Notes

Formation of a Methoxycarbonyl Group by Attack of Methanol on an Iron(II) Carbonyl Complex, assisted by Intramolecular Proton Transfer: *X*-Ray Structure Determination of $[Fe(CO)(PMe_3)_2(CNC_6H_{11})\{CO(OCH_3)\}\{C(CH_3)=NHC_6H_{11}\}]$-$BPh_4$†

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The reaction of $[Fe(CO)_2(PMe_3)_2\{C(=CH_2)N(C_6H_{11})C(=NHC_6H_{11})\}]I$ with CH_3OH gives $[Fe(CO)(PMe_3)_2(CNC_6H_{11})\{CO(OCH_3)\}\{C(CH_3)=NHC_6H_{11}\}]I$, which, with $NaBPh_4$, precipitates $[Fe(CO)(PMe_3)_2(CNC_6H_{11})\{CO(OCH_3)\}\{C(CH_3)=NHC_6H_{11}\}][BPh_4]$ (**2**). The molecular structure of (**2**) has been determined by single-crystal *X*-ray diffraction techniques. The complex shows octahedral symmetry with two PMe_3 ligands in the *trans* position, CO and CNC_6H_{11} ligands in the *cis* position, and the two remaining σ-bonded ligands [$-CO(OCH_3)$ and $-C(CH_3)=NHC_6H_{11}$] also in the *cis* position. The structure was confirmed by i.r. and ^1H n.m.r. spectroscopy.

Alkoxycarbonyl carbonyl complexes are believed to be intermediates in important catalytic reactions.[1] One of the most important of these processes is the carbonylation of alcohols.[2] The Monsanto low-pressure liquid-phase process for acetic acid production *via* Rh-catalysed carbonylation of methanol is one example that focuses attention on the importance of this reaction for practical use.[3]

The alkoxycarbonyl complexes can be obtained by attack of the anions OR^- on carbon monoxide co-ordinated to transition metals.[4,5] Attack of alcohols on carbon monoxide co-ordinated to transition metals in order to obtain esters or other derivatives is less common;[6] in these cases a proton acceptor is necessary to drive the reaction to completion.[6]

The present paper reports the results of nucleophilic attack of CH_3OH on a carbonyl group of a positively charged d^6 complex.[7,8]

Experimental

Dichloromethane was distilled from P_2O_5 and commercial methyl alcohol was used without further purification. The complex $[Fe(CO)_2(PMe_3)_2\{C(=CH_2)N(C_6H_{11})C(=NHC_6H_{11})\}]I$ (**1**) was prepared as previously described.[7,8] All reactions were carried out under nitrogen. Infrared spectra were recorded on a 983 Perkin-Elmer spectrophotometer. ^1H N.m.r. spectra were obtained with a JEOL CHL 60 spectrometer using $SiMe_4$ as internal reference. Elemental analyses were carried out with a Carlo Erba 1106 analyser. Chromatographic measurements were performed with a Carlo Erba 2350 Fractovap instrument.

Preparation of $[Fe(CO)(PMe_3)_2(CNC_6H_{11})\{CO(OCH_3)\}\{C(CH_3)=NHC_6H_{11}\}]BPh_4$ (**2**).—Complex (**1**) (0.3 g) was dissolved in CH_3OH (30 cm^3). To this solution $NaBPh_4$ (0.180 g) (molar ratio 1:1.1) was added. Slow crystallization was observed and white-yellow crystals were obtained, yield 20% (Found: C, 68.2; H, 8.25; N, 3.30. Calc. for $C_{48}H_{67}BFeN_2O_3P_2$: C, 67.9; H, 7.95; N, 3.30%).

Preparation of $[Fe(CO)(PMe_3)_2(CNC_6H_{11})\{CO(OCH_3)\}\{C(CD_3)=NDC_6H_{11}\}]BPh_4$ (**3**).—Complex (**1**) (0.2 g) was dissolved in CH_3OD (10 cm^3) and $NaBPh_4$ (0.120 g) (molar ratio 1:1) added. The solution was left at −18 °C. Slow crystallization of (**3**) was observed (four months). The complex showed the same behaviour as (**2**). In the i.r. spectrum the N–H stretching frequency at 3 198 cm^{-1} disappeared, but no N–D stretching was observed. The ^1H n.m.r. spectrum showed the disappearance of the band at τ 7.68 p.p.m. assigned to the $C-CH_3$ group.

Transformation of Complex (**2**) *into Complex* (**1**).—Complex (**2**) was dissolved in 1,2-dichloroethane (5×10^{-3} mol dm^{-3}). After 3 d it was transformed into complex (**1**), characterized previously.[7,8] During the reaction CH_3OH was produced and after distillation from the reaction mixture it was analysed by gas chromatography. The amount of CH_3OH corresponded to the stoicheiometric composition of complex (**2**).

X-*Ray Structure Determination of Complex* (**2**).—A crystal of dimensions 0.23 × 0.18 × 0.18 mm was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with graphite-monochromatized Mo-K_α radiation ($\lambda = 0.710\,69$ Å). The crystals are monoclinic. Cell dimensions were determined at room temperature by a least-squares calculation based on the setting angles of 25 reflections with 2θ in the range 15—20°.

Crystal data. $C_{48}H_{67}BFeN_2O_3P_2$, $M = 848.6$, $a = 17.874(3)$, $b = 20.481(3)$, $c = 13.236(3)$ Å, $\beta = 99.67(2)°$, $U = 4\,845.4$ Å^3, space group $P2_1/n$ (from systematic extinctions and intensity distribution statistics), $D_c = 1.178$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) = 3.89 cm^{-1}, $F(000) = 1\,816$.

Intensities were collected up to $2\theta = 50°$ using the ω—2θ scan technique, a scan range of 1.5°, and a scan speed of 0.05° s^{-1}. Owing to the poor quality of the crystal out of a total of

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† Carbonyl[1-(cyclohexyliminio)ethyl](cyclohexyl isocyanide)(methoxycarbonyl)bis(trimethylphosphine)iron(II) tetraphenylborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates for complex (**2**) (estimated standard deviations in parentheses refer to the last digit)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	0.027 5(1)	0.178 9(1)	0.413 1(2)
P(1)	−0.007 2(3)	0.092 3(2)	0.313 7(3)
P(2)	0.055 0(3)	0.272 9(2)	0.497 0(4)
O(1)	−0.047 7(8)	0.129 7(7)	0.576 0(11)
O(2)	−0.077 4(7)	0.254 2(7)	0.270 4(11)
O(3)	−0.125 1(8)	0.208 2(7)	0.393 1(11)
N(1)	0.163 4(9)	0.109 3(7)	0.531 5(10)
N(2)	0.057 9(8)	0.242 4(7)	0.229 9(10)
C(1)	0.067 2(13)	0.031 3(11)	0.304 4(17)
C(2)	−0.047 3(12)	0.106 5(10)	0.179 2(15)
C(3)	−0.081 6(11)	0.041 8(10)	0.354 5(15)
C(4)	0.066 3(18)	0.345 0(16)	0.424 0(24)
C(5)	0.150 5(15)	0.276 1(14)	0.583 3(20)
C(6)	−0.001 0(20)	0.294 5(18)	0.589 6(27)
C(7)	0.113 9(10)	0.137 5(8)	0.484 9(11)
C(8)	0.227 0(12)	0.073 5(10)	0.588 8(16)
C(9)	0.287 1(13)	0.122 0(11)	0.642 7(17)
C(10)	0.326 9(17)	0.142 9(15)	0.576 4(23)
C(11)	0.376 3(19)	0.081 6(16)	0.532 1(25)
C(12)	0.298 1(16)	0.052 6(14)	0.460 5(22)
C(13)	0.259 8(20)	0.026 1(17)	0.515 5(25)
C(14)	−0.019 9(10)	0.150 6(9)	0.509 6(14)
C(15)	0.088 3(9)	0.207 5(8)	0.309 4(12)
C(16)	0.095 2(12)	0.261 0(11)	0.136 4(16)
C(17)	0.037 2(13)	0.257 3(11)	0.043 6(16)
C(18)	0.074 1(16)	0.279 7(14)	−0.052 1(21)
C(19)	0.099 1(14)	0.347 0(13)	−0.029 7(19)
C(20)	0.160 7(19)	0.348 7(18)	0.063 6(25)
C(21)	0.121 4(17)	0.327 4(14)	0.158 0(22)
C(22)	0.171 6(11)	0.194 2(9)	0.312 9(14)
C(23)	−0.064 1(11)	0.218 3(10)	0.346 9(15)
C(24)	−0.199 5(15)	0.237 8(13)	0.346 3(18)
B	0.249 3(10)	0.012 0(9)	1.016 8(13)
C(25)	0.304 2(5)	−0.010 5(5)	0.930 8(7)
C(26)	0.272 1(5)	−0.047 0(5)	0.845 5(7)
C(27)	0.316 5(5)	−0.066 5(5)	0.773 7(7)
C(28)	0.393 1(5)	−0.049 4(5)	0.787 3(7)
C(29)	0.425 3(5)	−0.012 9(5)	0.872 7(7)
C(30)	0.380 8(5)	0.006 5(5)	0.944 4(7)
C(31)	0.172 3(5)	0.050 5(5)	0.952 0(7)
C(32)	0.101 6(5)	0.046 5(5)	0.983 2(7)
C(33)	0.039 4(5)	0.079 4(5)	0.928 3(7)
C(34)	0.047 8(5)	0.116 3(5)	0.842 3(7)
C(35)	0.118 5(5)	0.120 3(5)	0.811 2(7)
C(36)	0.180 7(5)	0.087 4(5)	0.866 0(7)
C(37)	0.221 7(6)	−0.052 5(5)	1.079 1(8)
C(38)	0.208 4(6)	−0.113 0(5)	1.031 1(8)
C(39)	0.179 9(6)	−0.164 6(5)	1.082 2(8)
C(40)	0.164 8(6)	−0.155 6(5)	1.181 3(8)
C(41)	0.178 1(6)	−0.095 1(5)	1.229 3(8)
C(42)	0.206 6(6)	−0.043 5(5)	1.178 2(8)
C(43)	0.296 1(6)	0.063 5(5)	1.100 6(7)
C(44)	0.279 3(6)	0.130 1(5)	1.097 5(7)
C(45)	0.320 3(6)	0.172 3(5)	1.168 9(7)
C(46)	0.378 0(6)	0.148 0(5)	1.243 5(7)
C(47)	0.394 8(6)	0.081 5(5)	1.246 7(7)
C(48)	0.353 9(6)	0.039 2(5)	1.175 2(7)

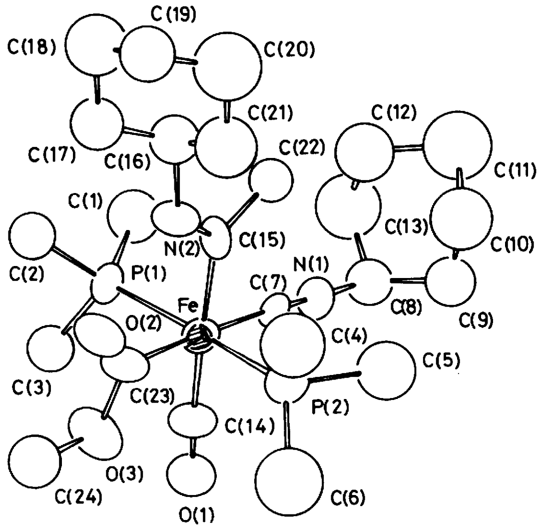

Figure. View of the cation $[Fe(CO)(PMe_3)_2(CNC_6H_{11})\{CO(OCH_3)\}\{C(CH_3)=NHC_6H_{11}\}]^+$ of (**2**)

8 750 independent measured reflections, only 2 173 having $I > 3\sigma(I)$ were retained for subsequent calculations. Three standard reflections, which were measured periodically, showed no apparent variation in intensity during data collection. The data were corrected for Lorentz and polarization factors. During the refinement an empirical absorption correction was applied according to the method of Walker and Stuart.[9] Correction factors were in the range 1.05—0.85.

The structure was solved by Patterson and Fourier methods and refined by the full-matrix least-squares method using the SHELX 76[10] package of programs. The phenyl groups were constrained to perfect hexagons (C–C = 1.395 Å) and refined as rigid groups. The hydrogen atoms (with the exception of those of the methyl groups) were included at calculated positions (C–H = 1.08 Å) with two overall isotropic parameters which refined to U = 0.17 and 0.11 Å^2 respectively for the H atoms of the cyclohexyl and phenyl groups. Anisotropic thermal parameters were refined for Fe, P, O, and N atoms, and for the carbon atoms directly co-ordinated to iron. Refinement converged at R = 0.089 and R' = 0.095 for 244 parameters and 2 173 observed reflections $\{R' = [\Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)]/(\Sigma w^{\frac{1}{2}}F_o)$, $w = [\sigma^2(F_o) + 0.0003F_o^{\,2}]^{-1}\}$. Atomic scattering factors were taken from ref. 10 for P, O, N, C, B, and H and from ref. 11 for Fe, the correction for anomalous dispersion being included.

Fractional atomic co-ordinates are listed in Table 1.

Results and Discussion

The Figure shows a view of the molecular structure of the cation of complex (**2**). Significant bond distances and angles are listed in Table 2. The complex shows octahedral geometry with two PMe_3 ligands in the *trans* position. In the planes perpendicular to the P–P axis lie a carbonyl ligand, an isocyanide ligand, and two *cis* bonds arising from the $-C(CH_3)=NHC_6H_{11}$ and $-CO(OCH_3)$ groups. The cyclohexyliminio and methoxycarbonyl groups are planar, as indicated by the calculated deviations of the atoms from their planes.* The Fe–P, Fe–CO, and Fe–CNC_6H_{11} bond distances are very close to those observed for similar iron complexes.[7,8,12,13] The Fe–$CO(OCH_3)$ [1.902(18) Å] and Fe–$C(CH_3)NC_6H_{11}$ [1.977(15) Å] distances are much shorter than those observed for iron–alkyl bonds (*ca.* 2.1 Å).[14,15]

The methyl group of the methoxycarbonyl is *cis* to the carbonyl oxygen; further, the methyl group of the cyclo-

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* FeC(15)C(22)N(2)C(16) and FeC(23)O(2)O(3) respectively.

Table 2. Significant bond distances (Å) and angles (°) in complex (**2**)

Fe–P(1)	2.233(5)	C(14)–O(1)	1.162(22)
Fe–P(2)	2.236(5)	C(15)–C(22)	1.507(21)
Fe–C(7)	1.875(15)	C(15)–N(2)	1.312(21)
Fe–C(14)	1.746(17)	C(16)–N(2)	1.549(24)
Fe–C(15)	1.977(15)	C(23)–O(2)	1.242(25)
Fe–C(23)	1.902(18)	C(23)–O(3)	1.353(21)
C(7)–N(1)	1.146(21)	C(24)–O(3)	1.498(27)
C(8)–N(1)	1.454(24)		

P(1)–Fe–P(2)	173.1(2)	Fe–P(2)–C(4)	118.5(9)
P(1)–Fe–C(7)	93.6(5)	Fe–P(2)–C(6)	115.5(7)
P(1)–Fe–C(14)	92.7(5)	Fe–P(2)–C(6)	117.3(10)
P(1)–Fe–C(15)	87.5(4)	Fe–C(7)–N(1)	175.3(14)
P(1)–Fe–C(23)	86.2(5)	C(9)–C(8)–N(1)	109.8(14)
P(2)–Fe–C(7)	92.5(5)	C(13)–C(8)–N(1)	109.4(17)
P(2)–Fe–C(14)	90.9(5)	Fe–C(14)–O(1)	176.0(13)
P(2)–Fe–C(15)	89.4(4)	Fe–C(15)–C(22)	125.5(10)
P(2)–Fe–C(23)	87.9(5)	Fe–C(15)–N(2)	121.1(10)
C(7)–Fe–C(14)	86.5(7)	C(22)–C(15)–N(2)	113.4(12)
C(7)–Fe–C(15)	89.1(6)	C(17)–C(16)–N(2)	108.5(14)
C(7)–Fe–C(23)	176.0(7)	C(21)–C(16)–N(2)	104.0(15)
C(14)–Fe–C(15)	175.6(6)	Fe–C(23)–O(2)	131.2(12)
C(14)–Fe–C(23)	89.5(7)	Fe–C(23)–O(3)	115.1(11)
C(15)–Fe–C(23)	94.9(6)	O(2)–C(23)–O(3)	113.6(14)
Fe–P(1)–C(1)	116.5(6)	C(7)–N(1)–C(8)	178.8(16)
Fe–P(1)–C(2)	118.2(6)	C(15)–N(2)–C(16)	126.8(12)
Fe–P(1)–C(3)	114.7(6)	C(23)–O(3)–C(24)	118.6(14)

hexyliminio ligand is *cis* to the cyclohexyl ring. This behaviour appears to be general[16] for the methoxycarbonyl group but not for the cyclohexyliminio group, for which the *cis* structure is observed in Mo complexes[17] and the *trans* structure in Pt complexes.[18]

The structure of complex (**2**) is confirmed by the i.r. and ^{1}H n.m.r. spectroscopic results. Complex (**2**) shows a band at 2 141 cm^{-1} assigned to the C=N stretching of the isocyanide ligand, a band at 1 986 cm^{-1} assigned to the C=O stretching, and a band at 1 558 cm^{-1} assigned to the C=N stretching of the $-C(CH_3)=NHC_6H_{11}$ group. A band at 1 597 cm^{-1} is tentatively assigned to the $CO(OCH_3)$ group. The ^{1}H n.m.r. spectrum shows a band at τ 6.58 p.p.m., assigned to the OCH_3 group of the methoxycarbonyl ligand, and a band at τ 7.68 p.p.m. assigned to the $C-CH_3$ group. This latter band disappears when complex (**2**) is prepared in CH_3OD, in which scrambling of the hydrogens of the $C=CH_2$ group of complex (**1**) with deuterium occurs.[8] The triplet at τ 8.72 p.p.m. (J = 4.2 Hz) confirms the *trans* position of the PMe_3 ligands.[19] Location of the iminium proton is more difficult; the band at 3 198 cm^{-1} in the i.r. spectrum, which disappears in complex (**3**), suggests that this proton is bonded to the iminic nitrogen. This is in agreement with the fact that, when alcohols react with carbonyl ligands to give alkoxycarbonyl groups, a base is necessary to bond the proton.[6] In complex (**1**) the iminic nitrogen acts as a base.

Formation of complex (**2**) from (**1**) is a reversible reaction and complex (**1**) is easily reobtained by dissolving (**2**) in CH_2Cl_2. This requires easy transfer of the proton to the alkoxy group, even though the rest of the process requires, successively, a complex rearrangement to give complex (**1**). The N(2) $\cdots$ O(2) separation of 2.57 Å is consistent with hydrogen bonding between these atoms and accounts for the easy transfer of the proton to the methoxycarbonyl group.

The reactivity of complex (**1**) confirms the lability of the heterocyclic structure, which is stabilized by subtle balancing of the electron density. This explains the difficulty of observing this structure with other isocyanide ligands.[8]

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