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Substitution reactions of dinuclear alkenyl-bridged iron-cobalt complexes with phosphines. Crystal structures of  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  and  $[(\text{CO})_2(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$

Isabel Moldes, Josep Ros \*

*Departament de Química, Universitat Autònoma de Barcelona, Bellaterra-08193, Barcelona (Spain)*

René Mathieu

*Laboratoire de Chimie de Coordination du C.N.R.S., Unité no. 8241 liée par convention à l'Université Paul Sabatier, 205 Route de Narbonne, 31077 Toulouse (France)*

Xavier Solans and Mercè Font-Bardía

*Departament de Cristal·lografia i Mineralogia, Universitat de Barcelona, Martí i Franqués s/n, 08028-Barcelona (Spain)*

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**Abstract**

The bridging alkenyl iron-cobalt complexes  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CR}^1=\text{CR}^2\text{H})$  ( $\text{R}^1 = \text{CO}_2\text{Me}$  or  $\text{CO}_2\text{Et}$  and  $\text{R}^2 = \text{H}$ ;  $\text{R}^1 = \text{H}$  and  $\text{R}^2 = \text{H}$  or Ph) react with one equivalent of  $\text{PMe}_2\text{Ph}$  or  $\text{PPh}_3$  to give monosubstituted complexes with the phosphine ligand coordinated to the iron atom. When  $\text{R}^1 = \text{CO}_2\text{Me}$  or  $\text{CO}_2\text{Et}$  and  $\text{R}^2 = \text{H}$ , addition of two equivalents of  $\text{PPh}_3$  produces complexes with two  $\text{PPh}_3$  ligands coordinated to each metal. The complex  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  also reacts with one equivalent of  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$  or  $\text{PPh}_2\text{H}$  to give monosubstituted complexes with the phosphine ligand bonded to the cobalt atom. The reaction of the complex  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  with  $\text{PPh}_3$  gives a complex with the phosphine coordinated to the iron atom, but addition of two phosphines gives complexes with one phosphine ligand bonded to each metal. The structures of the products  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  and  $[(\text{CO})_2(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  obtained from the reaction of the  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  complex with one and two equivalents of  $\text{PMe}_2\text{Ph}$ , respectively, have been determined by X-ray crystallography.

## Introduction

The development of satisfactory methods of synthesis of heterobimetallic complexes containing organic bridges is still a stimulating challenge in organometallic chemistry [1,2]. Different selectivities in the activation of organic substrates can play an important role in organic reactions [3]. In the last few years we have developed some methods of making, in varying yields, dinuclear iron-transition metal alkenyl-bridged complexes. Thus, we have shown that the dinuclear complexes  $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH=CRH})]^-$  ( $\text{R} = \text{H}$  or  $\text{Ph}$ ) react with  $\text{Co}_2(\text{CO})_8$  to give neutral  $[(\text{CO})_4\text{Fe-Co}(\text{CO})_3](\mu\text{-CH=CRH})$  compounds, and established the structure of the complex with  $\text{R} = \text{Ph}$  by an X-ray diffraction study [4,5]. The  $[(\text{CO})_4\text{Fe-Co}(\text{CO})_3](\mu\text{-CH=CH}_2)$  complex was shown to undergo an interesting thermal rearrangement to give producing trinuclear Fe-Co clusters with carbyne and vinylidene bridges. Related Fe-Co dinuclear compounds  $[(\text{CO})_4\text{Fe-Co}(\text{CO})_3](\mu\text{-R}^2\text{C=CH}_2)$  and  $[(\text{CO})_3\text{Fe-Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  were obtained from the reaction of the  $\eta^3$ -acryloyl derivatives  $[\text{Fe}(\mu^3\text{-R}^1\text{HC=CR}^2\text{C=O})(\text{CO})_3]^-$  ( $\text{R}^1 = \text{H}$  and  $\text{R}^2 = \text{CO}_2\text{Me}$  or  $\text{CO}_2\text{Et}$ ;  $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$ ) with  $\text{Co}_2(\text{CO})_8$  [6]. The same acryloyl anionic complexes were used in the synthesis of alkenyl bridged Fe-Ni derivatives [7]. The reactions of the  $[(\text{CO})_4\text{Fe-Co}(\text{CO})_3](\mu\text{-CH=CRH})$  complexes with  $\text{PMe}_2\text{Ph}$  revealed regiospecific selectivity leading to the formation of disubstituted complexes containing the two phosphines coordinated to iron [8]. This particular coordination induces a complete electronic reorganization of the molecule resulting in formation of an unsymmetrically bridging CO ligand.

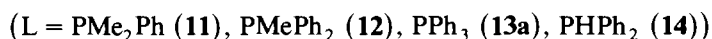
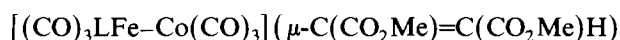
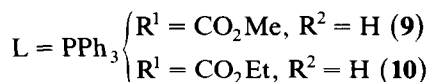
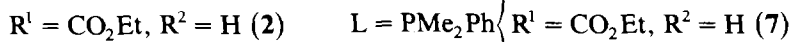
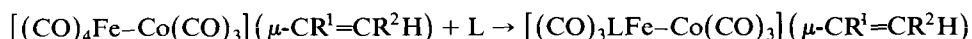
We describe here the substitution of CO ligands by phosphines in Fe-Co alkenyl bridged complexes of the type  $[(\text{CO})_4\text{Fe-Co}(\text{CO})_3](\mu\text{-CR}^1=\text{CHR}^2)$  ( $\text{R}^1 = \text{R}^2 = \text{H}$ ;  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Ph}$ ;  $\text{R}^1 = \text{CO}_2\text{Me}$  or  $\text{CO}_2\text{Et}$ ,  $\text{R}^2 = \text{H}$ ) and  $[(\text{CO})_3\text{Fe-Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$ . Monosubstituted and disubstituted complexes have been obtained from these reactions in good yields. The site of coordination of the phosphine ligands depends on the alkenyl bridge and the nature of the phosphine substituents. The structures of the iron- and cobalt-substituted compounds has been assigned on the basis of spectroscopic data and from the structures of  $[(\text{CO})_3\text{Fe-Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  and  $[(\text{CO})_2(\text{PMe}_2\text{Ph})\text{Fe-Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  determined by X-ray crystallography.

## Results and discussion

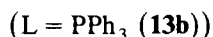
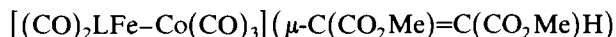
### *Monosubstituted complexes*

The complexes  $[(\text{CO})_4\text{Fe-Co}(\text{CO})_3](\mu\text{-CR}^1=\text{CR}^2\text{H})$  ( $\text{R}^1 = \text{CO}_2\text{Me}$  (1) or  $\text{CO}_2\text{Et}$  (2)) and  $\text{R}^2 = \text{H}$ ),  $[(\text{CO})_3\text{Fe-Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (3) and  $[(\text{CO})_4\text{Fe-Co}(\text{CO})_3](\mu\text{-CH=CPhH})$  (5) react at room temperature with one equivalent of phosphine to give new products resulting from the replacement of one CO by one phosphine ( $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$  and  $\text{PPhPh}_2$ ) ligand. All reactions were performed in dichloromethane solutions at room temperature and the products were crystallized from dichloromethane-methanol mixtures. The reaction with  $\text{PPh}_3$  yielded a mixture of products which were separated by column-chromatography on

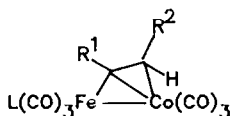
silica. The formation of the monosubstituted complexes can be represented as follows:



or



The elemental C and H analyses of the complexes obtained (except **14**, which could not be isolated as a solid) are in accordance with replacement of one CO by one phosphine ligand in the carbonyl complexes **1–3** and **5**. The IR spectra of products in dichloromethane solution in the  $\nu(\text{CO})$  region show bands of terminal CO ligands. Products **6**, **7**, **9** and **10** show the band for the ester C=O group at ca. 1680  $\text{cm}^{-1}$  whereas the complexes **11**, **13**, **13a**, **13b** and **14** display ester bands at 1680 and 1555  $\text{cm}^{-1}$ . The band at 1555  $\text{cm}^{-1}$  is indicative of the coordination of an ester group to a metal through an oxygen atom [9] as in complex **3**, suggesting that the chelated nature of the alkenyl bridge in **3** is not modified by coordination of the phosphine ligand. The pattern of the  $\nu(\text{CO})$  bands is identical for compounds **6–10**, suggesting that phosphine ligands are coordinated to the same metal. Except for complex **13b**, the products derived from complex **3** also display identical  $\nu(\text{CO})$  patterns, indicating that the substitution occurs at the same metal. The  $^1\text{H}$  NMR spectra of the monosubstituted complexes exhibit signals of alkenyl and phosphine ligands. The positions of the alkenyl signals almost coincide with those for the same groups in the unsubstituted complexes **1–3** and **5**, suggesting that the bridging ligands are not modified by coordination of phosphine ligand. The products **11**, **12**, **13a** and **14** that arise from complex **3** display a coupling of the alkenyl proton with the phosphorus atom of 9.6–13.6 Hz. The alkenyl hydrogen in product **13b** appears as a singlet at 4.19 ppm. In order to determine to which metal the phosphine ligand is coordinated we obtained the mass spectra of some  $\text{PMe}_2\text{Ph}$  derivatives which were suitably volatile to display optimal fragmentation. The mass spectra of products **6–8** and **11** show the parent ions ( $m/z = 536$  for **11**) or  $[\text{M}^+ - n\text{CO}]$  fragments for **6–8**. The  $[\text{FePMe}_2\text{Ph}]^+$  fragment is observed for complexes **6–8**, whereas product **11** gives the  $[\text{CoPMe}_2\text{Ph}]^+$  fragment. These observations suggest that the  $\text{PMe}_2\text{Ph}$  ligand is coordinated to iron in complexes **6–8** and to cobalt in complex **11**. Taking into account that complexes **6–10** display identical IR  $\nu(\text{CO})$



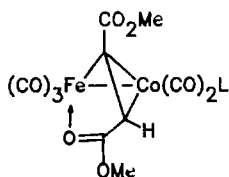
L	R <sup>1</sup>	R <sup>2</sup>	Complex
PMe <sub>2</sub> Ph	CO <sub>2</sub> Me	H	(6)
PMe <sub>2</sub> Ph	CO <sub>2</sub> Et	H	(7)
PMe <sub>2</sub> Ph	H	Ph	(8)
PPh <sub>3</sub>	CO <sub>2</sub> Me	H	(9)
PPh <sub>3</sub>	CO <sub>2</sub> Et	H	(10)

Fig. 1. Structure of complexes 6–10.

bands, we conclude that they contain the phosphine ligand attached to the iron atom. The coordination of the PPh<sub>3</sub> ligand to iron in the monosubstituted alkenyl complexes was also confirmed by the C–P coupling of the C<sub>α</sub> signal in the <sup>13</sup>C NMR spectrum of the complex **9** (which displays an identical IR  $\nu(\text{CO})$  pattern to those of complexes **6–8**, **10**). This spectrum shows the alkenyl carbon signals at 178.2 (d,  $J(\text{C–P}) = 5.1$  Hz,  $\text{C}(\text{CO}_2\text{Me})=\text{CH}_2$ ) and at 62.4 (s,  $\text{C}(\text{CO}_2\text{Me})=\text{CH}_2$ ) ppm. On the other hand, complexes **11**, **12**, **13a** and **14**, which also display an identical IR  $\nu(\text{CO})$  pattern, must have the phosphine ligand coordinated to cobalt. The coordination of the phosphine ligand to cobalt was confirmed by determination of the crystal structure of compound **11**. The different nature of complexes **13a** and **13b** was deduced from their <sup>31</sup>P NMR spectra; one signal is observed in each case, at 60.7 ppm (s, br) for **1a** and at 62.2 ppm (s) for **13b**. From the spectroscopic data we conclude that complex **13b** must have the PPh<sub>3</sub> ligand coordinated to iron. Figure 1 shows the structure of complexes 6–10 and Figs. 2 and 3 display the structures of monosubstituted complexes derived from complex 3.

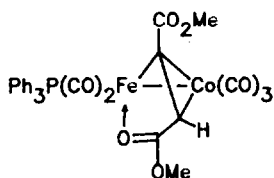
#### Disubstituted complexes

The reactions of  $[(\text{CO})_4\text{Fe–Co}(\text{CO})_3](\mu\text{-CR}^1=\text{CR}^2\text{H})$  ( $\text{R}^1 = \text{CO}_2\text{Me}$  (**1**) or  $\text{CO}_2\text{Et}$  (**2**)),  $[(\text{CO})_3\text{Fe–Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**3**) and  $[(\text{CO})_4\text{Fe–}$

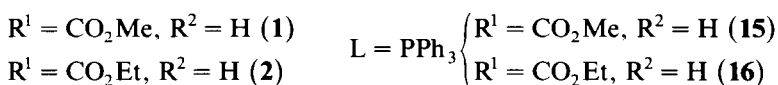
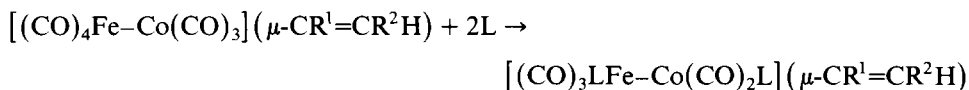


L	Complex
PMe <sub>2</sub> Ph	(11)
PMePh <sub>2</sub>	(12)
PPh <sub>3</sub>	(13a)
PPhPh <sub>2</sub>	(14)

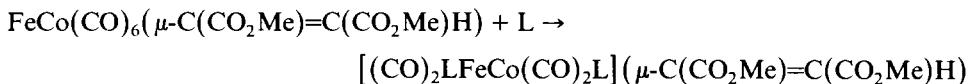
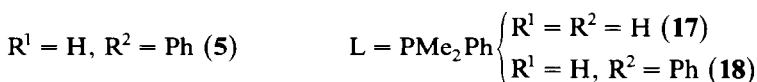
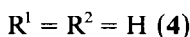
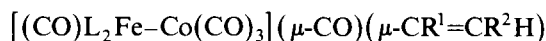
Fig. 2. Structure of complexes 11, 12, 13a and 14.

Fig. 3. Structure of complex **13b**.

$\text{Co}(\text{CO})_3](\mu\text{-CH}=\text{CRH})$  ( $\text{R} = \text{H}$  (**4**) or  $\text{Ph}$  (**5**)) with two equivalents of phosphine at room temperature give complexes resulting from the replacement of two CO by two phosphine ligands. The route to the disubstituted complexes can be represented as follows:



or



The elemental C and H analyses for the new complexes are consistent with the replacement of two CO ligands by two phosphines, except for complex **20**, which was obtained only as an oil. The IR spectra recorded in dichloromethane solutions, display bands attributable to terminal CO ligands in case of complexes **15**, **16** and **19–21**, and of both terminal and bridging CO ligands in the case of complexes **17** and **18**. Compounds **15** and **16** also show a band at ca.  $1670 \text{ cm}^{-1}$  characteristic of non coordinated C=O ester group, whereas complexes **19–21** show absorptions at ca.  $1669$  and  $1545 \text{ cm}^{-1}$ , respectively, corresponding to free and coordinated ester C=O groups. The  $^1\text{H}$  NMR spectra of disubstituted complexes display signals from the alkenyl bridge and phosphine ligands. Complexes **15** and **16** exhibit two signals for the terminal hydrogens of the alkenyl bridge; one these is a doublet as a result of coupling with one phosphorous atom. The  $^1\text{H}$  NMR spectra of complexes **17** and **18**, described in an earlier paper [8], show broad signals corresponding to alkenyl hydrogens coupled with two phosphorus atoms. Their  $^{31}\text{P}$ -decoupled  $^1\text{H}$  NMR spectra display signals with  $J_{\text{cis}} = 7.3$  and  $J_{\text{trans}} = 12 \text{ Hz}$  for **17** and  $J_{\text{trans}} = 12.3 \text{ Hz}$  for **18**. Complexes **19–21** give very similar spectra, with the alkenyl proton as a doublet with  $J(\text{H}-\text{P}) = 10\text{--}13.6 \text{ Hz}$ . The mass spectra of complexes **17** and **18** show

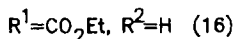
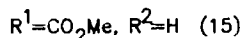
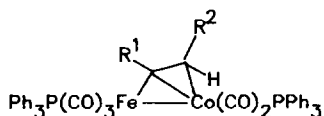


Fig. 4. Structure of complexes **15** and **16**.

the  $[\text{FePMe}_2\text{Ph}]^+$  fragment indicative of the coordination of phosphines to iron. The  $^{31}\text{P}$  NMR spectrum of complex **15** displays two signals, at 57.7 (s) and 68.0 (s, br), characteristic of coordination of  $\text{PPh}_3$  ligands to iron and cobalt atoms. The  $^{13}\text{C}$  NMR spectrum of complex **15** (which shows the same IR  $\nu(\text{CO})$  pattern as complexes **15**–**18**) has the alkenyl signals at 177.9 (t,  $J(\text{C}-\text{P}) = 4.6$  Hz,  $\text{C}(\text{CO}_2\text{Me})=\text{CH}_2$ ) and 64.7 (br,  $\text{C}(\text{CO}_2\text{Me})=\text{CH}_2$ ) ppm. The spectroscopic data for complexes **15** and **16** are in accord with a structure with one  $\text{PPh}_3$  attached to each metal, probably *trans* to the Fe–Co bond, as represented in Fig. 4. The previously reported [8] spectroscopic data for complexes **17** and **18** indicate a structure with the two  $\text{PMe}_2\text{Ph}$  ligands coordinated to iron. The X-ray structure of **17** also showed a bridging CO ligand formed either as a result of steric effects or by electronic reorganization after the coordination of the two  $\text{PMe}_2\text{Ph}$  ligands to the same metal. The structure of complexes **17** and **18** is shown in Fig. 5. Complexes **19**–**21** display a similar IR pattern, suggesting similar structures. The availability of the crystal structure of the complex  $[(\text{CO})_2(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**19**) allows us to postulate a structure with one phosphine coordinated to each metal for all these complexes. The general structure of complexes **19**–**21** is shown in Fig. 6.

From these results it appears that in Fe–Co complexes with  $\mu, \nu^2$ -alkenyl bridges ( $\mu\text{-CR}^1=\text{CR}^2\text{H}$ , with  $\text{R}^1 = \text{CO}_2\text{Me}$  or  $\text{CO}_2\text{Et}$  and  $\text{R}^2 = \text{H}$ ;  $\text{R}^1 = \text{H}$  and  $\text{R}^2 = \text{Ph}$ ) the substitution of one CO group by a phosphine ligand occurs at the iron centre. The substitution of a second CO group takes place at the cobalt atom when  $\text{R}^1$  is an electron-withdrawing group, but when  $\text{R}^1 = \text{H}$  and  $\text{R}^2 = \text{H}$  or  $\text{Ph}$  the two  $\text{PMe}_2\text{Ph}$  ligands coordinate to the iron atom. The substitution reactions in the complex  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**3**) are different. The coordination of one oxygen atom of an ester group seems to induce substitution at the cobalt centre except in the case of  $\text{PPh}_3$  ligand (the bulkiest phosphine used in this study).

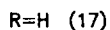
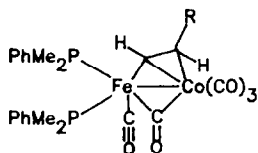
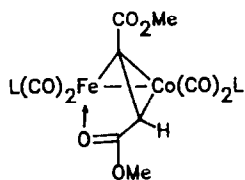


Fig. 5. Structure of complexes **17** and **18**.



$L = \text{PMe}_2\text{Ph}$  (19),  $\text{PMePh}_2$  (20) or  $\text{PPh}_3$  (21)

Fig. 6. Structure of complexes 19–21.

The second substitution is observed at the iron centre, yielding complexes with one phosphine bonded to Fe and the other to Co.

*Crystal structure of  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (11)*

Crystals of complex **11** suitable for an X-ray diffraction study were obtained by recrystallizations from dichloromethane–methanol mixtures. The crystal structure of complex **11** consists of discrete molecules linked by Van der Waals forces, as shown in Fig. 7. Table 1 shows the final atomic coordinates and Table 2 selected bond distances and angles. In the structure Fe and Co atoms are bridged by a  $\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H}$  ligand, and separated by a distance of 2.558(3) Å. This bond length is slightly shorter than that in the unsubstituted complex  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**3**) (2.593 Å) [6], but appreciably longer than that in the complex  $[(\text{CO})(\text{PMe}_2\text{Ph})_2\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CO})(\mu-\text{CH}=\text{CH}_2)$  (**17**) [8]. The 1,2-dimethoxyethenyl bridge is linked to iron by means of a  $\sigma$ -bond, with a Fe–C4 distance of 1.97(2) Å, and asymmetrically  $\pi$ -bonded to cobalt, with Co–C4 and Co–C3 distances of 1.98(1) and 2.11(1) Å. The methylcarboxylate groups are *trans* to the O1 atom coordinated to iron, with an Fe–O1 distance of 2.10(1) Å. The

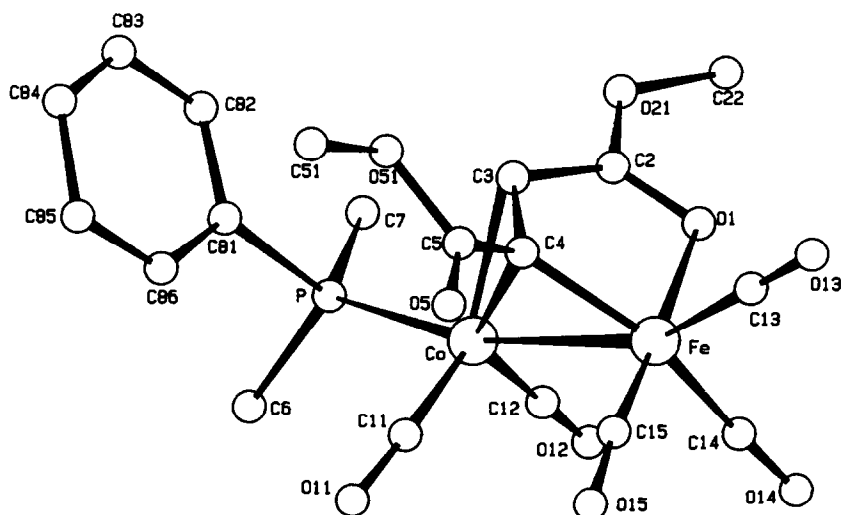


Fig. 7. Structure of complex **11** with the atom numbering scheme.

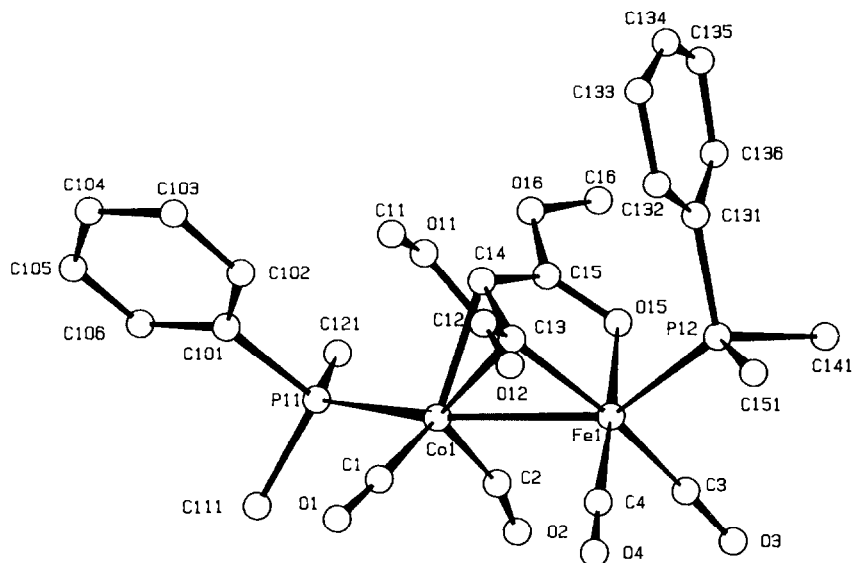


Fig. 8. Structure of complex **19** with the atom numbering scheme.

organic bridge forms an oxymetallacycle, with the iron atom forming a pseudoplane with the C14 and C15 atoms *trans* to C4 and O1 atoms, respectively. The short Fe–C15 bond distance of 1.60(2) Å is a consequence of the donor strength of the O1 atom. The remaining metal–carbonyl distances average 1.78 and 1.73 Å for the iron and cobalt atoms, respectively. The  $\text{PMe}_2\text{Ph}$  ligand is coordinated to cobalt with a Co–P distance of 1.286(4) Å. The *trans* disposition of the  $\text{PMe}_2\text{Ph}$  ligand probably causes the shortening of the Fe–Co bond with respect to the same distance in complex **3**.

*Crystal structure of  $[(\text{CO})_2(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**19**)*

As in complex **11**, monocrystals suitable for an X-ray diffraction study were obtained by recrystallizations from dichloromethane–methanol mixtures. The unit cell of **19** contains two independent molecules, related by a pseudocenter of inversion, which display only slight differences in geometry. The atom coordinates and some selected bond distances and angles are listed in Tables 3 and 4. The molecule of **19** can be regarded as made up of two  $\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}$  and  $\text{Co}(\text{CO})_2\text{PMe}_2\text{Ph}$  fragments linked by a Fe1–Co1 bond distance of 2.580(2) Å and a bridging  $\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H}$  ligand. The metal–metal bond is slightly shorter than that in the monosubstituted complex **11** but similar to the Fe–Co bond in compound  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**3**) compound [6]. As in the case of complexes **3** and **11**, the dimethoxycarbonyl bridge is  $\sigma$ -bonded to Fe1 and asymmetrically  $\pi$ -bonded to Co1, with Co1–C13 and Co1–C14 distances of 1.97(1) and 2.12(1) Å. The O15 atom of the ester group is linked to iron with a Fe1–O1 distance of 2.06(1) Å. The organic bridge and the Fe atom form an oxymetallacycle that also contains the C3 and C4 atoms. The  $\text{PMe}_2\text{Ph}$  ligands are coordinated to iron and cobalt atoms with Fe1–P12 and Co1–P11 bond lengths of



Table 1

Fractional atomic co-ordinates ( $\times 10^4$ ) with esd's in parentheses, for  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (11)

Atom	x	y	z
Fe	2885(5)	576(1)	1994(2)
Co	3568(2)	1217(1)	4234(2)
P	3622(3)	1834(2)	6054(4)
O(1)	1159(8)	585(5)	2803(11)
C(2)	1048(13)	1096(8)	3291(16)
O(21)	58(9)	1185(4)	3934(12)
C(22)	-890(15)	713(7)	4046(21)
C(3)	1882(12)	1566(6)	3152(14)
C(4)	2823(15)	1429(7)	2218(15)
C(5)	3363(13)	1844(9)	1409(17)
O(5)	4236(13)	1802(6)	768(14)
O(51)	2867(8)	2416(4)	1613(11)
C(51)	3473(14)	2869(7)	960(17)
C(6)	4957(12)	1773(7)	7497(15)
C(7)	2265(14)	1776(8)	7116(16)
C(81)	3665(12)	2597(6)	5539(13)
C(82)	2674(14)	2987(8)	5642(18)
C(83)	2751(18)	2569(10)	5280(25)
C(84)	3781(24)	3776(8)	4812(21)
C(85)	4866(17)	3404(7)	4687(18)
C(11)	5084(15)	1327(6)	3946(16)
O(11)	6152(10)	1424(6)	3829(12)
C(12)	2451(14)	600(7)	5324(16)
O(12)	3359(12)	190(5)	6073(13)
C(13)	2140(15)	445(6)	180(16)
O(13)	1662(12)	364(5)	-980(12)
C(14)	3096(14)	-151(8)	2685(18)
O(14)	3182(12)	-619(6)	3083(15)
C(15)	4242(20)	591(8)	1480(15)
O(15)	5267(12)	563(5)	1031(13)

2.221(3) and 2.175(3) Å respectively. The two phosphine ligands are nearly *trans* to the Fe-Co bond. The Co1-C2 and Fe1-C2 bond distances of 1.77(1) and 2.53(1) Å together with the Co1-C2-O2 and Fe1-Co1-C2 angles of 164.8(11) and 68.3(4)° are indicative of the semibridging nature of the C2O2 carbonyl ligand [10]. Probably the donor ability of the ester group and the  $\text{PMe}_2\text{Ph}$  ligand towards the Fe1 atom causes an electronic imbalance which is adjusted by transfer of charge from Fe to Co by means of a semibridging CO.

## Experimental

The new complexes were synthesized under nitrogen.  $^1\text{H}$  NMR spectra were recorded on a Bruker WP80 or a Bruker AM400 spectrometer with  $\text{CDCl}_3$  solutions. The  $\{^1\text{H}\}^{31}\text{P}$  and the  $\{^1\text{H}\}^{13}\text{C}$  spectra were recorded on a Bruker AM400 spectrometer in  $\text{CH}_2\text{Cl}_2$  and  $(\text{CD}_3)_2\text{CO}$  solutions, respectively. The  $^{31}\text{P}$  spectra were referenced to aqueous 85%  $\text{H}_3\text{PO}_4$ . The IR spectra were recorded in the  $\nu(\text{CO})$  region on a Perkin Elmer FT 1710 spectrophotometer with dichloromethane solu-

Table 2

Selected bond distances (Å) and angles (°) for  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**11**)

Co-Fe	2.558(3)	C(22)-O(21)	1.50(2)
O(1)-Fe	2.10(1)	C(4)-C(3)	1.45(2)
C(2)-Fe	2.72(2)	C(5)-C(4)	1.38(2)
C(4)-Fe	1.97(2)	O(5)-C(5)	1.18(2)
C(13)-Fe	1.78(2)	O(51)-C(5)	1.44(2)
C(14)-Fe	1.79(2)	C(51)-O(51)	1.41(2)
C(15)-Fe	1.60(2)	P-Co	2.186(4)
C(3)-Co	2.11(1)	C(4)-Co	1.98(1)
C(11)-Co	1.71(2)	C(12)-Co	1.75(2)
C(6)-P	1.83(1)	O(11)-C(11)	1.19(2)
C(7)-P	1.87(1)	O(12)-C(12)	1.18(2)
C(81)-P	1.82(1)	O(13)-C(13)	1.14(2)
C(2)-O(1)	1.27(2)	O(14)-C(14)	1.13(2)
O(21)-C(2)	1.30(2)	O(15)-C(15)	1.23(2)
C(3)-C(2)	1.42(2)		
O(1)-Fe-Co	83.4(3)	C(7)-P-C(6)	102.3(7)
C(2)-Fe-Co	62.9(3)	C(81)-P-Co	115.1(4)
C(2)-Fe-O(1)	26.7(4)	C(81)-P-C(6)	102.6(6)
C(4)-Fe-Co	49.8(4)	C(81)-P-C(7)	104.7(7)
C(4)-Fe-O(1)	84.8(6)	C(2)-O(1)-Fe	105.4(9)
C(4)-Fe-C(2)	58.8(6)	O(1)-C(2)-Fe	48.0(7)
C(13)-Fe-Co	153.9(5)	O(21)-C(2)-Fe	162.0(13)
C(13)-Fe-O(1)	91.2(6)	O(21)-C(2)-O(1)	115.3(15)
C(13)-Fe-C(2)	102.6(6)	C(3)-C(2)-Fe	77.7(9)
C(13)-Fe-C(4)	104.4(6)	C(3)-C(2)-O(1)	125.5(14)
C(14)-Fe-Co	104.0(5)	C(3)-C(2)-O(21)	119.2(16)
C(14)-Fe-O(1)	87.8(6)	C(22)-O(21)-C(2)	121.6(13)
C(14)-Fe-C(2)	108.6(6)	C(2)-C(3)-Co	100.8(9)
C(14)-Fe-C(4)	153.4(7)	C(4)-C(3)-Co	64.4(7)
C(14)-Fe-C(13)	101.3(7)	C(4)-C(3)-C(2)	113.0(14)
C(15)-Fe-Co	92.7(5)	Co-C(4)-Fe	80.7(6)
C(15)-Fe-O(1)	176.1(6)	C(3)-C(4)-Fe	108.3(12)
C(15)-Fe-C(2)	150.5(7)	C(3)-C(4)-Co	74.3(8)
C(15)-Fe-C(4)	93.1(8)	C(5)-C(4)-Fe	127.3(13)
C(15)-Fe-C(13)	92.6(7)	C(5)-C(4)-Co	121.6(11)
C(15)-Fe-C(14)	92.7(8)	C(5)-C(4)-C(3)	123.2(14)
P-Co-Fe	164.5(1)	O(5)-C(5)-C(4)	129.3(18)
C(3)-Co-Fe	72.6(4)	O(51)-C(5)-C(4)	11.5(11)
C(3)-Co-P	92.7(4)	O(51)-C(5)-O(5)	118.4(14)
C(4)-Co-Fe	49.5(5)	C(51)-O(51)-C(5)	114.6(11)
C(4)-Co-P	121.5(4)	C(82)-C(81)-P	123.3(12)
C(4)-Co-C(3)	41.3(5)	C(11)-Co-Fe	98.0(5)
C(11)-Co-P	95.4(5)	C(11)-Co-C(3)	130.8(6)
C(11)-Co-C(4)	95.6(7)	C(12)-Co-Fe	87.6(4)
C(12)-Co-P	94.8(4)	O(11)-C(11)-Co	175.7(13)
C(12)-Co-C(3)	116.9(6)	O(12)-C(12)-Co	178.7(14)
C(12)-Co-C(4)	133.1(7)	O(13)-C(13)-Fe	179.6(14)
C(12)-Co-C(11)	110.6(7)	O(14)-C(14)-Fe	176.9(15)
C(6)-P-Co	116.2(5)	O(15)-C(15)-Fe	175.2(14)
C(7)-P-Co	114.2(5)		

Table 3

Fractional atomic co-ordinates ( $\times 10^4$ ), with esd's in parentheses, for  $[(\text{CO})_2(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph}))(\mu\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})]$  (19)

Atom	x	y	z
Co(1)	24804(9)	10098(4)	71546(12)
Fe(1)	20219(9)	3441(4)	63935(13)
P(11)	2254(2)	1607(1)	7485(3)
P(12)	2210(2)	-54(1)	4876(3)
C(1)	3462(8)	986(3)	8118(11)
O(1)	4087(7)	993(3)	8755(9)
C(2)	1520(9)	853(3)	7808(11)
O(2)	921(6)	822(3)	8383(9)
C(3)	1155(8)	90(3)	7083(11)
O(3)	63686(9)	-80(2)	7553(8)
C(4)	2885(9)	120(3)	7470(12)
O(4)	3308(7)	-21(3)	8096(10)
C(11)	5054(7)	938(34)	4808(13)
O(11)	4121(5)	957(2)	4986(7)
C(12)	3818(7)	665(3)	5628(9)
O(12)	4265(5)	404(3)	6001(8)
C(13)	2869(7)	711(3)	5780(9)
C(14)	2359(6)	1020(2)	5229(8)
C(15)	1468(7)	922(3)	4947(9)
O(15)	1111(4)	620(2)	5249(6)
C(16)	103(6)	1068(3)	3883(10)
O(16)	1002(5)	1169(2)	4241(6)
C(101)	3029(7)	1944(3)	6905(10)
C(102)	3635(8)	1830(3)	6105(10)
C(103)	4214(8)	2087(4)	5610(11)
C(104)	4184(12)	2463(5)	5961(17)
C(105)	3621(13)	2572(5)	6801(19)
C(106)	3023(8)	2326(3)	7250(11)
C(111)	2267(10)	1725(4)	9109(12)
C(121)	1194(8)	1788(4)	6892(14)
C(131)	2487(11)	147(3)	3424(13)
C(132)	3358(18)	183(5)	3128(17)
C(133)	3605(16)	335(7)	2003(33)
C(134)	2877(19)	426(6)	1321(26)
C(135)	2021(16)	424(4)	1474(16)
C(136)	1818(12)	281(4)	2611(14)
C(141)	1222(9)	-326(4)	4478(14)
C(151)	3011(13)	-421(4)	5113(19)
Co(2)	24416(9)	-19481(3)	80133(11)
Fe(2)	29179(9)	-13164(4)	89823(12)
P(21)	2948(2)	-2494(1)	7465(2)
P(22)	2709(2)	-939(1)	10546(3)
C(5)	1452(7)	-1950(3)	7105(10)
O(5)	816(5)	-1953(2)	6482(7)
C(6)	3338(7)	-1714(3)	7357(10)
O(6)	3882(5)	-1654(2)	6690(7)
C(7)	2175(7)	-1074(3)	8001(9)
O(7)	1725(5)	-906(2)	7324(7)
C(8)	3810(7)	-1040(3)	8478(10)
O(8)	4387(5)	-862(2)	8173(8)
C(21)	-192(8)	-1335(4)	9393(14)
O(21)	702(5)	-1368(2)	9155(7)

Table 3 (continued)

Atom	x	y	z
C(22)	1081(7)	-1680(3)	9633(9)
O(22)	678(5)	-1913(2)	10175(8)
C(23)	2046(7)	-1693(3)	9478(8)
C(24)	2510(7)	-2025(3)	9924(9)
C(25)	3399(8)	-1937(3)	10269(9)
O(25)	3768(4)	-1634(2)	10048(6)
O(26)	3853(5)	-2214(2)	10884(7)
C(26)	4762(8)	-2153(4)	11242(13)
C(201)	2291(6)	-2912(3)	7731(8)
C(202)	2573(7)	-3268(3)	7449(9)
C(203)	2085(8)	-3588(3)	7616(10)
C(204)	1272(9)	-2553(3)	8052(11)
C(205)	920(7)	-3202(4)	8331(12)
C(206)	1450(7)	-2873(3)	8181(10)
C(211)	3106(8)	-2522(3)	5638(10)
C(221)	4033(8)	-2614(3)	8121(12)
C(231)	2449(9)	-1170(3)	11944(10)
C(232)	3243(10)	-1331(4)	12688(12)
C(233)	2937(15)	-1494(4)	13809(13)
C(234)	2085(16)	-1489(6)	14104(18)
C(235)	1389(16)	-1368(6)	13398(22)
C(236)	1604(12)	-1180(4)	12286(13)
C(241)	1835(18)	-580(5)	10323(17)
C(251)	2681(10)	-664(4)	10995(15)

tions. The mass spectra were obtained with a Hewlett-Packard 2985 GC/MS spectrometer. C and H elemental analyses were performed on a Perkin-Elmer 240-B analyzer.

The complexes  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CR}^1=\text{CR}^2\text{H})$  ( $\text{R}^1 = \text{CO}_2\text{Me}$  (**1**) or  $\text{CO}_2\text{Et}$  (**2**) and  $\text{R}^2 = \text{H}$ ) [6],  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CH}=\text{CRH})$  ( $\text{R} = \text{H}$  (**4**) or  $\text{Ph}$  (**5**)) [4,5] and  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**3**) [6] were prepared by published procedures. The syntheses and the spectroscopic data for complexes  $[(\text{CO})_3(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CR}^1=\text{CR}^2\text{H})$  ( $\text{R}^1 = \text{CO}_2\text{Me}$ ,  $\text{R}^2 = \text{H}$  (**6**) and  $\text{R}^1 = \text{CO}_2\text{Et}$ ,  $\text{R}^2 = \text{H}$  (**7**)) [6],  $[(\text{CO})_3(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_2](\mu-\text{CH}=\text{CPhH})$  (**8**) and  $[(\text{CO})(\text{PMe}_2\text{Ph})_2\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CO})(\mu-\text{CH}=\text{CRH})$  ( $\text{R} = \text{H}$  (**17**) or  $\text{Ph}$  (**18**)) [8] were described previously by our group but are been included here for comparison with the other phosphine-substituted compounds.

*Reaction of  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CR}^1=\text{CR}^2\text{H})$  ( $\text{R}^1 = \text{CO}_2\text{Me}$  (**1**) or  $\text{CO}_2\text{Et}$  (**2**) and  $\text{R}^2 = \text{H}$ ) with  $\text{PMe}_2\text{Ph}$  and  $\text{PPh}_3$ .*

*Addition of one equivalent of phosphine.* To a solution 0.3 g of  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CR}^1=\text{CR}^2\text{H})$  in 5 cm<sup>3</sup> of dichloromethane was added a stoichiometric amount of phosphine. The solution was stirred at room temperature for 15 min ( $\text{PMe}_2\text{Ph}$ ) or 30 min ( $\text{PPh}_3$ ) and then concentrated *in vacuo* and 2 cm<sup>3</sup> of methanol were added. The mixture was evaporated *in vacuo* until the crystals began to separate. The solution was kept for 1 h at -12°C and the product then filtered off and dried *in vacuo*. Yields were > 85% for complexes with  $\text{PMe}_2\text{Ph}$ : **5** and **7**; and 60% for complexes with  $\text{PPh}_3$ : **9** and **10**.

Table 4

Selected bond distances (Å) and angles (°) for [(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)Fe–Co(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)](μ-C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)H) (19)

Fe(1)–Co(1)	2.580(2)	Fe(2)–Co(2)	2.561(2)
P(11)–Co(1)	2.175(3)	P(21)–Co(2)	2.180(2)
C(1)–Co(1)	1.78(1)	C(6)–Co(2)	1.79(1)
C(2)–Co(1)	1.76(1)	C(23)–Co(2)	1.98(1)
C(13)–Co(1)	1.97(1)	C(24)–Co(2)	2.12(1)
C(14)–Co(1)	2.12(1)	P(22)–Fe(2)	2.220(3)
P(12)–Fe(1)	2.221(3)	C(6)–Fe(2)	2.40(1)
C(2)–Fe(1)	2.53(1)	C(7)–Fe(2)	1.74(1)
C(3)–Fe(1)	1.81(1)	C(8)–Fe(2)	1.79(1)
C(4)–Fe(1)	1.86(1)	C(23)–Fe(2)	1.99(1)
C(13)–Fe(1)	1.98(1)	C(5)–Co(2)	1.76(1)
O(15)–Fe(1)	2.06(1)	O(25)–Fe(2)	2.03(1)
O(1)–C(1)	1.15(2)	O(5)–C(5)	1.15(1)
O(2)–C(2)	1.15(2)	O(6)–C(6)	1.17(1)
O(3)–C(3)	1.15(2)	O(7)–C(7)	1.15(1)
O(4)–C(4)	1.07(27)	O(8)–C(8)	1.15(1)
O(11)–C(11)	1.45(1)	O(21)–C(21)	1.41(2)
C(12)–O(12)	1.35(1)	C(22)–O(21)	1.34(1)
O(12)–C(12)	1.21(1)	O(22)–C(22)	1.21(1)
C(13)–C(12)	1.48(1)	C(23)–C(22)	1.50(2)
C(14)–C(13)	1.45(1)	C(24)–C(23)	1.44(1)
C(15)–C(14)	1.42(1)	C(25)–C(24)	1.42(2)
O(15)–C(15)	1.26(1)	O(25)–C(25)	1.24(1)
O(16)–C(15)	1.34(1)	O(26)–C(25)	1.35(1)
O(16)–C(16)	1.45(1)	C(26)–O(26)	1.43(2)
C(1)–Co(1)–Fe(1)	110.6(4)	C(6)–Co(2)–Fe(2)	64.0(3)
C(1)–Co(1)–P(11)	94.7(4)	C(6)–Co(2)–P(21)	90.1(3)
C(2)–Co(1)–Fe(1)	68.3(4)	C(6)–Co(2)–C(5)	115.0(5)
C(2)–Co(1)–P(11)	95.3(4)	C(23)–Co(2)–Fe(2)	49.9(3)
C(2)–Co(1)–C(1)	115.5(6)	C(23)–Co(2)–P(21)	139.7(3)
C(13)–Co(1)–Fe(1)	49.4(3)	C(23)–Co(2)–C(5)	99.7(4)
C(13)–Co(1)–P(11)	135.2(3)	C(23)–Co(2)–C(6)	113.6(4)
C(13)–Co(1)–C(1)	98.6(5)	C(24)–Co(2)–Fe(2)	72.8(3)
C(13)–Co(1)–C(2)	116.4(5)	C(24)–Co(2)–P(21)	99.6(3)
C(14)–Co(1)–Fe(1)	71.6(2)	C(24)–Co(2)–C(5)	123.3(5)
C(14)–Co(1)–P(11)	98.5(3)	C(24)–Co(2)–C(6)	118.1(4)
C(14)–Co(1)–C(1)	127.8(5)	C(24)–Co(2)–C(23)	41.0(4)
C(14)–Co(1)–C(2)	113.2(5)	P(22)–Fe(2)–Co(2)	142.9(1)
C(14)–Co(1)–C(13)	41.4(4)	C(6)–Fe(2)–Co(2)	42.2(2)
P(12)–Fe(1)–Co(1)	141.1(1)	C(6)–Fe(2)–P(22)	172.8(3)
C(2)–Fe(1)–Co(1)	40.4(3)	C(7)–Fe(2)–Co(2)	90.9(3)
C(2)–Fe(1)–P(12)	167.0(3)	C(7)–Fe(2)–P(22)	93.7(3)
C(3)–Fe(1)–Co(1)	120.5(4)	C(7)–Fe(2)–C(6)	91.2(4)
C(3)–Fe(1)–P(12)	97.8(4)	C(8)–Fe(2)–Co(2)	123.1(4)
C(3)–Fe(1)–C(2)	80.5(5)	C(8)–Fe(2)–P(22)	93.7(4)
C(4)–Fe(1)–Co(1)	91.2(4)	C(8)–Fe(2)–C(6)	80.9(4)
C(4)–Fe(1)–P(12)	95.4(4)	C(8)–Fe(2)–C(7)	90.8(5)
C(4)–Fe(1)–C(2)	97.6(5)	C(23)–Fe(2)–Co(2)	49.7(3)
C(4)–Fe(1)–C(3)	90.5(5)	C(23)–Fe(2)–P(22)	93.2(3)
C(13)–Fe(1)–Co(1)	49.1(3)	C(23)–Fe(2)–C(6)	91.7(4)
C(13)–Fe(1)–P(12)	92.2(3)	C(23)–Fe(2)–C(7)	94.7(4)
C(13)–Fe(1)–C(2)	88.7(4)	C(23)–Fe(2)–C(8)	170.9(4)
C(13)–Fe(1)–C(3)	168.8(4)	C(25)–Fe(2)–Co(2)	64.4(2)

Table 4 (continued)

C(13)–Fe(1)–C(4)	93.5(5)	C(25)–Fe(2)–P(22)	97.5(2)
O(15)–Fe(1)–Co(1)	85.7(2)	C(25)–Fe(2)–C(6)	80.6(3)
O(15)–Fe(1)–P(12)	87.4(2)	C(25)–Fe(2)–C(7)	151.0(4)
O(15)–Fe(1)–C(2)	79.7(3)	C(25)–Fe(2)–C(8)	114.9(4)
O(15)–Fe(1)–C(3)	90.6(4)	C(25)–Fe(2)–C(23)	58.1(4)
O(15)–Fe(1)–C(4)	176.9(4)	O(25)–Fe(2)–Co(2)	85.0(2)
O(15)–Fe(1)–C(13)	84.9(3)	O(25)–Fe(2)–P(22)	90.1(2)
C(101)–P(11)–Co(1)	117.5(4)	O(25)–Fe(2)–C(6)	85.2(3)
C(111)–P(11)–Co(1)	113.1(4)	O(25)–Fe(2)–C(7)	175.8(4)
O(1)–C(1)–Co(1)	176.1(10)	O(25)–Fe(2)–C(8)	90.6(4)
Fe(1)–C(2)–Co(1)	71.3(4)	O(25)–Fe(2)–C(23)	83.4(3)
O(2)–C(2)–Co(1)	164.8(11)	O(25)–Fe(2)–C(25)	26.1(3)
O(2)–C(2)–Fe(1)	123.8(9)	O(5)–C(5)–Co(2)	178.1(10)
O(3)–C(3)–Fe(1)	176.7(10)	Fe(2)–C(6)–Co(2)	73.8(4)
O(4)–C(4)–Fe(1)	176.8(12)	O(6)–C(6)–Co(2)	159.2(8)
C(12)–O(11)–C(11)	114.1(8)	O(6)–C(6)–Fe(2)	127.0(7)

$[(\text{CO})_3(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Me})=\text{CH}_2)$  (**6**) (Found: C, 42.95; H, 3.20.  $\text{C}_{18}\text{H}_{16}\text{CoFeO}_8\text{P}$  calc.: C, 42.7; H, 3.15%). IR:  $\nu(\text{CO})$  2045m, 2004s, 1984s and 1670m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.86 (d,  $J$  7.4 Hz, 3H); 2.03 (d,  $J$  7.4 Hz, 3H); 3.18 (s, 1H); 3.60 (s, 1H); 3.61 (s, 3H) and 7.47 (m, 5H).  $\{^1\text{H}\}^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  26.17 (s).

$[(\text{CO})_3(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Et})=\text{CH}_2)$  (**7**) (Found: C, 43.6; H, 3.45.  $\text{C}_{19}\text{H}_{18}\text{CoFeO}_8\text{P}$  calc.: C, 43.85; H, 3.45%). IR:  $\nu(\text{CO})$  2050m, 2010s, 1990s and 1675m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.19 (t,  $J$  8 Hz, 3H); 1.79 (d,  $J$  4 Hz, 3H); 1.95 (d,  $J$  4Hz, 3H); 3.10 (s, 1H); 3.55 (s, 1H); 3.99 (q,  $J$  8 Hz, 2H) and 7.28 (s, 5H).

$[(\text{CO})_3(\text{PPh}_3)\text{Fe}-\text{Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Me})=\text{CH}_2)$  (**9**) (Found: C, 53.5; H, 3.31.  $\text{C}_{28}\text{H}_{20}\text{CoFeO}_8\text{P}$  calc.: C, 53.38; H, 3.17%). IR:  $\nu(\text{CO})$  2069m, 2028s, 1998vs and 1684  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.92 (s, 1H); 3.28 (s, 1H); 3.38 (s, 3H) and 7.45 (m, 15H).  $\{^1\text{H}\}^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  204.9 (CO); 176.1 (d,  $J(\text{C}-\text{P}) = 5.1$  Hz, C(CO<sub>2</sub>Me)=CH<sub>2</sub>); 134.1–128.4 (Ph); 62.4 (s, C(CO<sub>2</sub>Me)=CH<sub>2</sub>) and 51.8 (s, OCH<sub>3</sub>).

$[(\text{CO})_3(\text{PPh}_3)\text{Fe}-\text{Co}(\text{CO})_3](\mu\text{-C}(\text{CO}_2\text{Et})=\text{CH}_2)$  (**10**) (Found: C, 54.1; H, 3.5.  $\text{C}_{29}\text{H}_{23}\text{CoFeO}_8\text{P}$  calc.: C, 54.08; H, 3.41%). IR:  $\nu(\text{CO})$  2069m, 2007s, 1998vs and 1677m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.07 (t,  $J$  8 Hz, 3H); 3.37 (s, 1H); 3.75 (s, 1H); 3.896 (q,  $J$  8 Hz, 2H) and 7.50 (m, 15H).

*Addition of two equivalents of phosphine.* To a solution of 0.3 g of  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu\text{-CR}^1=\text{CR}^2\text{H})$  in 5  $\text{cm}^3$  of dichloromethane were added 2.5 equivalents of phosphine. The solution was stirred at room temperature for 1 h and the progress of the reaction monitored by IR spectroscopy. The solution at the end of the reaction contained two products, which were separated by chromatography on a silica column. The monosubstituted complex was eluted with a 1:4 dichloromethane–hexane mixture and the disubstituted complex with a 2:3 dichloromethane–hexane mixture. The second fraction was evaporated to dryness and crystallized from 3:2 dichloromethane–methanol mixture. Precipitation of the complex was completed at  $-12^\circ\text{C}$ . The product was filtered off and dried *in vacuo*. The yield was 50% for complexes **15** and **16**.

$[(\text{CO})_3(\text{PPh}_3)\text{Fe}-\text{Co}(\text{CO})_2(\text{PPh}_3)](\mu\text{-C}(\text{CO}_2\text{Me})=\text{CH}_2)$  (**15**) (Found: C, 61.6; H, 4.2.  $\text{C}_{45}\text{H}_{35}\text{CoFeO}_7\text{P}_2$  calc.: C, 62.54; H, 4.21%). IR:  $\nu(\text{CO})$  2049s, 1983vs, 1971sh,

1918m and 1671m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.84 (s, br, 4H); 3.31 (s, 1H) and 7.37 (m, 30H).  $\{^1\text{H}\}^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  205.5 (CO); 177.9 (t,  $J(\text{C}-\text{P}) = 4.6$  Hz,  $\text{C}(\text{CO}_2\text{Me})=\text{CH}_2$ ); 143.6 (br,  $\text{CO}_2\text{Me}$ ); 134.0–125.4 (Ph); 64.7 (br) and 51.0 (s,  $\text{OCH}_3$ ).

$[(\text{CO})_3(\text{PPh}_3)\text{Fe}-\text{Co}(\text{CO})_2(\text{PPh}_3)](\mu-\text{C}(\text{CO}_2\text{Me})=\text{CH}_2)$  (**16**) (Found: C, 62.1; H, 4.15.  $\text{C}_{46}\text{H}_{38}\text{CoFeO}_7\text{P}_2$  calc.: C, 62.91; H, 4.21%). IR:  $\nu(\text{CO})$  2048m, 1983vs, 1971s, 1917m and 1668m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.78 (t,  $J$  11.3 Hz, 3H); 2.95 (d,  $J(\text{P}-\text{H}) = 15.5$  Hz, 1H); 3.37 (s, 1H); 3.38 (m, 2H) and 7.44 (m, 30H).  $\{^1\text{H}\}^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  57.7 (s) and 68.0 (s, br).

*Reaction of complexes  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CH}=\text{CRH})$  ( $R = \text{H}$  (**4**) or  $\text{Ph}$  (**5**)) with  $\text{PMe}_2\text{Ph}$*

*Addition of one equivalent of phosphine.* To a stirred solution of 0.25 g of  $[(\text{CO})_4\text{FeCo}(\text{CO})_3](\mu-\text{CH}=\text{CPhH})$  in 5  $\text{cm}^3$  of dichloromethane was added an equivalent of  $\text{PMe}_2\text{Ph}$  with stirring. The mixture was stirred for 15 min at room temperature and then concentrated *in vacuo*. After addition of 3  $\text{cm}^3$  of methanol the solution was concentrated until a crystals appeared. Precipitation was completed at  $-12^\circ\text{C}$ , and the precipitate was then filtered off and dried *in vacuo*. The yield of complex **8** was  $> 80\%$ .

*Addition of two equivalents of phosphine.* To a solution of 0.25 g of complexes  $[(\text{CO})_4\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CH}=\text{CRH})$  ( $R = \text{H}$  (**4**) or (**5**)) in 5  $\text{cm}^3$  of dichloromethane was added a two-fold excess of  $\text{PMe}_2\text{Ph}$ . The solution was stirred for 30 min at room temperature and then evaporated to dryness *in vacuo*. The residue was dissolved in a minimum of dichloromethane and the product precipitated by addition of methanol and cooling to  $-12^\circ\text{C}$ . The red compounds **17** and **18** were obtained in  $> 80\%$  yield.

$[(\text{CO})_3(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CH}=\text{CPhH})$  (**8**) (Found: C, 49.7; H, 3.35.  $\text{C}_{22}\text{H}_{18}\text{CoFeO}_6\text{P}$  calc.: C, 50.40; H, 3.35%). IR:  $\nu(\text{CO})$  2045m, 2003s and 1987s  $\text{cm}^{-1}$ .  $\{^{31}\text{P}\}^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.81 (d,  $J$  1.4 Hz, 3H); 1.95 (d,  $J$  1.4 Hz, 3H); 4.93 (d,  $J$  11Hz, 1H); 7.85 (dd,  $J_1$  11,  $J_2$  12.5 Hz, 1H); 7.41 (br, 5H) and 7.55 (br, 5H).

$[(\text{CO})(\text{PMe}_2\text{Ph})_2\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CO})(\mu-\text{CH}=\text{CH}_2)$  (**17**) (Found: C, 50.25; H, 4.5.  $\text{C}_{23}\text{H}_{25}\text{CoFeO}_5\text{P}_2$  calc.: C, 49.20; H, 4.25%). IR:  $\nu(\text{CO})$  2037s, 1975s, 1958m and 1776  $\text{cm}^{-1}$ .  $\{^{31}\text{P}\}^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.47 (m, br, 12H); 2.39 (d,  $J$  7.3 Hz, 1H); 2.17 (d,  $J$  12 Hz, 1H); 7.34 (br, 5H); 7.39 (br, 5H) and 7.99 (dd,  $J_1$  7.3,  $J_2$  12 Hz, 1H).

$[(\text{CO})(\text{PMe}_2\text{Ph})_2\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{CO})(\mu-\text{CH}=\text{CPhH})$  (**18**) (Found: C, 54.5; H, 4.50.  $\text{C}_{29}\text{H}_{29}\text{CoFeO}_5\text{P}_2$  calc.: C, 54.40; H, 4.40%). IR:  $\nu(\text{CO})$  2034s, 1975s, 1962s, 1942m and 1775  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 2.53 (m, br, 12H); 2.80 (d,  $J$  12.3 Hz, 1H); 7.21 (br, 15H) and 8.00 (d,  $J$  12.3 Hz, 1H).

*Reaction of complex  $[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**3**) with the  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{PPh}_3$  and  $\text{PPhPh}_2$  ligands*

*Addition of one equivalent of phosphine.* To a stirred solution 0.5 g of complex **3** in 5  $\text{cm}^3$  of dichloromethane was added a stoichiometric amount of phosphine. The solution was stirred for 30 min at room temperature and the progress of the reaction monitored by IR spectroscopy. The solution was then concentrated *in vacuo* and 3  $\text{cm}^3$  of methanol were added. Concentration of the solution gave a crystalline

precipitate and crystallization was completed at  $-12^{\circ}\text{C}$  and the products were filtered off and dried *in vacuo*. The reaction with  $\text{PPh}_3$  yielded two products: **13a** and **13b**, which were separated by chromatography on a silica column (elution with a 1 : 3 dichloromethane–hexane mixture). The yields of the monosubstituted complexes **11**, **12**, **13a** + **13b** and **14** were 70%.

$[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**11**) (Found: C, 42.6; H, 3.4.  $\text{C}_{19}\text{H}_{18}\text{CoFeO}_9\text{P}$  calc.: C, 42.60; H, 3.19%). IR:  $\nu(\text{CO})$  at 2052s, 1998s, 1975w, 1940m, 1680m and  $1555\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.31 (s, 3H); 1.54 (s, 3H); 2.88 (s, 3H); 3.26 (s, 3H); 3.60 (d,  $J(\text{P}-\text{H}) = 9.6\text{ Hz}$ , 1H) and 7.34 (m, 5H).  $\{^1\text{H}\}^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  27.8 (s, br).

$[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PMePh}_2)](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**12**) (Found: C, 48.0; H, 3.41.  $\text{C}_{24}\text{H}_{20}\text{CoFeO}_9\text{P}$  calc.: C, 42.60; H, 3.34%). IR:  $\nu(\text{CO})$  2067s, 1998vs, 1932m, 1683m and  $1556\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.00 (d,  $J$  9.14 Hz, 3H); 3.17 (s, 3H); 3.60 (d,  $J(\text{P}-\text{H}) = 13.3\text{ Hz}$ , 1H); 3.74 (s, 3H) and 7.32 (m, 10H).

$[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PPh}_3)](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**13a**) and  $[(\text{CO})_2(\text{PPh}_3)\text{Fe}-\text{Co}(\text{CO})_3](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**13b**) (Found: C, 52.7; H, 3.45.  $\text{C}_{29}\text{H}_{22}\text{CoFeO}_9\text{P}$  calc.: C, 52.77; H, 3.33%). **13a** IR:  $\nu(\text{CO})$  2068s, 2000vs, 1927s, 1686m and  $1554\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.26 (s, 3H); 3.60 (d,  $J(\text{P}-\text{H}) = 11.2\text{ Hz}$ , 1H); 3.84 (s, 3H) and 7.41 (m, 15H).  $\{^1\text{H}\}^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  60.7 (s, br). **13b** IR:  $\nu(\text{CO})$  2049s, 2006vs, 1987s, 1684m and  $1559\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.15 (s, 3H); 3.39 (s, 3H); 4.19 (s, 1H) and (m, 15H).  $\{^1\text{H}\}^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  62.2 (s).

$[(\text{CO})_3\text{Fe}-\text{Co}(\text{CO})_2(\text{PPhPh}_2)](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**14**). IR:  $\nu(\text{CO})$  at 2068s, 2002vs, 1930sh, 1687m and  $1557\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.34 (s, 3H); 3.72 (d,  $J(\text{P}-\text{H}) = 13.6\text{ Hz}$ , 1H); 3.74 (s, 3H) and 6.55 (d,  $J(\text{P}-\text{H}) = 358.4\text{ Hz}$ , 1H).

*Addition of two equivalents of phosphine.* The method used was similar to that used for the reaction of complex **3** with one equivalent of phosphine, but in the present case the phosphine ligand was added in a two-fold excess. The progress of the reaction was monitored by IR spectroscopy, which showed that a 2 : 3 mixture of the mono and disubstituted complexes was obtained. The products were separated by chromatography on a silica column. The monosubstituted complexes were eluted with a 1 : 3 dichloromethane–hexane mixture and the disubstituted complexes then obtained in pure form by elution with a 2 : 3 dichloromethane mixture. Complexes **19–21** were obtained in 60% yield.

$[(\text{CO})_2(\text{PMe}_2\text{Ph})\text{Fe}-\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**19**) (Found: C, 48.2; H, 4.5.  $\text{C}_{26}\text{H}_{29}\text{CoFeO}_8\text{P}_2$  calc.: C, 48.34; H, 4.49%). IR:  $\nu(\text{CO})$  at 2008vs, 1952vs, 1869sh, 1669m and  $1542\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.71 (m, 12H); 3.11 (s, 3H); 3.50 (d,  $J(\text{P}-\text{H}) = 11.2\text{ Hz}$ , 1H); 3.72 (s, 3H) and 7.31 (m, 10H).

$[(\text{CO})_2(\text{PMePh}_2)\text{Fe}-\text{Co}(\text{CO})_2(\text{PMePh}_2)](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**20**). IR:  $\nu(\text{CO})$  2012 vs, 1956vs, 1873m, 1667m and  $1545\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.04 (m, 6H); 3.01 (s, 3H); 3.46 (d,  $J(\text{P}-\text{H}) = 13.6\text{ Hz}$ , 1H); 3.57 (s, 3H) and 7.28 (m, 20H).

$[(\text{CO})_2(\text{PPh}_3)\text{Fe}-\text{Co}(\text{CO})_2(\text{PPh}_3)](\mu-\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{H})$  (**21**) (Found: C, 62.7; H, 4.7.  $\text{C}_{45}\text{H}_{37}\text{CoFeO}_8\text{P}_2$  calc.: C, 61.79; H, 4.14%). IR:  $\nu(\text{CO})$  2010vs, 1957s, 1900m, 1669m and  $1553\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.84 (s, 3H); 3.34 (s, 3H); 3.52 (d,  $J(\text{P}-\text{H}) = 10\text{ Hz}$ , 1H) and 7.37 (m, 15H).



### Crystal structure determination

A.  $[(CO)_3Fe-Co(CO)_2(PMe_2Ph)](\mu-C(CO_2Me)=C(CO_2Me)H)$  (11). Crystal data.  $C_{19}H_{18}CoFeO_9P$ ,  $M = 504.1$ , monoclinic,  $a = 10.801(2)$ ,  $b = 22.949(5)$ ,  $c = 9.185(s)$  Å,  $\beta = 97.65(2)^\circ$ ,  $V = 2256(1)$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 25 automatically-centered reflections,  $\lambda = 0.71069$  Å), space group  $P2_1/n$ ,  $Z = 4$ ,  $D_c = 1.483$  g cm<sup>-3</sup>,  $\mu(Mo-K_\alpha) = 14.69$  cm<sup>-1</sup>,  $T = 298$  K.

Data collection and processing. Phillips PW-1100 diffractometer,  $\omega$ -scan technique with scan width  $1^\circ$ , scan speed  $0.03$  s<sup>-1</sup>, graphite-monochromated Mo- $K_\alpha$  radiation; 1635 independent reflections measured ( $2 \leq \theta \leq 25^\circ$ ), 1577 of which were assumed as observed. No significant intensity decay was observed. Lorentz-polarization, but not absorption, corrections were made.

Structure analysis and refinement. Direct methods (MULTAN80 system of programs) [11]. Full-matrix least-squares refinement (SHELX76 computer programs) [12]. The minimized function was  $\sum w \| F_o | - | F_c ||^2$ , where  $w = [\sigma^2(F_o) + 0.0068 | F_o |^2]^{-1}$ . Final  $R$  and  $R'$  values were 0.067 and 0.073, respectively.

B.  $[(CO)_2(PMe_2Ph)Fe-Co(CO)_2(PMe_2Ph)](\mu-C(CO_2Me)=C(CO_2Me)H)$  (19). Crystal data.  $C_{26}H_{29}CoFeO_8P_2$ .  $M = 647.25$ , monoclinic,  $a = 15.269(2)$ ,  $b = 35.361(6)$ ,  $c = 11.023(2)$  Å,  $\beta = 93.77(2)$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 25 automatically centred reflections,  $\lambda = 0.71069$  Å), space group  $P2_1/a$ ,  $Z = 8$ ,  $D_c = 1.447$  g cm<sup>-3</sup>,  $\mu(Mo-K_\alpha) = 12.34$  cm<sup>-1</sup>,  $T = 298$  K.

Data collection and processing. Phillips PW-1100 diffractometer,  $\omega$ -scan technique with scan width  $0.8^\circ$ , scan speed  $0.03^\circ$  s<sup>-1</sup>, graphite-monochromated Mo- $K_\alpha$  radiation; 4189 independent reflections measured ( $2 \leq \theta \leq 25^\circ$ ), 4009 of which were assumed as observed. No significant intensity decay was not observed. Lorentz-polarization, but not absorption, corrections were made.

Structure analysis and refinement. Direct methods (MULTAN80 system of programs) [11]. Full-matrix least-squares refinement (SHELX76 programs) [12]. The function minimized was  $\sum w \| F_o | - | F_c ||^2$  where  $w = [\sigma(F_c) + 0.0016 | F_o |^2]^{-1}$ . The final  $R$  and  $R'$  values were 0.05 and 0.053, respectively.

For both crystal structures tables of thermal parameters, complete lists of bond lengths and angles, and lists of structure factors are available from the authors.

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