Reaction of [FeCo(CO)$_7$(μ-CH=CRH)] (R = H or Ph) with Dimethylphenylphosphine. Synthesis and Structure of [FeCo(CO)$_4$(μ-CO)(PMe$_2$Ph)$_2$(μ-CH=CH$_2$)],† an Electronically Unbalanced Iron–Cobalt Complex

Isabel Moldes, Josep Ros,* and Ramón Yañez
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 a l'Université Paul Sabatier, 205 Route de Narbonne, 31077 Toulouse, France
Xavier Solans and Mercé Font-Bardía
Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, Gran Vía 585, 08007 Barcelona, Spain

The reaction of [FeCo(CO)$_7$(μ-CH=CRH)] (R = H or Ph) with PMe$_2$Ph leads to complexes [FeCo(CO)$_6$(PMe$_2$Ph)(μ-CH=CPhH)] and [FeCo(CO)$_5$(PMe$_2$Ph)$_2$(μ-CH=CRH)]. The disubstituted compounds contain two PMe$_2$Ph ligands linked to iron and two bridging ligands, carbonyl and vinyl. The structure of [FeCo(CO)$_4$(μ-CO)(PMe$_2$Ph)$_2$(μ-CH=CH$_2$)] has been solved by *X*-ray diffraction methods.

In recent papers we have described the synthesis and the structure of Fe–Co vinyl-bridged complexes [FeCo(CO)$_7$(μ-CH=CRH)] [R = H (**1**) or Ph (**2**)].[1,2] We are interested in their reactivity toward phosphines as two types of problems are envisaged. Nucleophilic attack of phosphines could occur on the vinyl ligand giving a phosphonium group as has previously been observed,[3] or at a metal centre with the question of metalloselectivity of the substitution reaction. Some examples of metalloselectivity have been observed in carbonyl substitution in mixed bi- or poly-nuclear species.[4–6]

In this note we present the results of the reactivity of complexes (**1**) and (**2**) towards PMe$_2$Ph and the *X*-ray structure of a disubstituted complex of (**1**) which shows that the replacement of two CO groups by phosphines induces a complete electronic redistribution in the molecule.

Results and Discussion

When the heterobinuclear complexes [FeCo(CO)$_7$(μ-CH=CRH)], [R = H (**1**) or Ph (**2**)] are treated with PMe$_2$Ph at room temperature, two types of products are obtained resulting from the mono- and di-substitution of carbonyl ligands by PMe$_2$Ph. In particular, the reaction of (**1**) with 1 or 2 equivalents of PMe$_2$Ph always gives only the disubstituted complex [FeCo(CO)$_5$(PMe$_2$Ph)$_2$(μ-CH=CH$_2$)] (**3**). Complex (**2**) reacts with 1 or 2 equivalents of PMe$_2$Ph leading to the formation of [FeCo(CO)$_6$(PMe$_2$Ph)(μ-CH=CPhH)] (**4**) and [FeCo(CO)$_5$(PMe$_2$Ph)$_2$(μ-CH=CPhH)] (**5**). The formation of disubstituted complexes (**3**) and (**5**) is characteristic in all these reactions. The resulting products were characterized by i.r., ^{1}H n.m.r., and mass spectroscopies and C and H elemental analyses.

The i.r. spectrum of complex (**4**) in the CO stretching region shows only terminal CO groups. The presence of one PMe$_2$Ph ligand and a 2-phenylethenyl bridge is confirmed by ^{1}H n.m.r. spectroscopy. The mass spectrum shows a peak $[M - 5\text{CO}]^+$ at m/z = 384, while the [FePMe$_2$Ph]$^+$ fragment is at m/z = 194 suggesting that the PMe$_2$Ph ligand is bonded to iron.[7]

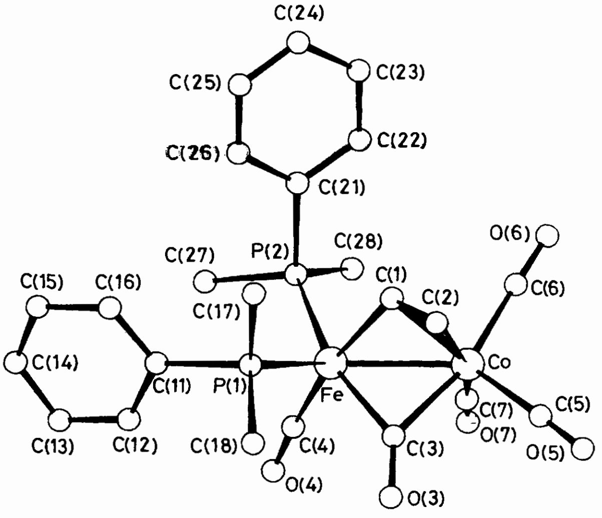

Figure. Structure of [FeCo(CO)$_4$(μ-CO)(PMe$_2$Ph)$_2$(μ-CH=CH$_2$)] (**3**) showing the atomic numbering scheme

Spectroscopic data for complexes (**3**) and (**5**) indicate the substitution of two CO ligands by two PMe$_2$Ph groups while the vinyl bridge remains unchanged. The i.r. spectra of the complexes are similar, characteristic of terminal CO ligands except for a band of medium intensity at *ca.* 1 775 cm^{-1} which can be attributed to a bridging CO group. The ^{1}H n.m.r. spectra at room temperature show broad signals corresponding to vinylic protons coupled with two phosphorus atoms. Thus for complex (**3**) only the ^{31}P-decoupled ^{1}H n.m.r. spectrum allows observation of a double doublet at 7.99 (J_1 = 7.3 and J_2 = 12) and doublets at 2.39 (J_1 = 7.3) and 2.17 p.p.m. (J_2 = 12 Hz) characteristic of a μ-η^2-bonded vinyl ligand. In the mass spectra only some fragments are observed of which the most significant are [FePMe$_2$Ph]$^+$ at m/z = 194 and [Fe(PMe$_2$Ph)$_2$]$^+$ at m/z = 332, suggesting that the two phosphines are linked to Fe. The fragment [CoPMe$_2$Ph]$^+$ at m/z = 197 was not observed.

In order to elucidate the nature of the disubstituted complexes, we have determined the *X*-ray structure of (**3**) (Figure). Selected bond lengths and angles are shown in Table 1. Complex (**3**) maintains the bimetallic vinyl bridge of the starting

---

† μ-Carbonyl-1,1,1,2-tetracarbonyl-2,2-bis(dimethylphenylphosphine)-μ-[vinyl-C^1(Co,Fe)C^2(Co)]-cobaltiron (*Co–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected bond distances (Å) and angles (°) for [FeCo(CO)$_4$(μ-CO)(PMe$_2$Ph)$_2$(μ-CH=CH$_2$)] (**3**)

Co–Fe	2.521(3)	C(1)–Co	2.063(14)	C(11)–P(1)	1.811(14)	C(2)–C(1)	1.426(19)
P(1)–Fe	2.193(5)	C(2)–Co	2.192(14)	C(17)–P(1)	1.795(17)	O(3)–C(3)	1.199(16)
P(2)–Fe	2.284(4)	C(3)–Co	1.987(16)	C(18)–P(1)	1.828(16)	O(4)–C(4)	1.142(18)
C(1)–Fe	1.929(14)	C(5)–Co	1.817(19)	C(21)–P(2)	1.809(16)	O(5)–C(5)	1.112(18)
C(3)–Fe	1.895(15)	C(6)–Co	1.813(19)	C(27)–P(2)	1.815(14)	O(6)–C(6)	1.134(18)
C(4)–Fe	1.769(20)	C(7)–Co	1.730(18)	C(28)–P(2)	1.841(17)	O(7)–C(7)	1.193(18)
P(1)–Fe–Co	130.5(1)	C(1)–Co–Fe	48.5(4)	C(7)–Co–Fe	87.9(5)	C(28)–P(2)–Fe	113.8(6)
P(2)–Fe–Co	107.9(1)	C(2)–Co–Fe	76.6(4)	C(7)–Co–C(1)	128.7(7)	C(28)–P(2)–C(21)	102.0(8)
P(2)–Fe–P(1)	106.4(2)	C(2)–Co–C(1)	39.0(5)	C(7)–Co–C(2)	164.4(7)	C(28)–P(2)–C(27)	101.9(9)
C(1)–Fe–Co	53.2(4)	C(3)–Co–Fe	47.9(4)	C(7)–Co–C(3)	88.8(7)	Co–C(1)–Fe	78.3(5)
C(1)–Fe–P(1)	91.6(4)	C(3)–Co–C(1)	80.2(6)	C(7)–Co–C(5)	100.7(8)	C(2)–C(1)–Fe	121.1(11)
C(1)–Fe–P(2)	91.6(4)	C(3)–Co–C(2)	79.8(6)	C(7)–Co–C(6)	92.8(7)	C(2)–C(1)–Co	75.4(8)
C(3)–Fe–Co	51.1(5)	C(5)–Co–Fe	139.2(5)	C(11)–P(1)–Fe	114.8(5)	C(1)–C(2)–Co	75.6(8)
C(3)–Fe–P(1)	99.6(5)	C(5)–Co–C(1)	129.4(7)	C(17)–P(1)–Fe	117.2(6)	Co–C(3)–Fe	81.0(6)
C(3)–Fe–P(2)	154.0(5)	C(5)–Co–C(2)	90.4(7)	C(17)–P(1)–C(11)	103.1(8)	O(3)–C(3)–Fe	139.6(13)
C(3)–Fe–C(1)	86.1(6)	C(5)–Co–C(3)	92.0(7)	C(18)–P(1)–Fe	115.4(6)	O(3)–C(3)–Co	138.9(12)
C(4)–Fe–Co	114.0(5)	C(6)–Co–Fe	118.2(5)	C(18)–P(1)–C(11)	102.9(8)	O(4)–C(4)–Fe	175.3(16)
C(4)–Fe–P(1)	100.6(5)	C(6)–Co–C(1)	87.9(7)	C(18)–P(1)–C(17)	101.4(9)	O(5)–C(5)–Co	177.0(17)
C(4)–Fe–P(2)	89.7(5)	C(6)–Co–C(2)	95.7(7)	C(21)–P(2)–Fe	118.7(5)	O(6)–C(6)–Co	178.3(16)
C(4)–Fe–C(1)	166.8(6)	C(6)–Co–C(3)	166.0(7)	C(27)–P(2)–Fe	116.0(6)	O(7)–C(7)–Co	178.2(15)
C(4)–Fe–C(3)	87.0(7)	C(6)–Co–C(5)	101.3(7)	C(27)–P(2)–C(21)	102.1(8)		

complex (**1**). The Fe and Co atoms are bridged by μ-CH=CH$_2$ and μ-CO ligands and separated by a distance of 2.521(3) Å consistent with the presence of a single bond.[8] This distance is short compared with those observed in other Fe–Co ethenyl-bridged complexes: [FeCo(CO)$_7$(μ-CH=CPhH)], 2.563(3) Å,[2] and [FeCo(CO)$_6${μ-MeOC(O)C=CHC(O)OMe}], 2.593(3) Å,[7] containing an electron-withdrawing organic bridge. The Fe atom is co-ordinated to two PMe$_2$Ph and one terminal CO ligands while the Co atom is bonded to three terminal CO ligands. The vinyl bridge is σ-bonded to Fe [1.929(14) Å] and unsymmetrically η^2-co-ordinated to Co [2.063(14) and 2.192(14) Å]. The bridging CO is unsymmetrically linked to Fe [1.895(15) Å] and to Co [1.987(16) Å]. The two PMe$_2$Ph ligands are in *cis* configuration [106.4(2)°] and the phosphorus atoms form a plane with Fe and C(3), perpendicular to the carbonyl C(4)O(4). The σ bond of the vinyl ligand is nearly *trans* to C(5)O(5) while C(1) and C(2) are pseudo-*trans* to C(7)O(7). The shortest metal–carbonyl distances are Fe–C(4) [1.769(20) Å] and Co–C(7) [1.730(18) Å] indicative of an increase in electronic density on metals also forming closest contacts between the metallic centres.

So it appears that substitution of two CO ligands by two PMe$_2$Ph is regiospecific and induces a complete electronic re-equilibration in the complex leading to a situation difficult to rationalize. The most important feature of the molecule is the presence of a bridging CO and according to a recent structural analysis of semibridging carbonyl ligands[9] the C(3)O(3) ligand can be considered as bridging slightly unsymmetrically. Taking into account the ligands around each metal centre and the metal–metal bond, this leads to a configuration in which Fe is surrounded by 17 valence electrons and Co by 19. However, if we neglect the metal–metal bond, iron is surrounded by 16 valence electrons, Co by 18, and the Fe–Co bond could then be considered as a donor from Co to Fe. So whatever the exact electronic situation, which is certainly between the two extreme situations described here, the increase in charge on Fe induced by CO substitution by phosphine ligands is distributed over the whole molecule through the formation of a bridging carbonyl ligand.

In conclusion, basic phosphines like PMe$_2$Ph attack the more electrophilic metal, even where one CO linked to Fe has been substituted by PMe$_2$Ph. This indicates that the formation of complexes (**1**) and (**2**) containing iron(I) and cobalt(0) centres is adequate.

Experimental

All reactions were performed under a nitrogen atmosphere. Proton n.m.r. spectra were recorded on a Bruker WP80 spectrometer in CDCl$_3$ solutions and ^{31}P-decoupled ^{1}H n.m.r. spectra on a Bruker WH90 spectrometer in CD$_2$Cl$_2$ solution. Infrared spectra were recorded in the ν(CO) region on a Beckman IR 20A spectrophotometer in cyclohexane solutions. Mass spectra were measured on a Hewlett-Packard 2985 GC/MS spectrometer. Analyses of C and H were performed on a Perkin-Elmer 240-B analyzer.

Preparations.—[FeCo(CO)$_6$(PMe$_2$Ph)(μ-CH=CPhH)] (**4**). To complex (**2**) (0.25 g) dissolved in dichloromethane (5 cm^3) was added a stoicheiometric amount of PMe$_2$Ph and the solution was stirred for 30 min at room temperature. The solution was evaporated to dryness and the residue crystallized in a dichloromethane–methanol mixture at −20 °C (Found: C, 49.70; H, 3.35. Calc. for C$_{22}$H$_{18}$CoFeO$_6$P: C, 50.40; H, 3.45%). I.r.: ν(CO) at 2 045m, 2 003s, and 1 987s cm^{-1}. ^{1}H N.m.r. (CDCl$_3$): δ 1.81 (d, 3 H, *J* 1.4), 1.95 (d, 3 H, *J* 1.4), 4.93 (d, 1 H, *J* 11), 7.85 (dd, 1 H, J_1 11, J_2 12.5 Hz), 7.41 (br, 5 H), and 7.55 p.p.m. (br, 5 H).

[FeCo(CO)$_4$(μ-CO)(PMe$_2$Ph)$_2$(μ-CH=CRH)] [R = H (**3**) *or* Ph (**5**)]. Complex (**1**) or (**2**) (0.25 g) was dissolved in dichloromethane (5 cm^3) and a two-fold excess of PMe$_2$Ph was added. The solution was stirred for 30 min at room temperature and then evaporated to dryness. Dissolving the residue in a dichloromethane–methanol mixture and cooling to −20 °C gave red crystals of (**3**) or (**5**) in good yield. Complex (**3**) (Found: C, 50.25; H, 4.50. Calc. for C$_{23}$H$_{25}$CoFeO$_5$P$_2$: C, 49.20; H, 4.25%). I.r.: ν(CO) at 2 037s, 1 975s, 1 958m, and 1 776m cm^{-1}. ^{1}H-{^{31}P} N.m.r. (CD$_2$Cl$_2$): 1.47 (br m, 12 H), 2.39 (d, 1 H, J_1 7.3), 2.17 (d, 1 H, J_2 12), 7.34 (br, 5 H), 7.39 (br, 5 H), and 7.99 p.p.m. (dd, 1 H, J_1 7.3, J_2 12 Hz). Complex (**5**) (Found: C, 54.45; H, 4.50. Calc. for C$_{29}$H$_{29}$CoFeO$_5$P$_2$: C, 54.40; H, 4.40%). I.r.: ν(CO) at 2 034s, 1 975s, 1 962s, 1 942m, and 1 775m cm^{-1}. ^{1}H N.m.r. (CDCl$_3$): 2.53 (br m, 12 H), 3.80 (d, 1 H, *J* 12.3), 7.21 (br, 15 H), and 8.00 p.p.m. (d, 1 H, *J* 12.3 Hz).

Table 2. Fractional atomic co-ordinates (× 10^4) (with estimated standard deviations in parentheses) for $[FeCo(CO)_4(\mu\text{-}CO)(PMe_2Ph)_2(\mu\text{-}CH{=}CH_2)]$ (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	7 370(2)	2 639(2)	4 507(2)	C(25)	7 464(17)	−762(25)	6 943(23)
Co	6 665(2)	1 320(2)	2 114(3)	C(26)	7 862(13)	242(18)	6 520(23)
P(1)	6 506(3)	3 695(4)	6 916(5)	C(27)	9 550(13)	2 300(17)	5 657(23)
C(11)	7 366(13)	4 508(16)	8 259(17)	C(28)	9 503(15)	525(20)	2 561(21)
C(12)	8 120(15)	5 553(19)	8 145(22)	C(1)	6 302(11)	1 168(15)	4 154(16)
C(13)	8 813(16)	6 169(21)	9 084(24)	C(2)	5 281(11)	1 274(16)	3 953(16)
C(14)	8 788(19)	5 739(27)	10 165(28)	C(3)	6 637(12)	3 251(16)	3 585(17)
C(15)	8 078(24)	4 762(26)	10 355(25)	O(3)	6 398(9)	4 283(11)	3 709(13)
C(16)	7 354(16)	4 144(18)	9 373(21)	C(4)	8 415(15)	3 849(18)	4 367(18)
C(17)	5 537(15)	2 724(18)	7 737(18)	O(4)	9 059(10)	4 634(13)	4 204(14)
C(18)	5 691(15)	5 054(18)	7 343(20)	C(5)	5 768(14)	1 518(16)	1 149(20)
P(2)	8 597(3)	1 387(4)	4 466(5)	O(5)	5 200(11)	1 684(13)	618(16)
C(21)	8 104(12)	33(15)	5 004(18)	C(6)	6 812(13)	−476(19)	1 118(20)
C(22)	7 882(14)	−1 278(17)	3 923(20)	O(6)	6 897(11)	−1 600(13)	467(16)
C(23)	7 445(15)	−2 271(19)	4 424(27)	C(7)	7 910(14)	1 640(16)	1 079(19)
C(24)	7 273(15)	−2 028(23)	5 916(33)	O(7)	8 769(10)	1 825(12)	339(14)

Crystallography.—*Crystal data for* (**3**). $C_{23}H_{25}CoFeO_5P_2$, *M* = 556.2, triclinic, *a* = 12.936(3), *b* = 11.292(3), *c* = 10.124(3) Å, α = 117.74(2), β = 73.20(2), γ = 100.17(2)°, *U* = 1 251(1) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P\bar{1}$, *Z* = 2, D_c = 1.475 g cm^{-3}. Poor quality red crystals of dimensions 0.1 × 0.1 × 0.15 mm; $\mu(\text{Mo-}K_\alpha)$ = 14.40 cm^{-1}, *T* = 288 K.

Data collection and processing. Phillips PW-1100 diffractometer, ω-scan technique with scan width 0.8°, scan speed 0.03° s^{-1}, graphite-monochromated Mo-K_α radiation; 1 928 reflections measured ($\theta \leqslant 25°$), 1 484 unique with $I \geqslant 2.5\sigma(I)$. Significant intensity decay was not observed. Lorentz polarization but not absorption corrections were made.

Structure analysis and refinement. Direct methods using the MULTAN [10] system of computer programs. Full-matrix least-squares refinement (isotropic and anisotropic). The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0036|F_o|^2]^{-1}$. Final *R* and *R'* values 0.063 and 0.065. The largest peak in the final difference synthesis was 0.4 e Å^{-3}, 1.2 Å from C(1). The maximum shift-to-error ratio is 0.4 for C(3). The computer programs were as given in refs. 10 and 11. Fractional co-ordinates are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We are grateful to C.A.I.C.YT. of Spain for financial support, N.A.T.O. Scientific Affairs Division for a travel grant, and Fluka AG for reagents.

References

1 J. Ros and R. Mathieu, *Organometallics*, 1983, **2**, 771.

2 I. Moldes, J. Ros, R. Yañez, X. Solans, M. Font-Altaba, and R. Mathieu, *J. Organomet. Chem.*, 1986, **315**, C22.

3 K. Henrick, M. McPartlin, A. J. Deeming, S. Hasso, and P. Manning, *J. Chem. Soc., Dalton Trans.*, 1982, 899.

4 D. J. Robinson, E. A. Darling, and N. J. Coville, *J. Organomet. Chem.*, 1986, **310**, 203.

5 S. Guesmis, P. H. Dixneuf, N. J. Taylor, and A. J. Carty, *J. Organomet. Chem.*, 1986, **303**, C47.

6 M. Hidai, H. Matsuzaka, Y. Koyasu, and Y. Uchida, *J. Chem. Soc., Chem. Commun.*, 1986, 1451.

7 I. Moldes, J. Ros, R. Mathieu, X. Solans, and M. Font-Bardía, *J. Chem. Soc., Dalton Trans.*, 1987, 1619.

8 D. A. Roberts and G. L. Geoffroy, 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, ch. 40, p. 803.

9 R. H. Crabtree and M. Lavin, *Inorg. Chem.*, 1986, **25**, 805.

10 P. Main, S. E. Fiske, S. L. Hull, L. Lessinger, G. Germain, J. P. Declerq, and M. M. Woolfson, MULTAN, An Automatic System of Computer Programs for Crystal Structure Determination from *X*-Ray Diffraction Data, Universities of York and Louvain, 1980.

11 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

Received 17*th July* 1987; *Paper* 7/1281