups from planarity.

The formation of the bis-substituted derivatives is expected to occur through intermediates in which only one carbonyl group in $[\pi\text{-}RC_5H_4Fe(CO)_2]_2$ ($R = H, CH_3$) has been replaced by the ditertiary phosphine or arsine ligands. By monitoring the reactions of $[\pi\text{-}RC_5H_4Fe(CO)_2]_2$ with the various chelating ligands by means of infrared spectroscopy it was observed that intermediate products were formed

TABLE 2

INFRARED SPECTROSCOPIC DATA

Compound	ν(C–O)^a (cm^{-1})	Other peaks (cm^{-1})^{a,d}
[π-$C_5H_5Fe(CO)_2$]$_2$	2005 (m), 1961 (s), 1793 (s)^b	
[π-$C_5H_5Fe(CO)$]$_2$- $(C_6H_5)_2PCH_2P(C_6H_5)_2$	1734 (vw), 1690 (s)^b 1722 (vw), 1677 (s)^c	3067 (w), 3052 (w), 2950 (w), 1481 (w), 1431 (s), 1417 (w), 1371 (w), 1361 (w), 1355 (w), 1308 (w), 1183 (w), 1157 (w), 1112 (w), 1093 (m), 1070 (w), 1027 (w), 1009 (w), 998 (w), 903 (w), 836 (w), 818 (m), 773 (w), 738 (s), 713 (m), 692 (s), 661 (vs), 614 (w), 581 (m), 525 (s), 498 (m), 485 (w), 465 (w), 440 (w), 422 (w)
[π-$C_5H_5Fe(CO)$]$_2$- $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	1730 (vw), 1693 (s)^b 1719 (vw), 1678 (s)^c	3067 (w), 3047 (w), 2993 (w), 2904 (w), 1478 (w), 1429 (m), 1412 (w), 1352 (w), 1302 (w), 1178 (w), 1110 (w), 1089 (m), 1064 (w), 1011 (w), 1007 (w), 994 (w), 900 (w), 841 (w), 831 (w), 812 (m), 800 (w), 742 (m), 691 (vs), 671 (vs), 644 (s), 611 (w), 584 (w), 573 (m), 549 (w), 519 (s), 500 (w), 486 (w), 459 (w), 432 (m)
[π-$C_5H_5Fe(CO)$]$_2$- $(C_6H_5)_2PC_3H_6P(C_6H_5)_2$	1725 (vw), 1687 (s)^b	3070 (w), 3050 (w), 2921 (m), 2905 (w), 2846 (w), 1480 (w), 1448 (w), 1433 (s), 1420 (w), 1359 (w), 1331 (w), 1310 (w), 1275 (w), 1182 (w), 1156 (w), 1129 (w), 1119 (w), 1092 (m), 1069 (w), 1038 (m), 1012 (w), 998 (w), 970 (w), 948 (w), 910 (w), 844 (w), 834 (w), 818 (m), 802 (w), 743 (s), 696 (s), 660 (vs), 636 (w), 617 (w) , 579 (m), 507 (s), 452 (w), 428 (w)
[π-$C_5H_5Fe(CO)$]$_2$- $(C_6H_5)_2PC_2H_2P(C_6H_5)_2$	1705 (s)^b 1733 (vw), 1691 (s)^c	3064 (w), 3048 (w), 2970 (w), 1479 (w), 1430 (m), 1354 (w), 1306 (w), 1180 (w), 1154 (w), 1112 (w), 1089 (m), 1067 (w), 1024 (w), 1010 (w), 997 (w), 907 (w), 833 (w), 814 (m), 800 (w), 743 (m), 716 (w), 693 (s),648 (vs), 616 (w), 588 (w), 563 (s), 512 (m), 506 (w), 488 (w), 432 (w), 421 (w)
[π-$C_5H_5Fe(CO)$]$_2$- $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	1732 (vw), 1687 (s)^c	3090 (w), 3048 (w), 2984 (w), 2962 (w), 2923 (w), 2862 (w), 1479 (w), 1430 (m), 1376 (w), 1353 (w), 1310 (w), 1184 (w), 1151 (w), 1090 (m),1058 (m), 1006 (w), 998 (w), 923 (w), 878 (m), 834 (w), 812 (m), 758 (m), 745 (w), 696 (vs), 670 (s), 629 (s), 611 (w), 590 (w), 578 (w), 560 (w), 539 (s), 513 (m), 504 (w), 470 (w), 446 (w)
[π-$C_5H_5Fe(CO)$]$_2$- $(C_6H_5)_2AsCH_2As(C_6H_5)_2$	1719 (vw), 1675 (s)^c	3060 (w), 3040 (w), 2990 (w), 1478 (w), 1430 (m), 1336 (w), 1300 (w), 1179 (w), 1108 (w), 1073 (w), 1052 (w), 1020 (w), 1004 (w), 994 (w), 830 (w), 811 (w), 731 (m), 690 (s), 665 (vs), 587 (w), 578 (m), 466 (w), 456 (w), 370 (w), 328 (w), 311 (w)

[π-$C_5H_5Fe(CO)]_2$- $(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$	1675 (s)[c]	
[π-$CH_3C_5H_4Fe(CO)]_2$- $(C_6H_5)_2PCH_2P(C_6H_5)_2$	1728 (w), 1685 (s)[b] 1717 (w), 1672 (s)[c]	3070 (w), 3050 (w), 2958 (w), 1431 (m), 1368 (w), 1305 (w), 1180 (w),1153 (w), 1115 (w), 1091 (m), 1024 (w), 1015 (w), 997 (w), 924 (w), 804 (w), 770 (w), 738 (s), 712 (w), 692 (m), 660 (vs), 628 (w), 614 (vw),581 (m), 527 (m), 498 (w), 438 (w)
[π-$CH_3C_5H_4Fe(CO)]_2$- $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	1718 (vw), 1676 (s)[c]	3090 (w), 3072 (w), 3046 (w), 2908 (w), 1481 (w), 1431 (m), 1414 (w), 1371 (w), 1308 (w), 1265 (w), 1182 (w), 1093 (m), 1069 (w), 1027 (w), 998 (w), 928 (w), 847 (w), 808 (w), 746 (m), 693 (vs), 674 (vs), 648 (s),629 (w), 616 (w), 578 (m), 552 (s), 522 (s), 518 (w), 492 (w), 466 (w), 438 (w), 362 (w)
[π-$CH_3C_5H_4Fe(CO)]_2$- $(C_6H_5)_2PC_2H_2P(C_6H_5)_2$	1734 (w), 1700 (s)[b] 1723 (w), 1687 (s)[c]	
[π-$CH_3C_5H_4Fe(CO)]_2$- $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	1683 (s)[c]	3070 (w), 3048 (w), 2975 (w), 2915 (w), 1478 (w), 1429 (m), 1372 (w), 1309 (w), 1180 (w), 1150 (w), 1089 (m), 1058 (m), 1022 (w), 923 (m), 877 (s), 804 (m), 758 (m), 743 (w), 695 (vs), 688 (s), 628 (s), 611 (w), 600 (w) 590 (w), 577 (w), 558 (w), 538 (s), 511 (m), 470 (w), 444 (w), 367 (w)

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[a] w=weak, m=medium, s=strong, vs=very strong. [b] Measured in cyclohexane. [c] Measured in carbon tetrachloride. [d] Measured in KBr discs.

whose C–O stretching peaks decreased in intensity with the formation of [π-RC_5H_4-$Fe(CO)]_2L$. As shown in Table 3 the frequencies of these bands correspond with those of compounds of the type (π-$C_5H_5)_2Fe_2(CO)_3L$ (L = tertiary phosphine) containing one terminal and two bridging carbonyl groups. This suggests that the formation of [π-$RC_5H_4Fe(CO)]_2L$ occurs by stepwise loss of the terminal carbonyl groups in [π-$RC_5H_4Fe(CO)_2]_2$. Attempts to isolate the "mono-substituted" intermediates proved unsuccessful, however. Irrespective of the ligand to parent carbonyl ratio and the reaction time an appreciable quantity of the bis-substituted compound was always formed and attempts to separate the two derivatives chromatographically resulted in decomposition of the "mono-substituted" compound on the column.

The reactions of [π-$RC_5H_4Fe(CO)_2]_2$ (R = H, CH_3) with the various ditertiary phosphine and arsine ligands were observed to afford further products which were readily separated from those discussed above by methanol extraction. The yield of these yellow derivatives was found to depend on the ligand involved and the mode of reaction. Thus while a benzene solution of [π-$CH_3C_5H_4Fe(CO)_2]_2$ and $(C_6H_5)_2$-$PN(C_2H_5)P(C_6H_5)_2$ exposed to ultraviolet light for 17 h yielded these compounds as the sole products, there was no evidence for their formation in the reaction of [π-$CH_3C_5H_4Fe(CO)_2]_2$ with $(C_6H_5)_2PCH_2P(C_6H_5)_2$ in refluxing benzene. The infrared spectra of the mixtures obtained from the methanol extraction contain two peaks in the terminal carbonyl stretching region of variable relative intensity at approximately 1950 and 1910 cm^{-1}. These do not correspond with any of those for the known $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ derivatives of iron carbonyl. The difficulty in obtaining these compounds in pure form has thus far prevented their characterisation.

In a previous study[13] it was shown that replacement of a single terminal carbonyl group in [π-$C_5H_5Fe(CO)_2]_2$ by tertiary phosphine or phosphite ligands resulted in a lowering of the frequency of the bridging carbonyl stretching band of the order 50 cm^{-1}. It is now observed as shown in Table 2 that substitution of both terminal carbonyl groups in the above parent compound by ditertiary phosphine or arsine ligands effects a considerably larger decrease in this frequency. The decrease in the frequency of terminal and ketonic carbonyl stretching modes in metal carbonyl derivatives as a result of carbonyl replacement by phosphorus and arsenic donor ligands has been explained in terms of an increase in π-bonding between the metal atom and the remaining carbonyl groups. These ligands with overall stronger (σ–π) donor ability than carbon monoxide effect an increase in the electron density on the metal atom. This is redistributed into the anti-bonding orbitals of the carbonyl groups thereby decreasing the C–O bond order[14]. Based on the results presented above, it is now suggested that a similar π-bonding mechanism operates between metal atoms and bridging carbonyl groups in metal carbonyl derivatives *i.e.* there is an effective π-overlap between metal d_π orbitals and C–O π-antibonding orbitals.

As shown in Table 4, the NMR spectra of the bis-substituted compounds [π-$C_5H_5Fe(CO)]_2(C_6H_5)_2PR'P(C_6H_5)_2$ [R' = CH_2, C_2H_4, C_3H_6, C_2H_2 and N-(C_2H_5)] contain a single cyclopentadienyl proton resonance which is between τ 0.46 and 0.71 ppm to high field of the corresponding peak in the spectrum of the parent dimer [π-$C_5H_5Fe(CO)_2]_2$. This high field shift is readily explained in terms of an increase in the electron density on the iron atom as a result of the replacement of a carbonyl group by an overall stronger (σ–π) donor. There was no evidence for coupling between the phosphorus and cyclopentadienyl hydrogen nuclei in these bis-substituted

TABLE 3

C–O STRETCHING FREQUENCIES OF

(a). The intermediates in the formation of $[\pi\text{-RC}_5\text{H}_4\text{Fe(CO)}]_2\text{L}^a$ (cm^{-1})

R=H,	L=$(C_6H_5)_2PCH_2P(C_6H_5)_2$	1927 (s), 1725 (s)
	$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	1922 (s), 1725 (s)
	$(C_6H_5)_2PC_3H_6P(C_6H_5)_2$	Not measured
	$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$	Not observed
	$(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	~1925 (s), 1721 (s)
	$(C_6H_5)_2AsCH_2As(C_6H_5)_2$	~1925 (s), 1722 (s)
	$(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$	~1925 (s), 1719 (s)
R=CH_3,	L=$(C_6H_5)_2PCH_2P(C_6H_5)_2$	~1925 (s), 1720 (s)
	$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	~1925 (s), 1720 (s)
	$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$	~1925 (s), 1721 (s)
	$(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	~1925 (s), 1719 (s)

(b). The monosubstituted derivatives $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{L}'^a$ (cm^{-1})

L'=$P(C_2H_5)_3$	1927 (s), 1725 (s)
$P(C_6H_5)_2C_2H_5$	1932 (s), 1726 (s)

[a] Measured in dichloromethane.

derivatives although such coupling has previously been observed for the monosubstituted compounds $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{L}$ (L=tertiary phosphine ligand)[13].

The NMR spectra of the ditertiary phosphine derivatives of $[\pi\text{-CH}_3\text{C}_5\text{H}_4\text{Fe(CO)}_2]_2$ contain two peaks which can be assigned to cyclopentadienyl protons. To a first approximation the intensities of these resonances are equal but are observed to vary slightly from compound to compound; the low field peak is always the stronger. Further for the compounds $[\pi\text{-CH}_3\text{C}_5\text{H}_4\text{Fe(CO)}]_2(\text{C}_6\text{H}_5)_2\text{PR}'\text{P}(\text{C}_6\text{H}_5)_2$ [R'=CH_2, $N(C_2H_5)$] the peaks are broad and asymmetric with that at lower τ containing two maxima. There is only one strong resonance in the spectra of $[\pi\text{-CH}_3\text{C}_5\text{H}_4\text{Fe(CO)}]_2(\text{C}_6\text{H}_5)_2\text{PR}'\text{P}(\text{C}_6\text{H}_5)_2$ [R'=CH_2, C_2H_4, $N(C_2H_5)$] which can be assigned to methyl protons although very weak peaks to higher field may be associated with these protons. Interestingly the chemical shifts of the cyclopentadienyl and methyl resonances are observed to vary with temperature. It is thus apparent that the chemical shifts of the α and β cyclopentadienyl protons of $[\pi\text{-CH}_3\text{C}_5\text{H}_4\text{Fe(CO)}]_2(\text{C}_6\text{H}_5)_2\text{PR}'\text{P}(\text{C}_6\text{H}_5)_2$ [R'=CH_2, C_2H_4, $N(C_2H_5)$] are different in contrast to those of $[\pi\text{-CH}_3\text{C}_5\text{H}_4\text{Fe(CO)}_2]_2$ which are found to be the same. A chemical shift difference between the α and β protons has recently been established for compounds of the type $\pi\text{-CH}_3\text{C}_5\text{H}_4\text{Mo(CO)}_3\text{X}$ (X=halogen)[15]. The temperature dependence of the NMR spectra of the bis-substituted derivatives of $[\text{CH}_3\text{C}_5\text{H}_4\text{Fe(CO)}_2]_2$ suggests that several isomers or conformers exist in solution in equilibrium. A full NMR study is required to clarify the spectral data, however.

The ligand proton peaks associated with the group R' in the spectra of the compounds $[\pi\text{-RC}_5\text{H}_4\text{Fe(CO)}]_2(\text{C}_6\text{H}_5)_2\text{PR}'\text{P}(\text{C}_6\text{H}_5)_2$ [R=H, R'=CH_2, C_2H_4, C_2H_2, $N(C_2H_5)$; R=CH_3, R'=CH_2, C_2H_4, $N(C_2H_5)$] are at considerably higher field than the corresponding peaks in the spectra of the free ligand. As a result of metal–ligand bonding the negative inductive effect of the phosphorus in the above ligands would be expected to be increased and thereby in terms of a diamagnetic shielding

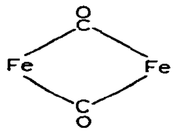
TABLE 4

PROTON MAGNETIC RESONANCE DATA

Compound	Resonances[a,b]			
	C_6H_5[c]	C_5H_5	CH_3	MC_nH_mM (M = P or As)
$[\pi\text{-}C_5H_5Fe(CO)_2]_2$		5.21		
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PCH_2P(C_6H_5)_2$	2.74 b	5.73		8.27 b
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	2.35 b	5.82		8.39 b
	2.57 d, b			8.65 b
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PC_3H_6P(C_6H_5)_2$	2.33 b	5.92		8.63 b
	2.62			9.12 b
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PC_2H_2P(C_6H_5)_2$	2.53 b	5.78		3.51 st
	2.64 d, b			
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	2.52 b	5.91		7.47 m (CH_2)
				10.05 t (CH_3)
$[\pi\text{-}C_5H_5Fe(CO)]_2(C_6H_5)_2AsCH_2As(C_6H_5)_2$	2.67 b	5.67		8.73 b
$[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$		5.45	7.95	
$[\pi\text{-}CH_3C_5H_4Fe(CO)]_2(C_6H_5)_2PCH_2P(C_6H_5)_2$	2.66 b	5.78	7.58	8.71 b
	2.78 b	5.85 b	7.92[d]	
		6.09 b		
$[\pi\text{-}CH_3C_5H_4Fe(CO)]_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	2.33 b	5.85	7.94	8.71 b
	2.57 d, b	6.47	8.50[d]	
$[\pi\text{-}CH_3C_5H_4Fe(CO)]_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	2.42 p	5.87	8.12	7.51 m, b (CH_2)
	2.53 b	5.96 b	8.23[d]	10.21 t (CH_3)
		6.28 b	8.33[d]	
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	2.70 m			7.20 t (*J* 1.6 Hz)
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	2.71 m			7.87 t (*J* 3.9 Hz)
$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$	2.73 m			e
$(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$	2.50 m			6.59 m (CH_2)
				9.23 t (CH_3)
				($J \simeq 7$ Hz)

[a] τ scale measured in $CDCl_3$ at 38° (TMS reference). [b] Abbreviations: b, broad; d, doublet; t, triplet; st, sextet; m, multiplet. [c] Values refer to centres of asymmetric peaks. [d] Assignment is tentative. [e] Peaks lie under C_6H_5 resonance.

mechanism the peaks associated with R would be expected to be shifted to lower field. This has indeed been observed for $M(CO)_4(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ (M = Cr, Mo, W)[16] and $\pi\text{-}C_5H_5Mo(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2X$ (X = Cl, I)[17]. The high field shift in the compounds discussed above must be attributed to other shielding effects. Based on infrared evidence it was suggested above that π-bonding occurs between the iron atoms and the bridging carbonyl groups in the bis-substituted derivatives $[\pi\text{-}RC_5H_4Fe(CO)]_2L$ (R = H, CH_3). A mechanism thus exists for the delocalisation of π-electrons in the planar



moiety. A ring current in this system would readily account for the high field shift of the resonances associated with the hydrogen atoms situated below the plane of the ring.

EXPERIMENTAL

The ligands cis-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$[18], $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n=1$, 2, 3)[19] and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$[20] were synthesised according to literature methods and slight modifications of them while $(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$ ($n=1$, 2) as well as $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ were obtained commercially (Strem Chemicals). All experiments were performed under a nitrogen atmosphere. Petroleum ether refers to that with b.p. 40–60°. The photochemical reactions employed a Hanovia medium pressure mercury arc photochemical reactor. The chromatographic separations were effected on an alumina column (50 × 1.5 cm; Woelm acid washed alumina, activity III). The infrared and NMR spectra were recorded on a Perkin–Elmer model 621 grating spectrophotometer and a Varian A60 instrument respectively. Conductivities were determined by established methods. The molecular weights were measured using a Mechrolab vapour pressure osmometer. The elemental analyses (C, H, P) were performed by the Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany. The iron analyses were determined by an Atomic Absorption Spectroscopic method using a Techtron AA4 instrument.

General methods of synthesis of the bis-substituted derivatives

(*i*). A mixture of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ or $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ and the appropriate ligand in benzene (*ca.* 80 ml) was refluxed until the reaction was complete as indicated by infrared spectroscopy. The solution was filtered and the solvent removed under reduced pressure. The residue was crystallised and the pure compound dried *in vacuo* at room temperature or at 80°.

(*ii*). $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and the appropriate ligand in benzene (*ca.* 120 ml) were irradiated with ultraviolet light until the reaction was complete as indicated by infrared spectroscopy. The solution was filtered and the solvent removed under reduced pressure. Purification was achieved as described in (*i*).

Dicarbonyl[bis(diphenylphosphino)methane]di-π-cyclopentadienyldiiron

The product obtained by reacting $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (2.0 g, 5.6 mmole) and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (3.4 g, 8.9 mmole) for 36 h as described in (*i*) was washed with acetone to remove excess ligand. The residue was crystallised from benzene/petroleum ether and recrystallised from dichloromethane/petroleum ether.

Dicarbonyl[1,2-bis(diphenylphosphino)ethane]di-π-cyclopentadienyldiiron

The product obtained by reacting $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (2.0 g, 5.6 mmole) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (3.4 g, 8.5 mmole) for 10 h as described in (*i*) was washed with acetone to remove excess ligand. The residue was crystallised from benzene/petroleum ether and recrystallised from dichloromethane/petroleum ether.

Dicarbonyl[1,3-bis(diphenylphosphino)propane]di-π-cyclopentadienyldiiron

The product obtained by reacting $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.0 g, 2.8 mmole) and

$(C_6H_5)_2PC_3H_6P(C_6H_5)_2$ (1.7 g, 4.1 mmole) for 10 h as described in (*i*) was washed with acetone to remove excess ligand. The residue was crystallised from benzene/petroleum ether and recrystallised from dichloromethane/petroleum ether.

Dicarbonyl[1,2-bis(diphenylphosphino)ethylene]di-π-cyclopentadienyldiiron

The product obtained by reacting $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.5 g, 1.4 mmole) and *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ (1.1 g, 2.8 mmole) for 2 h as described in (*i*) was washed with methanol and warm petroleum ether to remove excess ligand and side-products. The residue was crystallised from benzene/petroleum ether.

Dicarbonyl[bis(diphenylphosphino)ethylamine]di-π-cyclopentadienyldiiron

The product obtained by reacting $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.5 g, 1.4 mmole) and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ (0.9 g, 2.2 mmole) for 42 h as described in (*i*) was washed with methanol to remove excess ligand and side-products. The residue was crystallised from benzene/petroleum ether and recrystallised from dichloromethane/petroleum ether.

Dicarbonyl[bis(diphenylarsino)methane]di-π-cyclopentadienyldiiron

The product obtained by reacting $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.5 g, 1.4 mmole) and $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ (1.0 g, 2.1 mmole) for 88 h as described in (*ii*) was washed with methanol to remove excess ligand and side-products. The residue was crystallised from benzene/petroleum ether.

Dicarbonyl[1,2-bis(diphenylarsino)ethane]di-π-cyclopentadienyldiiron

The product obtained by reacting $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.5 g, 1.4 mmole) and $(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$ (1.0 g, 2.0 mmole) for 39 h as described in (*ii*) was dissolved a minimum of benzene and transferred to an alumina column. The column was eluted in turn with petroleum ether (b.p. 60–80°), cyclohexane and benzene to remove excess ligand and side-products (yellow band). Elution with dichloromethane afforded a green band which was collected. The solvent was removed to afford a green oil. Attempts to crystallise this oil were unsuccessful.

Dicarbonyl[bis(diphenylphosphino)methane]bis-π-(methylcyclopentadienyl)diiron

The product obtained by reacting $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ (0.5 g, 1.3 mmole) and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.77 g, 2.0 mmole) for 136 h as described in (*i*) was washed with methanol to remove excess ligand. The residue was crystallised from benzene/petroleum ether and recrystallised from dichloromethane/petroleum ether.

Dicarbonyl[1,2-bis(diphenylphosphino)ethane]bis-π-(methylcyclopentadienyl)diiron

The product obtained by reacting $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ (0.5 g, 1.3 mmole) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.78 g, 2.0 mmole) for 20 h as described in (*i*) was washed with methanol to remove excess ligand. The residue was crystallised from benzene/petroleum ether and recrystallised from dichloromethane/petroleum ether.

Dicarbonyl[1,2-bis(diphenylphosphino)ethylene]bis-π-(methylcyclopentadienyl)diiron

The product obtained by reacting $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ (0.5 g, 1.3 mmole) and *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ (0.78 g, 2.0 mmole) for 33 h as described in (*i*) was washed with methanol to remove excess ligand and side-products. Attempts to crystallise the green oily residue were unsuccessful.

Dicarbonyl[bis(diphenylphosphino)ethylamine]bis-π-(methylcyclopentadienyl)diiron

The product obtained by reacting $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ (0.5 g, 1.3 mmole) and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ (0.8 g, 2.0 mmole) for 60 h as described in (*i*) was washed with methanol to remove excess ligand and side-products. The residue was crystallised from benzene/petroleum ether and recrystallised from dichloromethane/petroleum ether.

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