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MÖSSBAUER SPECTROSCOPIC STUDIES OF SOME DINUCLEAR η-CYCLOPENTADIENYL DERIVATIVES OF IRON

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Summary

Mössbauer spectra have been recorded at 77 K for *cis*- and *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ ($L = P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{—}i\text{-}C_3H_7)_3$, $P(OC_6H_5)_3$, $P(C_2H_5)_3$ and $P(C_3H_7)_3$, $[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2\,PRP(C_6H_5)_2]$ ($R = CH_2$, C_2H_4 and $N(C_2H_5)$), $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$, $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5P(C_2H_5)_3]$, $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4L_2]$ ($L = P(OC_6H_5)_3$ and $P(C_2H_5)_3$), $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$, $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$, $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4L]$ ($L = P(OCH_3)_3$ and $P(C_6H_5)_3$) and $[\{Fe(\eta\text{-}CH_3C_5H_4)(CO)_2\}_2X]B(C_6H_5)_4$ (X = Cl, Br and I). Many of the compounds contain non-equivalent iron environments, and in such cases the assignments of the various lines in the spectra to the individual iron atoms are discussed in detail. The results are interpreted in terms of probable structures for the derivatives and the bonding properties of the ligands involved.

Introduction

Previous reports from these laboratories have described certain aspects of the chemistry of some bridged derivatives of iron. The investigations included a study of the reactivity of the bridging sulphido derivatives $[Fe(CO)_3SR]_2$ (R = alkyl or aryl group) towards monodentate and bidentate group V donor ligands [1—3], a study of the redox properties of $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ (R = alkyl or

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aryl group) [4], the synthesis of some novel substituted derivatives of $[Fe_2(CO)_9]$ such as $[Fe_2(CO)_7(C_2H_5O)_2POP(OC_2H_5)_2]$ and $[Fe_2(CO)_5\{(C_2H_5O)_2POP(OC_2H_5)_2\}_2]$ [5], the reactions of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ with halogens and tertiary and ditertiary phosphines [6—9], and the synthesis and reactivity of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$ containing both a bridging phosphino and a bridging carbonyl group [10]. Extensive use was made of Mössbauer spectroscopy in these investigations and the earlier reports described its application, in particular, in the structural studies of the substituted derivatives of $[Fe(CO)_3SR]_2$ [1] and the bonding studies of $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2^{x+}$ ($x = 0,1$ or 2) [4].

This paper describes the Mössbauer spectra of a number of products obtained from the reactions of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$. The results have provided an insight into the bonding characteristics of the various ligands involved and have thrown light on a number of specific structural problems. Several workers have warned of the need for caution in using Mössbauer spectroscopy to infer molecular structure in organometallic compounds [11—13], particularly those containing organic groups such as $\eta\text{-}C_5H_5$ [12,13]. These reservations have been based on the apparent failure of the technique, in a few isolated cases, to detect non-equivalence of iron environments where it is known definitely to exist. The results presented in this paper are relevant to this problem because they help to define the extent to which the technique is sensitive to particular environmental differences in several restricted series of compounds containing non-equivalent iron atoms.

Results and discussion

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ ($L = CO$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, $P(OC_6H_5)_3$, $P(C_2H_5)_3$, and $P(C_3H_7)_3$)

The Mössbauer spectra of *cis*- and *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (Fig. 1) have been measured and the parameters obtained (Table 1) are in good agreement with those reported earlier [14]. As indicated, the data are essentially insensitive to the structural differences between the two isomers.

On first inspection the spectra of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ ($L = P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{—}i\text{-}C_3H_7)_3$, and $P(OC_6H_5)_3$) (Fig. 2) consist of only two peaks and thereby reveal no apparent difference in the inidividual iron resonances. Sim-

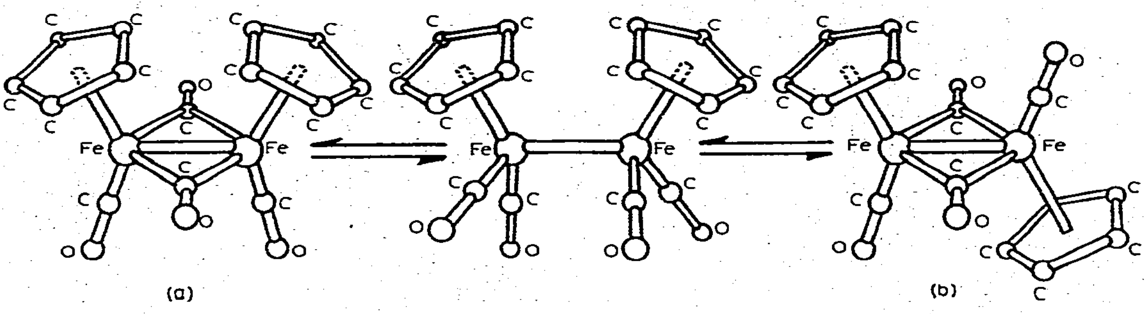

Fig. 1. Structures of *cis*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (a), and *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (b); ref. 11 and 31.

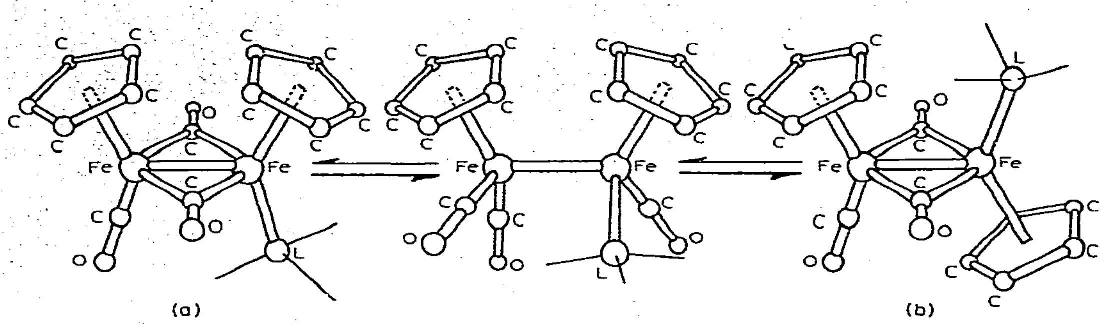

Fig. 2. Proposed structures of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ ($L = P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{—}i\text{-}C_3H_7)_3$, $P(OC_6H_5)_3$, $P(C_2H_5)_3$ or $P(C_3H_7)_3$); see ref. 32 for crystal structure determination of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OC_6H_5)_3]$.

ilar behaviour has been reported for the monosubstituted acetylenic diphosphine derivative $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2]$ [12]. In contrast, the spectra of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ ($L = P(C_2H_5)_3$ and $P(C_3H_7)_3$) clearly reveal the expected non-equivalence in the iron environments. This is illustrated in Fig. 3

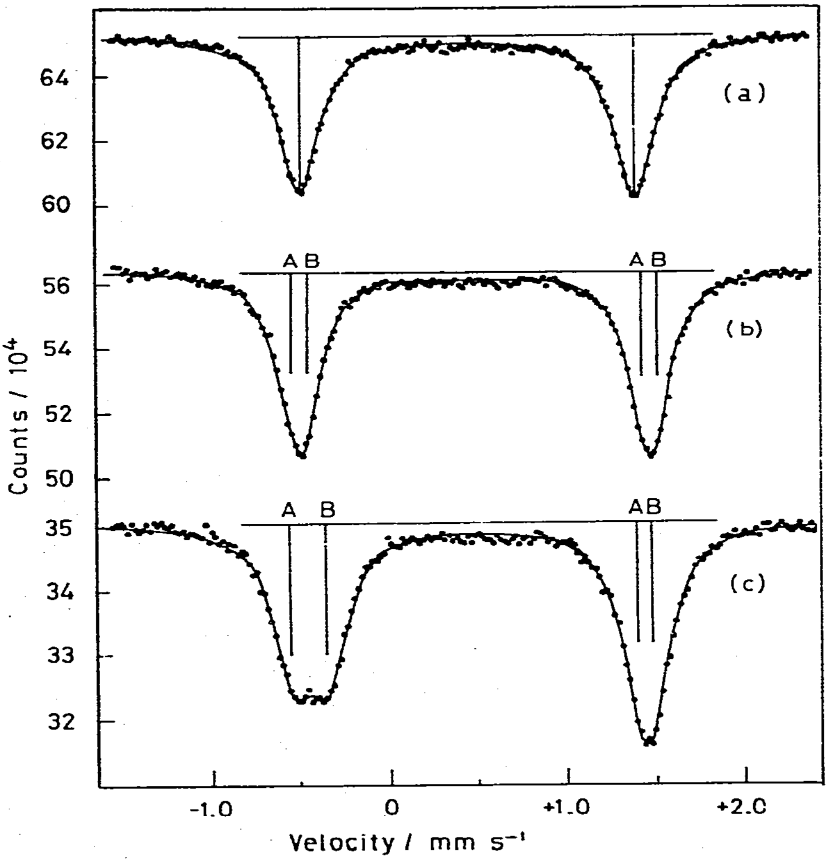

Fig. 3. Mössbauer spectra at 77 K of *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (a), $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OC_6H_5)_3]$ (b), and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(C_3H_7)_3]$ (c).

TABLE 1

MÖSSBAUER SPECTROSCOPIC DATA AT 77 K

Compound	Line Assignment	Chemical isomer shift [a,b] δ(mm s^{-1})	Quadrupole splitting [c] Δ(mm s^{-1})	Widths at half height [c] Γ(mm s^{-1})	Chi-squared/ degrees of freedom
cis-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$		0.22	1.92	0.25, 0.25	252/193 [d]
trans-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$		0.23	1.90	0.27, 0.27	241/193 [d]
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OCH_3)_3]$	$Fe_A(1,3)$	0.19	1.92	0.25, 0.25	276/193 [e]
	$Fe_B(2,4)$	0.30	1.93	0.25, 0.25	
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OC_2H_5)_3]$	$Fe_A(1,3)$	0.20	1.90	0.23, 0.23	287/193 [e]
	$Fe_B(2,4)$	0.30	1.91	0.23, 0.23	
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(O\text{-}i\text{-}C_3H_7)_3]$	$Fe_A(1,3)$	0.23	1.88	0.25, 0.25	418/193 [e]
	$Fe_B(2,4)$	0.30	1.91	0.25, 0.25	
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OC_6H_5)_3]$	$Fe_A(1,3)$	0.22	1.97	0.23, 0.23	464/193 [e]
	$Fe_B(2,4)$	0.30	1.98	0.23, 0.23	
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(C_2H_5)_3]$	$Fe_A(1,3)$	0.20	1.92	0.24, 0.24	326/193 [e]
	$Fe_B(2,4)$	0.34	1.84	0.24, 0.24	
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(C_3H_7)_3]$	$Fe_A(1,3)$	0.20	1.95	0.26, 0.26	297/193 [e]
	$Fe_B(2,4)$	0.34	1.84	0.26, 0.26	
$[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]$		0.30	1.84	0.44, 0.44	212/192 [d]
$[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$		0.31	1.88	0.25, 0.25	271/247 [d]
$[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$		0.29	1.90	0.32, 0.32	211/192 [d]

$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$	$Fe_A(2,3)$	0.09	1.75	0.30, 0.30	319/187 [e]
	$Fe_B(1,4)$	−0.09	2.38	0.30, 0.30	
$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5P(C_2H_5)_3]$	$Fe_A(2,3)$	0.09	1.72	0.28, 0.28	277/191 [e]
	$Fe_B(1,4)$	−0.10	2.54	0.28, 0.28	
$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(OC_6H_5)_3\}_2]$	$Fe_A(2,3)$	0.15	1.77	0.27, 0.30	393/187 [d]
	$Fe_B(1,4)$	−0.11	2.65	0.26, 0.25	
$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(C_2H_5)_3\}_2]$	$Fe_A(2,3)$	0.20	1.72	0.28, 0.28	268/191 [e]
	$Fe_B(1,4)$	−0.09	2.56	0.28, 0.28	
$[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$	$Fe_A(2,4)$	0.22	1.78	0.34, 0.29	322/187 [d,e]
	$Fe_B(1,3)$	−0.10	2.15	0.31, 0.29	
$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$	$Fe_A(1,4)$	0.19	1.80	0.25, 0.23	379/188 [f]
	$Fe_B(2,3)$	0.05	1.39	0.25, 0.28	
$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(OCH_3)_3]$	$Fe_A(1,4)$	0.18	1.98	0.27, 0.27	371/192 [e]
	$Fe_B(2,3)$	0.07	1.51	0.27, 0.27	
$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(C_6H_5)_3]$	$Fe_A(1,4)$	0.18	2.12	0.25, 0.24	1289/187 [d,g]
	$Fe_B(2,3)$	0.11	1.51	0.29, 0.30	
$[\{Fe(\eta\text{-}C_5H_4CH_3)(CO)_2\}_2Cl]B(C_6H_5)_4$		0.24	1.90	0.38, 0.38	643/191 [d]
$[\{Fe(\eta\text{-}C_5H_4CH_3)(CO)_2\}_2Br]B(C_6H_5)_4$		0.24	1.86	0.38, 0.38	375/192 [d]
$[\{Fe(\eta\text{-}C_5H_4CH_3)(CO)_2\}_2I]B(C_6H_5)_4$		0.23	1.83	0.35, 0.35	355/192 [d]

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[a] Relative to metallic iron at 295 K. [b] Confidence limits of ±0.01 and ±0.02 mm s^{-1} are placed on the parameters from the two-peak and four-peak spectra respectively. [c] ±0.02 or ±0.04, see footnote *b*. [d] All parameters unconstrained during curve fit. [e] Intensities and widths at half height constrained as follows: $I_1 = I_2, I_3 = I_4, \Gamma_1 = \Gamma_2 = \Gamma_3 = \Gamma_4$, where the peaks are numbered from 1 to 4 in order of increasing velocity. [f] $I_1 = I_2, \Gamma_1 = \Gamma_2$. [g] Unacceptably high chi-squared reflects slight impurity contribution to spectrum; the additional component falls mainly in the region between the principal absorption peaks and does not have any significant effect on the parameters.

where the spectrum of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(C_3H_7)_3]$ is compared with those of *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OC_6H_5)_3]$. In view of this the spectra of all the monosubstituted derivatives have been treated as the result of two slightly non-coincident doublets. Two line combinations 1,3; 2,4 or 1,4; 2,3 are possible but the latter can be eliminated because it gives rise to chemical isomer shift data which require the electron density change at both metal atoms on replacement of a carbonyl group by the ligand L to be roughly equal. This situation is highly unlikely. Rather it is expected that the Mössbauer parameters for the non-substituted iron atom (Fe_A) in each derivative will be similar to those of the parent dimer and in fact the 1,3 combination gives rise to a centroid which is essentially invariant throughout the series and is roughly equal to that for $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$.

As revealed by the data presented in Table 1 substitution of a terminal carbonyl by a tertiary phosphite results in an increase in the chemical isomer shift of the iron involved (Fe_B) by ca. 0.08 mm s^{-1}, whereas for a tertiary phosphine an even greater increase in chemical isomer shift is observed (0.12 mm s^{-1}). This indicates a decrease in *s*-electron density at the iron nucleus on substitution. Previous work has shown that the stretching frequencies of the carbonyl groups in these compounds decrease progressively along the series parent carbonyl > phosphite derivatives > phosphine derivatives, consistent with an increase in the (σ—π)-donor properties of the substituting ligand along this series [6]. The increase in the chemical isomer shift is thus attributed to an increase in the shielding of the iron *s*-electron density, rather than to a reduction in the *s*-orbital population. It is instructive to compare these trends with those reported for replacement of a carbonyl group in $[Fe(CO)_5]$ by a tertiary phosphine or phosphite [15] As shown in Table 2 the substitution is invariably accompanied by a decrease in the chemical isomer shift, and this can be accounted for in terms of the bonding characteristics of the four remaining carbonyl groups. The latter are able to

TABLE 2

MÖSSBAUER PARAMETERS FOR SOME PHOSPHINE AND PHOSPHITE DERIVATIVES OF $[Fe(CO)_5]$

Compound	Chemical isomer shift [a] δ (mm s^{-1})	Quadrupole splitting [b] $\frac{1}{2}e^2qQ$(mm s^{-1})	Temperature (K)	Refs.
$[Fe(CO)_5]$	—0.09	+2.57	78	26, 21
$[Fe(CO)_4P(C_6H_5)_3]$	—0.12	+2.42	78	21, 24
$[Fe(CO)_3\{P(C_6H_5)_3\}_2]$	—0.10	+2.76	78	27
$[Fe(CO)_4P\{N(CH_3)_2\}_3]$	—0.14	2.22 [c]	78	24
$[Fe(CO)_3\{P[N(CH_3)_2]_3\}_2]$	—0.14	2.27 [c]	78	24
$[Fe_2(CO)_8(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$	—0.10	+2.79	80	21, 20
$[Fe(CO)_3(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$	—0.17	—2.12	80	21, 20
$[Fe(CO)_4P(OCH_3)_3]$		+2.27	4.2	28
$[Fe(CO)_3\{P(OCH_3)_3\}_2]$	—0.22	2.28 [c]	ca. 295	28, 29
$[Fe(CO)_4P(OC_2H_5)_3]$	—0.12	2.31 [c]	78	30
$[Fe(CO)_3\{P(OC_6H_5)_3\}_2]$	—0.20	2.60 [c]	ca. 295	29

[a] Relative to metallic iron at 295 K. [b] *Q* is positive for $^{57}Fe^m$. [c] Sign not determined but presumed to be positive.

delocalize the shielding electron density away from the iron such that the stronger σ-donor effect of the phosphine, relative to carbon monoxide, is the dominant factor contributing to the change in chemical isomer shift. In the case of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ any additional shielding electron density on the iron atoms is less easily redistributed (η-cyclopentadienyl and bridging carbonyl groups are poor π-acceptors) and as a result the chemical isomer shifts appear now to be governed primarily by the relative π-acceptor abilities of the ligands L.

These results show clearly that in carbonyl-containing systems the change in chemical isomer shift accompanying the substitution of one particular ligand by another is strongly dependent on the bonding characteristics of the other ligands present. An important consequence of this fact is that the concept of partial chemical isomer shifts is rather limited in systems of this type; this problem has been discussed recently by Bancroft and Libbey in a study of carbonyl complexes of iron(II) [16].

$[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$ ($R = CH_2$, C_2H_4, *and* $N(C_2H_5)$)

The bis-substituted derivatives $[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$ ($R = CH_2$, C_2H_4, and $N(C_2H_5)$) give symmetrical two-line Mössbauer spectra, with parameters (Table 1) which are very similar to those assigned to the substituted iron atoms in the monosubstituted compounds $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$, thereby adding weight to the interpretation of the spectra of the latter. The results are therefore consistent with the symmetrical structure (Fig. 4) proposed earlier [7] and confirmed recently by X-ray crystallography [17].

$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4L'L'']$ ($L' = L'' = CO$; $L' = CO$, $L'' = P(C_2H_5)_3$; $L' = L'' = P(OC_6H_5)_3$; $L' = L'' = P(C_2H_5)_3$; *and* $L'L'' = (C_6H_5)_2PCH_2P(C_6H_5)_2$)

The Mössbauer spectrum (Fig. 5a) of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$ consists of a pair of quadrupole split doublets with overlapping right-hand limbs, indicative of dissimilar iron environments. The four peaks in this spectrum can be paired in one of two ways, 1, 3; 2, 4 or 1, 4; 2, 3. However, the second combination is favoured as being more consistent with the proposed structure (Fig. 6) [10]. On this basis the chemical isomer shift ($\delta = -0.09$ mm sec^{-1}, relative to iron) and quadrupole splitting ($\Delta = 2.38$ mm sec^{-1}) for the outer pair of lines are typical [15] * of the trigonal bipyramidal environment suggested for Fe_B,

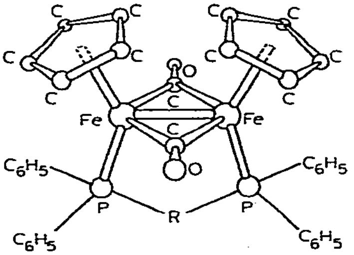

Fig. 4. Proposed structure of $[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]$ ($R = CH_2$, C_2H_4 or $N(C_2H_5)$): this structure has been confirmed for $R = CH_2$, ref. 17.

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* See also refs. in Table 2.

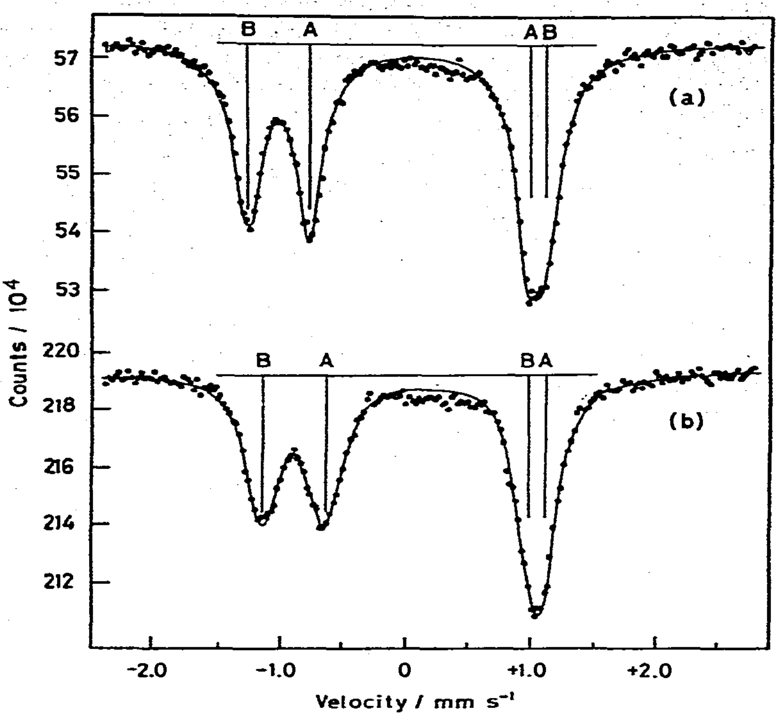

Fig. 5. Mössbauer spectra at 77 K of [$Fe_2(\eta$-$C_5H_5)P(C_6H_5)_2(CO)_4L'L''$] (L' = L'' = CO (a) L'L'' = $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (b)).

and the chemical isomer shift (δ = +0.09 mm sec^{-1}) for the inner pair of lines is very similar to that observed for derivatives of the type [$Fe(\eta$-$C_5H_5)(CO)_2L$] [18] in which the iron environment resembles that of Fe_A.

Mono- and bis-substituted derivatives of [$Fe_2(\eta$-$C_5H_5)P(C_6H_5)_2(CO)_6$] have been synthesised but significantly they could not be obtained by direct substitution of a carbonyl group in the parent compound [10]. Instead their formation was achieved by reaction of the bridging carbonyl derivative [$Fe_2(\eta$-$C_5H_5)$-$P(C_6H_5)_2(CO)_5$] (Fig. 7) with the appropriate ligand in solution under thermal conditions [10]. One monosubstituted derivative, [$Fe_2(\eta$-$C_5H_5)P(C_6H_5)_2(CO)_5$-

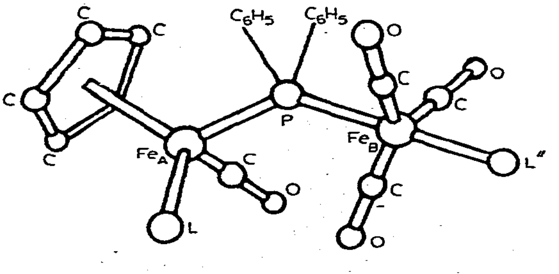

Fig. 6. Proposed structures of [$Fe_2(\eta$-$C_5H_5)P(C_6H_5)(CO)_6$] (L' = L'' = CO), [$Fe_2(\eta$-$C_5H_5)P(C_6H_5)_2(CO)_5P$-$(C_2H_5)_3$] (L' = CO; L'' = $P(C_2H_5)_3$) and [$Fe_2(\eta$-$C_5H_5)P(C_6H_5)_2(CO)_4\{P(OC_6H_5)_3\}_2$] and [$Fe_2(\eta$-$C_5H_5)P$-$(C_6H_5)_2(CO)_4\{P(C_2H_5)_3\}_2$] (L' = L'' = $P(OC_6H_5)_3$ or $P(C_2H_5)_3$).

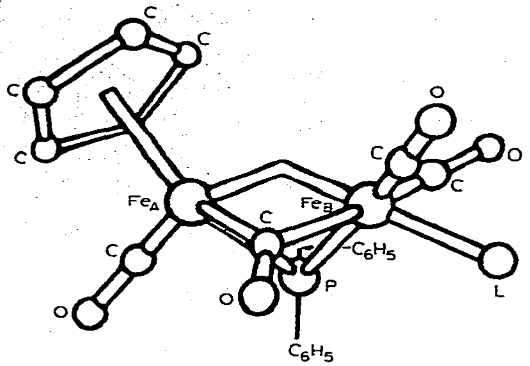

Fig. 7. Proposed structures of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$ (L = CO), $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(OCH_3)_3]$ (L = $P(OCH_3)_3$) and $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(C_6H_5)_3]$ (L = $P(C_6H_5)_3$).

$P(C_2H_5)_3]$, two bis-substituted compounds $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(OC_6H_5)_3\}_2]$ and $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(C_2H_5)_3\}_2]$, and one bridged derivative, $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$, have been studied by means of Mössbauer spectroscopy.

All four compounds afford spectra which can be satisfactorily computed as four-peak fits. Although two line combinations, 1,3; 2,4 and 1,4; 2,3, are possible the former can be immediately eliminated for $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5P(C_2H_5)_3]$, because, irrespective of the line combination chosen for $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$, replacement of a carbonyl group in the latter by triethylphosphine produces equal changes in the chemical isomer shifts of the two iron atoms. This situation, similar to that described for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$, is highly unlikely. Inspection of the chemical isomer shift and quadrupole splitting data for the monosubstituted triethylphosphine derivative and its parent compound (Table 1) reveals that one resonance remains unchanged with respect to both δ and Δ on substitution. This resonance has already been assigned to the iron bonded to the cyclopentadienyl group and it therefore follows that substitution has occurred at the cyclopentadienyl-free iron. Although the changes in the Mössbauer parameters for this iron are small the increase in quadrupole splitting from 2.38 to 2.54 mm sec^{-1} is significant. The small decrease in chemical isomer shift from -0.09 to -0.10 mm sec^{-1} is within the experimental error, implying that any increase in the *s*-electron density at the iron due to the stronger σ-donor properties of the triethylphosphine ligand is approximately compensated by an increase in the shielding 3*d*-electron density.

Again two line combinations are possible for $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(C_2H_5)_3\}_2]$ but, on the basis that only one iron atom is expected to reveal any real change in chemical isomer shift on replacement of a carbonyl group in $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5P(C_2H_5)_3]$ by triethylphosphine, combination 1,3; 2,4 can be eliminated. The line combination 1,4; 2,3 is also preferred for $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(OC_6H_5)_3\}_2]$. The alternative choice is unacceptable because the chemical isomer shift for the doublet 1,3 is unrealistically low; also the changes which occur in the centroids of both doublets in going from $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)(CO)_6]$ to $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(OC_6H_5)_3\}_2]$ are unacceptably high for monosubstitution by a tertiary phosphite; bis-substitution at a single iron atom is ruled out because both doublets shift. Substitution of a carbonyl group in the monosubstituted derivatives $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5L]$ ($L = P(OC_6H_5)_3$ or $P(C_2H_5)_3$) by $P(OC_6H_5)_3$ or $P(C_2H_5)_3$ respectively is thus seen to induce increases in the chemical isomer shift at the cyclopentadienyl-bearing iron atom of 0.06 and 0.11 mm s^{-1} respectively. The data therefore confirm the proposal made previously, on the basis of infrared evidence [10], that this is the site of substitution. They also indicate that the substitution is accompanied by a decrease in *s*-electron density at the iron nucleus, attributable to an increase in the shielding *3d*-electron density as described earlier in the text for the monosubstituted derivatives of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$. The near constancy of the parameters for the tricarbonyl-bearing iron atom is consistent with this unit remaining unchanged.

For the ditertiary phosphine derivative $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$ the line combination 1,3; 2,4 is preferred (Fig. 5b). The alternative 1,4; 2,3 implies that in going from $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$ to $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$ almost identical changes occur both in the chemical isomer shift and in the quadrupole splitting at each iron atom. This is highly unlikely; on the basis of the results discussed above, substitution of a carbonyl on the cyclopentadienyl-bearing iron by a tertiary phosphine will lead to a much greater change in chemical isomer shift than substitution of a carbonyl on the cyclopentadienyl-free iron. Further evidence in favour of the 1,3; 2,4 assignment is the similarity of the chemical isomer shift in $[Fe(\eta\text{-}C_5H_5)(CO)P(C_6H_5)_2]_2$ (0.26 mm s^{-1} relative to iron) [19] with that for the cyclopentadienyl-containing iron. The changes in chemical isomer shift observed on replacement of two carbonyl groups in $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$ by $(C_6H_5)_2PCH_2P(C_6H_5)_2$ are very similar to those produced by bis-substitution with triethylphosphine i.e. a large increase for Fe_A but a negligible change for Fe_B. However in contrast to $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(C_2H_5)_3\}_2]$ there is a decrease in the quadrupole splitting for the cyclopentadienyl-free iron in going from $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$ to $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$.

Cullen et al. have suggested that the Mössbauer quadrupole splittings might be used to distinguish between *cis*- and *trans*- bis-substituted derivatives of a trigonal bipyramidal iron(0) complex [20]. This conclusion was based on data of the type shown in Table 2, which reveals that replacement of a second carbonyl group in an $Fe(CO)_4L$ moiety to give an apical—apical $Fe(CO)_3L_2$ species (L = tertiary phosphine or phosphite) is invariably accompanied by an increase in the quadrupole splitting, whereas the generation of a *cis*-$Fe(CO)_3$(L—L) species (e.g. $[Fe(CO)_3(C_6H_5)_2PCH_2P(C_6H_5)_2]$) is accompanied by a substantial decrease in this parameter. In the present study (Table 1) there is an increase in the quadrupole splitting for the cyclopentadienyl-free iron in going from $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$ to $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5P(C_2H_5)_3]$, $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(OC_6H_5)_3\}_2]$ and $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(C_2H_5)_3\}_2]$ consistent with substitution of a carbonyl ligand *trans* to the bridging $P(C_6H_5)_2$ group as deduced previously from infrared measurements [10]. However, as mentioned earlier, in going from $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_6]$ to $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$ there is a decrease in the quadrupole splitting for the cyclopentadienyl-free iron, consistent with coordination of the ditertiary phosphine *cis* rather than *trans* to the $P(C_6H_5)_2$ group as expected on stereochemical grounds. The differences in the infrared spectra of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\{P(C_2H_5)_3\}_2]$ and $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$ in the C—O stretching region have also been explained in terms of *trans* and *cis* coordination [10]. For reasons discussed at length by Clark et al. [21] it is doubtful whether the present Mössbauer data allow a more detailed specification of the geometry of the iron atom in $[\{Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4\}(C_6H_5)_2PCH_2P(C_6H_5)_2]$. These authors have demonstrated, in the case of $[Fe(CO)_3(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$, that even if the sign of the quadrupole coupling constant and the magnitude of the asymmetry parameter are known (from magnetic perturbation measurements) it is still not possible to distinguish between structures having C_{2v} and C_s symmetry.

$[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4L]$ ($L = CO$, $P(OCH_3)_3$, *and* $P(C_6H_5)_3$)

No ambiguity arises in the pairing of the peaks in the Mössbauer spectrum of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$ as two of them are coincident. The resulting chemical isomer shift values are entirely consistent with the proposed structure (Fig. 7) [10], the doublet with lower chemical isomer shift being assigned to the tricarbonyl-bearing iron atom (Fe_B) and the other doublet to the cyclopentadienyl-containing iron atom (Fe_A). It is appropriate to compare the chemical isomer shifts for this compound with those for the closely related compounds $[Fe(CO)_3P(C_6H_5)_2]_2$ [19] and $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$. The chemical isomer shift for Fe_B of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$ (0.05 mm s^{-1}) is apprecialby greater than that for $[Fe(CO)_3P(C_6H_5)_2]_2$ (-0.02 mm s^{-1}), whereas the value for $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (0.22 mm s^{-1}) is only slightly larger than that for Fe_A of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$ (0.19 mm s^{-1}). It is therefore apparent that replacement of a bridging carbonyl bonded to an $Fe(CO)_3$ unit, by a bridging phosphino group, effects a larger increase in *s*-electron density at the iron nucleus than a similar replacement involving an $Fe(\eta\text{-}C_5H_5)(CO)$ moiety. As before this can be explained in terms of the bonding properties of the ligands attached to the respective iron atoms. Thus the shielding electron density which accumulates on the tricarbonyl-bearing iron, as a result of the replacement of the bridging carbonyl by the bridging phosphino ligand, is redistributed to a large extent into the π^*-antibonding orbitals of the terminal carbonyls and the nett result is a decrease in the chemical isomer shift due to the better σ-donor properties of the phosphino group compared with the bridging carbonyl. The cyclopentadienyl-containing iron however cannot respond to the same extent and, because of the greater accumulation of shielding electron density, the effective increase in the *s*-electron density at the iron nucleus is smaller.

Both $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(OCH_3)_3]$ and $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(C_6H_5)_3]$, substituted derivatives of $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$, afford four-peak Mössbauer spectra and again two line-combinations are possible. For the line combination 1,3; 2,4 the centroid of the low-velocity doublet (1,3) remains virtually unchanged upon substitution, whereas the centroid of the high-velocity doublet (2,4) varies in position. For the alternative line combination (1,4; 2,3) the situation is reversed, with the high velocity doublet (1,4) remaining fixed and the low-velocity doublet (2,3) shifting to more positive velocity. This time assignment is only possible by comparison with data for other systems. We have shown previously that carbonyl replacement in $[Fe(CO)_3SC_6H_5]_2$ by triphenylphosphine to give $[Fe(CO)_2P(C_6H_5)_3SC_6H_5]_2$ is accompanied by a slight increase (0.04 mm s^{-1}) in the chemical isomer shift while trimethyl phosphite substitution in $[Fe(CO)_3SCH_3]_2$ to give $[Fe(CO)_2P(OCH_3)_3SCH_3]_2$ effects a slight decrease (0.02 mm s^{-1}) in this parameter [1]. Similar, though not necessarily identical, shifts are expected to accompany substitution of a terminal carbonyl group of the $Fe(CO)_3$ moiety in $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$. For the reasons discussed above, and as revealed in fact by the results for the series of compounds of the type $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$, much larger changes in chemical isomer shift are expected to accompany carbonyl substitution on an $Fe(\eta\text{-}C_5H_5)(CO)$ moiety; replacement of a terminal carbonyl in $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ by trimethyl phosphite and triphenyl phosphine produced increases in the chemical isomer shift of 0.08 and 0.12 mm s^{-1} respectively. These latter changes are much larger than those which occur in the centroid of the high-velocity doublet (2,4) * on going from $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_5]$ to $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(OCH_3)_3]$ and $[Fe_2(\eta\text{-}C_5H_5)P(C_6H_5)_2(CO)_4P(C_6H_5)_3]$ and as a consequence the line-combination 1,4; 2,3 is preferred for the latter compounds. This in turn implies that substitution occurs at the cyclopentadienyl-free iron, consistent with the infrared evidence [10].

$[\{Fe(\eta\text{-}C_5H_4CH_3)(CO)_2\}_2X]B(C_6H_5)_4$ *(X = Cl, Br, and I)*

Halogenation of $[Fe(\eta\text{-}C_5H_4R)(CO)_2]_2$ (R = H or CH_3) affords as intermediates in the formation of $[Fe(\eta\text{-}C_5H_4R)(CO)_2X]$ (X = halogen), bridged halogeno species of the type $[\{Fe(\eta\text{-}C_5H_4R)(CO)_2\}_2X]^+$ [8]. The Mössbauer spectra of $[\{Fe(\eta\text{-}C_5H_4CH_3)(CO)_2\}_2X]B(C_6H_5)_4$ (X = Cl, Br and I) have been measured and found to contain doublets with linewidths which are slightly broader than expected for samples containing a unique iron environment. The line-broadening may imply slight structural non-equivalence of the iron environments in these compounds but a more likely explanation is that these compounds occur as more than one conformer in the solid state, as has been suggested for $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(SC_2H_5)]A$ (A = SbF_6 or $B(C_6H_5)_4$) in solution [22] and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(SnCl_2)]$ in the solid state [23]. The chemical isomer shift is seen to be constant throughout the series, which indicates that the *s*-electron density at the iron nucleus is the same irrespective of the halogen present. This behaviour is common in series of carbonyl complexes containing different halogens, and has been attributed to the fact that increased σ-donation on going from chlorine to iodine is compensated by decreased π-back-donation of shielding *d*-electron density [24]. However, in the case of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2X]PF_6$ (X = Cl, Br and I) a decrease in the chemical isomer shift from the bridging chloro to the bridging iodo derivative was observed [25] indicative of an increase in *s*-electron density at the iron nucleus along this series.

Experimental

The Mössbauer spectra were obtained on powdered samples cooled to 77 K in a Texas Instrument Inc. Cryoflask, model CLF-3. Two spectrometers were used.

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* For the 1,3; 2,4 combination doublet 2,4 would be assigned to the cyclopentadienyl-containing iron on the basis that this iron will resonate at more positive velocity than the cyclopentadienyl-free iron.

The first was a Nuclear Science and Engineering Corporation instrument, model AM-1, coupled with a 400-channel R.I.D.L. analyser, model 34-12B, and the second comprised an MVT3 transducer, an MD3 drive amplifier and an MFG3 waveform generator from Elscint Limited, Israel, all coupled with a Northern Scientific Inc. NS630 multichannel analyser. The radioactive source was a nominal 25 mCi of ^{57}Co diffused into a rhodium matrix, as supplied by the Radiochemical Centre, Amersham. The data were analysed by least-squares curve-fitting programs developed by Dr. T.C. Gibb. Various constraints were applied to the halfwidths and intensities in the analysis of the more complex spectra, to prevent the computer from giving unrealistic fits; further details are given in the footnotes to Table 1.

The compounds studied were synthesized by methods published previously [6—8, 10].

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