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# Stabilization of dimethyliron(II) and methylcobalt(I) complexes bearing a hemilabile 2-benzoylpyridine ligand in octahedral and square-pyramidal coordination

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### ABSTRACT

Octahedral *cis*-Fe(CH<sub>3</sub>)<sub>2</sub>{2-(benzoyl)pyridyl-*N*,*O*}(PMe<sub>3</sub>)<sub>2</sub> (**1**), square-pyramidal Co(CH<sub>3</sub>){2-(benzoyl)pyridyl-*N*,*O*}(PMe<sub>3</sub>)<sub>2</sub> (**2**), and triangular-planar Ni{2-(benzoyl)pyridyl- $\eta^2$ -*C*,*O*}(PMe<sub>3</sub>)<sub>2</sub> (**3**) have been synthesized by reaction of 2-benzoylpyridine with thermally labile Fe(CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> and Co(CH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub> complexes. With Ni(CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>, reductive elimination of ethane is observed when a  $\eta^2$ -*C*,*O*-coordination is constituted. The complexes were investigated by NMR spectroscopic methods and the molecular structures of **1** and **2** were determined by X-ray crystallography.

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### 1. Introduction

The interest in complexes containing a 2-benzoylpyridine [N,O] coordination is substantiated by their hemilability that facilitates substrate binding and can stabilize reactive intermediates of transition metals [1].

As a rare example of an isolable product, a palladium center with N,O-coordination has been described, where carbon monoxide/alkene insertion into the Pd–C bond is observed [2]. A rhodium complex containing a related dipyridylketone backbone, by insertion of ethene forms a five-membered oxametallacycle [3]. These can be seen as model compounds for studying the growth of an alkyl-metal chain.

Furthermore, in the case of 2-benzoylpyridine the interest in neutral N,O ligands is based on the above-mentioned properties and the relation with isoelectronic benzophenones and -imines which *Murai* demonstrated at ruthenium centers for catalyzed functionalization at the *ortho* position with 100% regioselectivity [4].

The main feature from most previously reported reactions of  $Co(CH_3)(PMe_3)_4$  and  $Fe(CH_3)_2(PMe_3)_4$  (Scheme 1) containing thermally labile methyl groups, is C–H activation of various organic

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substrates, assisted by [N, O, P] coordinating donor functions (D) [5]. The reaction pathway for the newly formed M–C bond is irreversible, since methane does not cleave a Fe–C or Co–C bond which does occur with dihydrogen [6].

Our recent study of C–H activation was concerned with vinylicand aromatic C–H bonds of 1,4-CH/N exchanged azadiene systems in 2-vinylphenylpyridine (**A**), benzophenoneimine (**B**) [7], and isoelectronic benzophenone prechelating ligands (**C**) [8], containing a set of hard (carbon)/soft (oxygen, nitrogen) donor atoms. Cyclometalation was observed under mild conditions (-70 °C), with high regioselectivity. The reactions proceeded by evolution of methane forming stable five-membered [C,N]- or [C,O]-metallacycles (Scheme 2).

Our interest in the related 2-benzoylpyridine (**D**) is substantiated by the combination of soft/soft ligand donor effects and the presence of further possible coordination sites, with isoelectronic constitution as in **A**, **B**, and **C**. Typically [N,O]-coordination is observed, other activation sites appear likely (indicated by arrow) where the question of preference in N/O donor or five-/six-membered ring coordination by C–H activation with Fe(CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>, Co(CH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>, and Ni(CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> arises.

The [N,O] coordination chemistry of 2-benzyolpyridine has been well described previously with many transition metals for example with Zn [9], Mn [10], Cu [11], Ru [12], or Rh [13], typically carrying additional sets of hard donor atoms [Cl, O, N]. Surprisingly there are only few literature reports of organometallic compounds bearing 2-benzoylpyridine, described for Rh [14], Pd [15], Ru [16],

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M= Co, Fe

Scheme 1. C-H activation with methyliron and methylcobalt.



M = Co, FeH

Scheme 2. 18 Electron-chelates of cobalt(I) and iron(II).

Fe [17], Re [18], whereas only one methylpalladium complex has been described [19].

Here we report the results of our studies on the reactivity of methyl(Fe, Co, Ni) complexes with 2-benzoylpyridine.

### 2. Experimental

### 2.1. General considerations

All air-sensitive and volatile materials were handled using standard vacuum techniques, und were kept under argon. Microanalyses: Kolbe Microanylytical Laboratory, Mühlheim/Ruhr, Germany. Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. Chemicals 2-benzoylpyridine (Merck/Schuchardt) were used as purchased. Literature methods were applied for the preparation of trimethylphosphine [41], [Fe-Me<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>] [42], [CoMe(PMe<sub>3</sub>)<sub>4</sub>] [43], and [NiMe<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>] [44]. And IR: Nujol mulls between KBR discs, Bruker spectrophotometer type FRA 106. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra (500 MHz, 125 MHz, and 202 MHz, respectively) were recorded with a Bruker Bruker DRX 500 spectrometer. <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} resonances were obtained with broad-band proton decoupling.

### 2.1.1. Preparation of cis-dimethyl-[2-(benzoylpyridine)κN,κO]bis(trimethylphosphine)-iron(II) (**1**)

2-Benzoylpyridine (366 mg, 1.99 mmol) in 30 mL of diethyl ether were combined at -70 °C with FeMe<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (786 mg, 1.99 mmol) in 80 mL of diethyl ether. During warm-up evolution of gas was noticed, and a red brown color was attained. The mixture was kept at 20 °C for 3 h. The volatiles were removed in vacuo and the solid residue was extracted with two 70 mL portions of

diethyl ether and the solution cooled to -27 °C to afford rhombic crystals with brown faces of **1**. Yield 723 mg (86%); m.p. 82–84 °C (dec.). IR (Nujol):  $v = 1577 \text{ cm}^{-1}$  m (v C=C); 1492 cm<sup>-1</sup> m (v C=O); 1192 w, 1173 w ( $\delta_{\rm s}$  Fe–CH<sub>3</sub>); 937 s ( $\rho_{\rm 1}$  PCH<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, [D<sub>8</sub>]THF, 293 K):  $\delta = 0.31$  (s(br), 3H, Fe–CH<sub>3</sub>); 0.51 (s(br), 3H, Fe–CH<sub>3</sub>); 0.95 (s(br), 9H, PCH<sub>3</sub>), 1.25 (s(br), 9H, PCH<sub>3</sub>), 6.52–8.51 (m, 9H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>8</sub>]THF, 293 K):  $\delta = 17.3$  (m, PCH<sub>3</sub>); 111.9 (s, CH); 121.3 (s, CH); 122.5 (s, CH); 123.8 (s, CH); 126.0 (s, CH); 126.3 (s, CH); 129.8 (s, CH); 146.4 (s, C); 152.4 (s, CH); 154.1 (s, C=N); 160.1 (s, C=O). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, [D<sub>8</sub>]THF, 203 K, ppm):  $\delta = -15.6$  (d, <sup>2</sup>*J*<sub>P,P</sub> = 56.2 Hz, 1P, PCH<sub>3</sub>), 10.7 (d, <sup>2</sup>*J*<sub>P,P</sub> = 56.2 Hz, 1P, PCH<sub>3</sub>). *Anal.* Calc. for C<sub>20</sub>H<sub>33</sub>Fe-NOP<sub>2</sub> (421.3): C, 57.02; H, 7.90; N, 3.32. Found: C, 56.97; H, 8.12; N, 3.36%.

### 2.1.2. Preparation of methyl-[2-(benzoylpyridine)-

### *κN*,*κ*O]bis(trimethylphosphine)cobalt(I) (**2**)

2-Benzoylpyridine (324 mg, 1.77 mmol) in 50 mL of THF were combined at -70 °C with CoMe(PMe<sub>3</sub>)<sub>4</sub> (670 mg, 1.77 mmol) in 50 mL of THF with a color change from red to dark blue within 3 h, while the mixture is coming to r.t. After further stirring for 3 h at 20 °C, all volatiles were removed in vacuo and the solid residue was extracted with two 80 mL portions of diethylether. From the solution 460 mg of dark blue quadrangular crystals were obtained at 4 °C which proved suitable for X-ray diffraction. Upon cooling to -27 °C a second fraction of **2** was collected and combined with the first. Yield 602 mg (83%); m.p. 91–93 °C (dec.). IR (Nujol): v = 1579 cm<sup>-1</sup> m (v C=C); 1485 cm<sup>-1</sup> m (v C=O); 1172 w ( $\delta_s$  Co-CH<sub>3</sub>); 935 s ( $\rho_1$  PCH<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, [D<sub>8</sub>]THF, 293 K, ppm):  $\delta = 0.51$  (s, 3H, Co-CH<sub>3</sub>); 1.27 (s(br), 18H, PCH<sub>3</sub>); 6.65 (t,  ${}^{3}J_{H,H} = 7.3$  Hz, 1H, Ar-H); 7.09 (t,  ${}^{3}J_{H,H} = 7.5$  Hz, 1H, Ar-H); 7.53 (dd,  ${}^{3}J_{H,H} = 6.6$  Hz,  ${}^{3}J_{H,H} = 9.2$  Hz, 1H, Ar-H); 7.84 (t,

<sup>3</sup>*J*<sub>H,H</sub> = 5.5 Hz, 1H, Ar-H); 8.02 (d, <sup>3</sup>*J*<sub>H,H</sub> = 8.3 Hz, 1H, Ar-H); 8.12 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 7.4 Hz, <sup>3</sup>*J*<sub>P,H</sub> = 12.0 Hz, 2H, Ar-H); 8.44 (t, <sup>4</sup>*J*<sub>P,H</sub> = 5.9 Hz, 1H, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>8</sub>]THF, 293 K, ppm):  $\delta$  = -29.3 (m, Co-CH<sub>3</sub>); 16.3 (d, <sup>1</sup>*J*<sub>P,C</sub> = 16.2 Hz, PCH<sub>3</sub>); 111.9 (s, CH); 121.9 (s, CH); 123.1 (s, CH); 124.3 (s, CH); 126.8 (s, CH); 130.3 (s, CH); 146.9 (s, C); 152.9 (s, CH); 154.7 (s, C=N); 160.8 (s, C=O). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, [D<sub>8</sub>]THF, 203 K, ppm):  $\delta$  = -5.7 (s(br), 2P, PCH<sub>3</sub>). *Anal.* Calc. for C<sub>19</sub>H<sub>30</sub>CoNOP<sub>2</sub> (409.3): C, 55.75; H, 7.39; P, 15.13. Found: C, 55.60; H, 7.19; P, 15.28%.



# 2.1.3. Preparation of [2-(benzoylpyridine)- $\eta^2$ -C,O]bis (trimethylphosphine)nickel(0) (**3**)

To a solution of NiMe<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (837 mg, 2.64 mmol) in 50 mL pentane (483 mg, 2.64 mmol) of 2-benzoylpyridine dissolved in 50 mL diethyl ether were added dropwise at - 70 °C. During warm up the yellow solution darkens, accompanied with gas evolution (ethane) and a yellow powder starts to precipitate. After 6 h the mixture was filtered through a sinter disc (G3). The remaining solid was washed with 50 mL ice-cold pentane affording an analytical pure, highly sensitive sample of **3** in (593 mg) 57% yield; m.p. 91–94 °C (dec.). Efforts to get crystals suitable for X-ray diffraction failed with solutions of pentane, ether, and THF or mixtures thereof. IR (Nujol):  $v = 1579 \text{ cm}^{-1} \text{ m} (v \text{ C=C})$ ; 924 s ( $\rho_1 \text{ PCH}_3$ ). <sup>1</sup>H NMR (500 MHz, [D<sub>8</sub>]THF, 293 K, ppm): *δ* = 1.15 (s(br), 18H, PCH<sub>3</sub>); 7.37 (m, 3H, Ar-H); 7.53 (t,  ${}^{3}J_{H,H} = 8.1 \text{ Hz}$ , 1H, Ar-H); 7.88 (t,  ${}^{3}J_{H,H}$  = 8.1 Hz, 1H, Ar-H); 8.14 (m, 3H, Ar-H); 8.61 (d,  ${}^{3}J_{H,H}$  = 7.5 Hz, 1H, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>8</sub>]THF, 293 K, ppm):  $\delta$  = 15.3 (d,  ${}^{1}J_{P,C}$  = 19.2 Hz, PCH<sub>3</sub>); 16.3 (d,  ${}^{1}J_{P,C}$  = 21.3 Hz, PCH<sub>3</sub>); 122.3 (s, CH); 125.2 (s, CH); 127.1 (s, CH); 130.1 (s, CH); 132.8 (s, CH); 135.5 (s, CH); 147.1 (s, NiC=O); 154.7 (s, CN). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz,  $[D_8]$ THF, 293 K, ppm):  $\delta = 0.9$  (s(br), 2P, PCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, [D<sub>8</sub>]THF, 203 K, ppm):  $\delta = -12.4$  (d,  ${}^{2}J_{P,P} = 57.1$  Hz, 1P, PCH<sub>3</sub>), -15.3 (d,  ${}^{2}J_{P,P}$  = 57.1 Hz, 1P, PCH<sub>3</sub>). Anal. Calc. for C<sub>18</sub>H<sub>27</sub>NNiOP<sub>2</sub> (394.06): C, 54.86; H, 6.91; N, 3.55; P, 15.72. Found: C, 54.30; H, 7.31; N, 3.42; P, 15.18.

### 2.1.4. X-ray structure determinations

Data collection was performed on a STOE IPDSII image plate detector Mo K $\alpha$  radiation ( $\lambda$  = 0.71019 Å). Details of the crystal structure are given in Table 1. Data collection: Stoe XAREA [44]. Cell refinement: Stoe x-AREA [45]. Data reduction: Stoe x-RED [45]. The structure was solved by direct methods using SHELXS-97 [46], and anisotropic displacement parameters were applied to nonhydrogen atoms in a full-matrix least-squares refinement based on  $F^2$  using SHELXL-97 [46]. In the title compounds, the hydrogen atoms on C were placed at calculated positions (C–H = 0.93 Å, 0.96 Å for methyl groups) and were allowed to ride on the parent atom [Uiso(H) = 1.2U(C) for CH groups and Uiso(H) = 1.5U(C) for methyl groups]. For (1) the disordered PMe<sub>3</sub> group could be treated with a split model with site occupation factors of 0.58(1) for C211-C231 and 0.42(1) for C212-C232 each. The disordered P(2)Me<sub>3</sub> group in (2) was similarly split into C141-C161 with s.o.f = 0.61(1) and C142-C162 with s.o.f. = 0.39(1) but with isotropic model. However, it was not possible to model the apparent disorder of P(1)Me<sub>3</sub> group accordingly, so the large a.d.p.'s of C17–C19 have no physical relevance.

### 3. Results and discussion

When simply combining the starting materials  $Fe(CH_3)_2(PMe_3)_4$ with 2-benzoylpyridine in diethyl ether (Eq. (1)) at -70 °C a slow color change from red to brown is observed when the reaction mixture is allowed to warm to 20 °C during 3 h.



From concentrated ether solutions at -27 °C dark red-brown, rhombic crystals of **1** were isolated which remained unchanged under air for 3 h, although their solutions are decomposed within a few seconds if air is admitted. High yields up to 86% of **1** were obtained when crystallization was neglected and the product simply washed with ice-cold pentane, which afforded an analytically pure sample.

By IR a bathochromic coordination shift of the C=O stretching frequency to  $1490 \text{ cm}^{-1}$  is observed next to a less intensive band at  $1173 \text{ cm}^{-1}$  which is attributed to the deformation band of the remaining methyl group in the product complex.

By dynamic NMR spectroscopy mobility of ligands is recognized by broad singlet resonances for the two methyl groups at 0.31 ppm and 0.51 ppm caused by reversible dissociation of the trimethylphosphine ligands.

When the sample is cooled to -70 °C the  ${}^{31}P{}^{1}H{}$  NMR spectrum exhibits signals at -15.6 ppm as doublet ( ${}^{2}J_{P,P}$  = 56.2 Hz, 1P), and at 10.7 ppm as doublet ( ${}^{2}J_{P,P}$  = 56.2 Hz, 1P) for the trimethylphos-

# Table 1 Crystal data for compounds 1 and 2

	1	2
Empirical formula	C <sub>20</sub> H <sub>33</sub> FeNOP <sub>2</sub>	C <sub>19</sub> H <sub>30</sub> CoNOP <sub>2</sub>
Molecular mass	421.26	409.31
Crystal size (mm)	$0.44 \times 0.40 \times 0.20$	$0.50 \times 0.45 \times 0.45$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	7.9965(11)	13.274(2)
b (Å)	12.866(2)	7.409(2)
c (Å)	21.641(4)	22.928(9)
β(°)	96.253(13)	106.190(13)
V (Å <sup>3</sup> )	2213.3(6)	2165.5(9)
Ζ	4	4
$D_{\text{calc.}}(g/\text{cm}^3)$	1.264	1.255
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.834	0.946
Temperature (K)	150(2)	150(2)
$\Theta$ -Range (°)	$1.84 \leqslant arrow \Theta \leqslant 27.17$	$1.60 \leqslant artheta \leqslant 27.07$
Index ranges	$-9 \leqslant h \leqslant 10$	$-16 \leqslant h \leqslant 16$
	$-16 \leqslant k \leqslant 16$	$-9 \leqslant k \leqslant 9$
	$-27 \leqslant l \leqslant 27$	$-29 \leqslant l \leqslant 29$
Number of reflections measured	31064	29068
Number of unique data (R <sub>int</sub> )	4776 (0.0758)	4699 (0.0504)
Parameters	255	221
Restraints	18	15
Goodness-of-fit on F <sup>2</sup>	1.078	1.044
$R_1 \ [I \geqslant 2\sigma(I)]$	0.0338	0.0415
$wR_2$ (all data)	0.0915	0.1160

phine ligands. The range of coupling constants corresponds with *cis* disposed trimethylphosphine ligands [20].

These data establish the only probable geometry around iron as octahedral, with two phosphines and the methyl groups in *cis* positions. From the NMR spectra, the single set of resonances indicates that only one of two possible configurational isomers is present, which could be methyl *trans* either to oxygen or nitrogen.

### 3.1. Reaction with CoCH<sub>3</sub>(PMe<sub>3</sub>)<sub>4</sub>

When combined with 2-benzoylpyridine in tetrahydrofuran, a solution of  $CoCH_3(PMe_3)_4$  during warm up turns green-blue, indicating the coordination the of the aromatic backbone forming complex **2** according to (Eq. (2)).



From concentrated pentane solutions at -27 °C crystals were obtained which were suitable for X-ray diffraction. The molecular structure (Fig. 1) displays an octahedrally coordinated iron(II) atom with two *cis*-disposed methyl groups, two *cis*-disposed trimethylphosphine ligands, and the neutral [N,O] chelating ligand with a bite angle of (O1–Fe1–N1 = 80.46(6)°), completes the coordination sphere. The sum of internal angles in the five-membered chelate ring (539°) indicates planarity and donor positions along the three main axes of the octahedron deviate by less than 12° from linearity.

The slightly shorter Fe–C bond with (Fe1–C1 = 2.045(2) Å) lies opposite to the softer trimethylphosphine donor P2 and the longer (Fe1–C2 = 2.055(2) Å) is subject to the influence of the harder oxygen donor atom of the 2-benzyolpyridine. The strong *trans* influence of the C1 atom is observed by an elongated distance (Fe1–P2 = 2.3097(5) Å) when compared with the weaker pyridyl anchoring group (N1), *trans* to P1 (2.1950(6) Å) which is ca. 11 pm shorter. The Fe–N and Fe–O bond lengths are as observed in other iron(II) complexes containing oxygen and nitrogen donor atoms [21].

The C=O bond lengths with C8–O1 = 1.294(2) Å is elongated, when compared with free benzoylpyridine (1.213 Å) [22], but is still to be regarded as a double bond. Related 2-pyridylalcoholato ligands in W, Zr, Ti, and Mo complexes show C–O single bond length in the range of 1.386–1.427 Å [23]. A related structure of **1** is described with a cationic acylFe(II) complex bearing 2-benzo-ylpyridine [17].

Most methyliron complexes described in literature carry an additional set of stabilizing phosphine [24], and/or cyclopentadiene [25], ligands, but to the best of our knowledge, iron-methyl complexes containing oxygen donor atoms in the ligand sphere have not been described. Recently, with nitrogen ligands of the tris(pyrazolyl)borato-type [26], and dimine-pincer type [27], methyliron complexes were studied.

Moreover, dimethyliron complexes are very rare, only three have been structurally described to date [28].

The balanced N,O coordination of the 2-benzoylpyridine can stabilize two thermally labile methyl functions of iron(II)  $[Fe(CH_3)_2(PMe_3)_4]$ , which are easily removed by other substrate molecules through C–H activation, or by extended reaction periods when reductive elimination is observed and zerovalent  $[Fe(PMe_3)_4]$  is produced [29].

To our surprise the methyl group remained attached to the metal after reaction. The complex was obtained in 83% yield. Crystals of **2** form large blue sticks with shiny surfaces that slowly decompose in air although their solutions decompose within a few seconds if air is admitted, similar to **1**. Typically cobalt(I) complexes in trigonal bipyramidal coordination with similar sets of donor atoms attain an orange to red color. The unusual blue color of complex **2** appears to be a direct consequence of a square-pyramidal coordination and hemilabile bonding.

The infrared spectrum displays the expected bathochromic shift of the carbonyl stretching frequency, 1485 cm<sup>-1</sup> (v C=O), with weak intensity, similar as observed for 1 and ortho-metalated benzophenone Co(I) (1484 cm<sup>-1</sup>) [30], when coordinated to the metal. The  ${}^{31}P{}^{1}H$  NMR spectrum features a broad singlet at -5.7 ppm, which is not resolved upon cooling the sample to 203 K. There can be two reasons for this exchange broadening in pentacoordinated systems: we have either dissociation of PMe<sub>3</sub>-groups or fast exchange of ligand positions in a pseudorotation process involving square-pyramidal and trigonal bipyramidal coordination geometries. Similar, on the relatively slow <sup>1</sup>H NMR timescale, the fast reversible ligand mobility of the trimethylphosphine ligands, conduct a collapse of the  ${}^{3}J(P,H)$  coupling between the Co–CH<sub>3</sub> group and the phosphorus nuclei. Typically, <sup>3</sup>J(P,H) couplings in the <sup>1</sup>H NMR spectrum are observed in more rigid, octahedral coordination, in the range between 3 and 8 Hz. The singlet resonance of the Co–CH<sub>3</sub> group (0.51 ppm) in the <sup>1</sup>H NMR spectrum corresponds with a high field shift in the  ${}^{13}C{}^{1}H$  NMR at -29.3 ppm (Co-CH<sub>3</sub>), observed as multiplet (nuclear spin I: Co = 7/2).

An X-ray diffraction confirmed for the solid state the constitution derived from solution NMR spectra. The ORTEP plot of **2** is shown in Fig. 2. The molecular structure of **2** closely resembles a pentacoordinated cobalt(I) center in square-pyramidal coordination surrounded by an apical trimethylphosphine ligand (P2), the methyl group (C1) in *trans* configuration of the oxygen donor atom, a trimethylphosphine ligand (P1) and the chelating [N,O] (2-benzyolpyridine) ligand spanning the four basal sites.

The essential feature of a the square-pyramidal coordination is described by the four angles between the apical P2 donor atom and the four equatorial ligand positions (P1, C1, O1 and N1) with  $102.47(3)^{\circ}$ ,  $95.06(10)^{\circ}$ ,  $100.94(6)^{\circ}$  and  $100.20(6)^{\circ}$ , respectively. The basal angles vary between  $88^{\circ}$  and  $94^{\circ}$  with the smallest for the [N,O] bite angle at  $82.05(8)^{\circ}$ . The dimensions in the chelate ring

(2)



**Fig. 1.** Molecular structure of **1**. Anisotropic displacement ellipsoids are plotted at the 50% probability level. Minor part of disordered P(1)Me<sub>3</sub> group omitted. Selected distances [Å] and angles [°]: Fe1-C1 2.045(2), Fe1-C2 2.055(2), Fe1-N1 1.9860(15), Fe1-O1 1.9071(13), Fe1-P1 2.1950(6), Fe1-P2 2.3097(5), C8-O1 1.294(2); O1-Fe1-N1 80.46(5), O1-Fe1-C2 175.75(7), N1-Fe1-P1 168.77(4), C1-Fe1-P2 171.84(6), C1-Fe1-C2 86.69(8), P1-Fe1-P2 96.57(2).



**Fig. 2.** Molecular structure of **2**. Anisotropic displacement ellipsoids are plotted at the 50% probability level. Minor part of disordered P(2)Me<sub>3</sub> group omitted. Selected distances [Å] and angles [°]: Co1-C1 1.995(3), Co1-N1 1.918(2), Co1-O1 1.9207(17), Co1-P1 2.1736(8), Co1-P2 2.1735(10), C7-O1 1.307(3); O1-Co1-N1 82.05(8), O1-Co1-C1 163.98(11), N1-Co1-P1 156.86(6), N1-Co1-C1 94.36(11), O1-Co1-P1 89.10(6), P2-Co1-P1 102.47(3), C1-Co1-P2 95.06(10), O1-Co1-P2 100.94(6), N1-Co1-P2 100.20(6).

are normal, and the bite angle of the chelating 2-benzoylpyridine [N,O] ligand with  $(O1-Co1-N1 = 82.05(8)^\circ)$ , within experimental

error equals those of the monoanionic benzophenone [C,O] coordination (83.49(7)°) or monoanionic [C,N] coordination of 2-vinylpy-





ripdine ligands  $(80.5(1)^\circ)$  [7,30], only 1.5° more augmented than in **1** and the sum of internal angles (539.1) is as expected for an almost planar five-membered metallacycle.

Similar ranges for Co–CH<sub>3</sub> bond lengths (Co1–C1 = 1.995 Å) are also observed for other cobalt compounds with a comparable set of donor atoms, independent of the oxidation state. The cobalt–phosphorus distances, Co1–P1 = 2.1736(8) Å and Co1–P2 = 2.1735(10) Å are equal and are well in the range of Co–P distances observed in pentacoordinated Co(I)–PR<sub>3</sub> complexes [31], indicating a balanced *trans* influence in this coordination mode.

The sigma coordinated C=O-group (C7-O1 = 1.307(3) Å) is again only slightly elongated compared with free 2-benzoylpyridine, but much shorter as described for 2-pyridylalcoholato complexes as aforementioned in the iron case.

Typically the methyl group of  $Co(CH_3)(PMe_3)_4$  is thermally labile and the basic behavior easily activates C–H bonds of various organic substrates with release of methane. However, previously it was only possible in reactions with strong  $\pi$ -acceptor ligands to keep the methyl group attached to the metal in a low oxidation [32,33].

To the best of our knowledge, a square-pyramidal configuration of low-valent Co(I) has not been described so far which is typical for Cobalt(II) with tri- or tetradentate ligands [34]. Most pentacoordinated cobalt(I) complexes attain a trigonal bipyramidal coordination, and only a few methylcobalt complexes are known in +II and +III oxidation states. Low-valent methylcobalt(I) complexes were recently studied with pincer-type ligands of bis-iminopyridines [35], and bis-*N*-heterocyclic carbenes [36], or with strong  $\pi$ -acceptor ligands as diazo-cylopentadienes and fulvenes [32,33]. To date the longest Co–CH<sub>3</sub> distance (2.081 Å) has been reported for a methyltricarbonyl(tricyclohexylphosphine)cobalt(I) [37].

### 3.1.1. Reaction with Ni(CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

At variance with reactions of **1** and **2** under similar conditions, reductive elimination is observed during 6 h, when  $Ni(CH_3)_2$  (PMe<sub>3</sub>)<sub>3</sub> reacts with 2-benzoylpyridine in pentane/diethyl ether (1:1). (Scheme 3).

From pentane the light yellow powder of **3** is deposited -27 °C, that is extremely air-sensitive and melts at 91–94 °C under decomposition. Crystallization from different solvents to get suitable crystals for X-ray diffraction proved unsuccessful.

The loss of both methyl substituents can be derived from the  ${}^{1}$ H NMR data for **3**, and the multiplicity of the signals indicates mirror symmetry of the molecule.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum in THF at 25 °C, consists of singlet resonance at 0.9 ppm, indicating dissociation of for the trimethylphosphine ligands, which is split into doublet ( ${}^{2}J_{P,P} = 57.1$  Hz) and separated into two peaks accompanied by high field shift (-12.4 ppm and -15.3 ppm) when the sample is cooled to -70 °C. An essential feature is observed in the  $\eta^{2}$ -C=O resonance of the  ${}^{13}$ C{<sup>1</sup>H} NMR spectrum by high field shift to 147.1 ppm when compared with **1** and **2** (**1**: 160.1 ppm, **2**: 160.8 ppm) and the free 2-benzoylpyridine (193.7 ppm, C=O).

The two methyl groups are easily eliminated by release of ethane in a reductive elimination process forming the zerovalent nickel complex 3 prior to an alternative sigma-N,O coordination of 2benzvolpvridine. Similar reductive elimination of dimethyl nickel has been described in reactions with PPh<sub>2</sub>-donor ligands [38]. We propose from NMR spectra a bonding mode as in a zerovalent nickel complex of  $(\eta^2-C=O)$  benzophenone, which was previously described without detection of the C=O resonance in  ${}^{13}C{}^{1}H$ NMR [39]. Additionally, in a related study with Ni(CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and thiobenzophenones, we observed reductive elimination by release of ethane. The X-ray structure reveals a three coordinated nickel(0) center with two trimethylphosphine ligands, almost coplanar to the  $\pi$ -coordinated  $\eta^2 C=S$  fragment. The phenylrings of the coordinated thiobenzophenone are in fan type conformation and the closest aromatic ortho carbon atoms with 3.2 and 3.6 Å, are far away from bonding interactions [40]. It appears a similar bonding situation in 3, for 2-benzoylpyridine attached to the nickel atom, without incorporating the N-donor atom.

### 4. Conclusion

A regiospecific displacement of two trimethylphosphine ligands is achieved with a neutral hemilabile [N,O]-coordinating 2-benzoylpyridine ligand in reaction with  $Fe(CH_3)_2(PMe_3)_4$  and  $Co(CH_3)(PMe_3)_4$ . In both cases the methyl groups remain attached to the metal after reaction. The N,O coordination is capable of stabilizing these thermally labile methyl groups of iron(II) (1) in an octahedral, and for cobalt(I) (2) in a square-pyramidal environment. By contrast, in a reaction with Ni(CH\_3)\_2(PMe\_3)\_3 reductive elimination of ethane is initiated and a zerovalent nickel complex **3** is formed.

Surprisingly, in all reactions described here there was no evidence for a C–H activation of available aromatic C–H bonds, which was previously observed for isoelectronic systems. As the metals retain their low oxidation states with an attached methyl group, these compounds can be seen as model substances for studying a growing alkyl-metal chain by subsequent insertion of ethene or carbon monoxide in the metal–carbon bond. Experiments with this aim are currently under way.

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### **Appendix A. Supplementary material**

CCDC 681203 and 681204 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc .cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2008.09.021.

### References

[1] (a) K. Frankcombe, K.J. Cavell, R. Knott, B. Yates, Chem. Commun. (1996) 781; (b) C. Jablonski, Z. Zhou, J. Bridson, Inorg. Chim. Acta 254 (1997) 315; (c) H. Jin, K.J. Cavell, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1995) 2159;

(d) S.Y. Desjardins, K.J. Cavell, J.L. Hoare, B.W. Skelton, A.N. Sobolev, A.H. White, W. Keim, J. Organomet. Chem. 544 (1997) 163;

(e) A.J. Canty, P.R. Trail, B.W. Skelton, A.H. White, Inorg. Chim. Acta 255 (1997) 117

[2] (a) M.J. Green, G.J.P. Britovsek, K.J. Cavell, B.W. Skelton, A.H. White, Chem. Commun (1996) 1563.

(b) M.J. Green, G.J.P. Britovsek, K.J. Cavell, F. Gerhards, B.F. Yates, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1998) 1137.

- [3] C. Godard, S.B. Duckett, S. Parsons, R.N. Perutz, Chem. Commun. (2003) 2332.
- [4] F. Kakiuchi, S. Murai, Acc. Chem. Res. 35 (2002) 826.
- [5] (a) H.-F. Klein, U. Lemke, M. Lemke, A. Brand, Organometallics 17 (1998) 4196; (b) H.-F. Klein, R. Beck, U. Flörke, H.J. Haupt, Eur. J. Inorg. Chem. (2003) 1380; (c) H.-F. Klein, S. Camadanli, R. Beck, U. Flörke, Chem. Commun. (2005) 381.
- [6] H.-F. Klein, S. Schneider, M. He, U. Flörke, H.J. Haupt, Eur. J. Inorg. Chem. (2000) 2295.
- [7] H.-F. Klein, S. Camadanli, R. Beck, D. Leukel, U. Flörke, Angew. Chem., Int. Ed. 44 (2005) 975.
- [8] S. Camadanli, R. Beck, U. Flörke, H.-F. Klein, Dalton Trans. (2008), doi:10.1039/ h813419g
- [9] Zn (a) A. Schneider, H. Vahrenkamp, Z. Anorg. Allg. Chem. 629 (2003) 2122; (b) C. Sudbrake, H. Vahrenkamp, Inorg. Chim. Acta 318 (2001) 23.
- [10] Mn (a) M.A.M. Abu-Youssef, A. Escuer, D. Gatteschi, M.A.S. Goher, F.A. Mautner, R. Vicente, Inorg. Chem. 38 (1999) 5716; (b) C.J. Milios, T.C. Stamatatos, P. Kyritsis, A. Terzis, C.P. Raptopoulou, R.
- Vicente, A. Escuer, S.P. Perlepes, Eur. J. Inorg. Chem. (2004) 2885. [11] Cu: (a) M.A.S. Goher, T.C.W. Mak, Inorg. Chim. Acta 99 (1985) 223;
- (b) M.A.S. Goher, A.E.H. Abdou, W.-H. Yip, T.C.W. Mak, Polyhedron 12 (1993) 2981. (c) M.A.S. Goher, R.-J. Wang, T.C.W. Mak, J. Coord. Chem. 38 (1996) 151;
- (d) F.A. Mautner, M.A.S. Goher, A.E.H. Abdou, Polyhedron 12 (1993) 2815. [12] Ru: (a) S.L. Queiroz, A.A. Batista, M.P. de Araujo, R.C. Bianchini, G. Oliva, J. Ellena, B.R. James, Can. J. Chem. 81 (2003) 1263; (b) D.L. Reger, J.R. Gardinier, M.D. Smith, Inorg. Chim. Acta 352 (2003) 151;
- (c) D.L. Reger, J.R. Gardinier, M.D. Smith, P.K. Pellechia, Inorg. Chem. 42 (2003) 482 [13] Rh D.J. de Geest, P.J. Steel, Aust. J. Chem. 48 (1995) 1573.
- [14] Rh: (a) G. Matsubayashi, S. Akazawa, Polyhedron 4 (1985) 419; (b) A.P. Martinez, M.P. Garcia, F.J. Lahoz, L.A. Oró, Inorg. Chim. Acta 347 (2003) 86.
- [15] Pd: (a) L.R. Falvello, M.M. Garcia, I. Lazaro, R. Navarro, E.P. Urriolabeitia, New J. Chem. 23 (1999) 227;
- (b) J.M. Casas, L.R. Falvello, J. Fornies, A. Martin, Inorg. Chem. 35 (1996) 56.
- [16] Ru D. Zuccaccia, G. Bellachioma, G. Cardaci, C. Zuccaccia, A. Macchioni, Discuss. Faraday Soc. (2006) 1963.
- [17] Fe: G. Bellachioma, G. Cardaci, V. Gramlich, A. Macchioni, M. Valentini, C. Zuccaccia, Organometallics 17 (1998) 5025.
- [18] Re: M.L. Creber, K.G. Orrel, A.G. Osborne, V. Sik, M.B. Hursthouse, M.E. Light, Polyhedron 20 (2001) 1973.
- [19] M.J. Green, G.J.P. Britovsek, K.J. Cavell, F. Gerhards, B.F. Yates, K. Frankcombe, B.W. Skelton, A.H. White, J. Organomet. Chem. 533 (1997) 201.
- [20] P.E. Garrou, Chem. Rev. 81 (1981) 229.
- [21] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton. Trans. (1989) S1.
- [22] M. Sievert, R. Dienelt, H. Bock, Acta Crystallogr., Sect. C 54 (1998) 674.
- [23] (a) P.A. van der Schaaf, R.A.T.M. Abbenhuis, D.M. Grove, W.J.J. Smeets, A.L. Spek, G. van Koten, Chem. Commun. (1993) 504;

(c) I. Kim, Y. Nishihara, R.F. Jordan, R.D. Rogers, A.L. Rheingold, G.P.A. Yap, Organometallics 16 (1997) 3314;

(d) B.E. Schultz, S.F. Gheller, M.C. Muetterties, M.J. Scott, R.H. Holm, J. Am. Chem. Soc. 115 (1993) 2714.

[24] (a) L.D. Field, H.L. Li, B.A. Messerle, R.J. Smernik, P. Turner, Discuss. Faraday (2004) 1418;

(b) M. Tilset, I. Fjeldahl, J.-R. Hamon, P. Hamon, L. Toupet, J.-Y. Saillard, K. Costuas, A. Haynes, J. Am. Chem. Soc. 123 (2001) 9984.

[25] (a) T. Katayama, Y. Morimoto, M. Yuge, M. Uno, S. Takahashi, Organometallics 18 (1999) 3087; (b) A.S. Batsanov, B.M. Bridgewater, J.A.K. Howard, A.K. Hughes, C. Wilson, J.

Organomet. Chem. 590 (1999) 169.

- [26] (a) J. Vela, S. Vaddadi, T.R. Cundari, J.M. Smith, E.A. Gregory, R.J. Lachicotte, C.J. Flaschenriem, P.L. Holland, Organometallics 23 (2004) 5226;
- (b) J.L. Kisko, T. Hascall, G. Parkin, J. Am. Chem. Soc. 120 (1998) 10561.
- [27] (a) J. Scott, S. Gambarotta, I. Korobkov, P.H.M. Budzelaar, Organometallics 24 (2005) 6298; (b) M.W. Bouwkamp, S.C. Bart, E.J. Hawrelak, R.J. Trovitch, E. Lobkovsky, P.J.
- Chirik, Chem. Commun. (2005) 3406. [28] (a) X. Fang, B.L. Scott, J.G. Watkin, G.J. Kubas, Organometallics 20 (2001)
  - 2413: (b) C. Venturi, G. Bellachioma, G. Cardaci, A. Macchioni, C. Zuccaccia, Inorg. Chim. Acta 358 (2005) 3815;

(c) W.K. Wong, K.W. Chiu, G. Wilkinson, A.J. Howes, M. Motevalli, M.B. Hursthouse, Polyhedron 4 (1985) 603.

[29] R. Beck, H.-F. Klein, unpublished results.

R. Beck et al./Inorganica Chimica Acta 362 (2009) 1984-1990

- [30] S. Camadanli, Dissertation, Technische Universität Darmstadt, 2005.
- [31] H.-F. Klein, R. Beck, U. Flörke, H.-J. Haupt, Eur. J. Inorg. Chem. (2003) 853.
- [32] H.-F. Klein, E. Auer, T. Jung, C. Röhr, Organometallics 14 (1995) 2725.
- [33] H.-F. Klein, K. Ellrich, B. Hammerschmitt, U. Koch, G. Cordier, Z. Naturforsch. Teil B45 (1990) 1291.
- [34] (a) C. Zimmermann, F.W. Heinemann, A. Grohmann, Eur. J. Inorg. Chem. (2005) 3506

(b) C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Zanobini, F. Laschi, A. Sommazzi, Eur. J. Inorg. Chem. (2003) 1620.

[35] (a) N. Kleigrewe, W. Steffen, T. Blömker, G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, J.-C. Wasilke, G. Wu, G.C. Bazan, J. Am. Chem. Soc. 127 (2005) 13955; (b) M.J. Humphries, K.P. Tellmann, V.C. Gibson, A.J.P. White, D.J. Williams, Organometallics 24 (2005) 2039; (c) T.M. Kooistra, Q. Knijnenburg, J.M.M. Smits, A.D. Horton, P.H.M. Budzelaar,

A.W. Gal, Angew. Chem., Int. Ed. 40 (2001) 4719.

- [36] A.A. Danopoulos, J.A. Wright, W.B. Motherwell, S. Ellwood, Organometallics 23 (2004) 4807.
- [37] S.A. Llewellyn, M.L.H. Green, A.R. Cowley, J. Organomet. Chem. 690 (2005) 2358.
- [38] R. Beck, Dissertation, Technische Universität Darmstadt, 2001.
- [39] (a) T.T. Tsou, J.C. Huffman, J.K. Kochi, Inorg. Chem. 18 (1979) 2311;
- (b) D.J. Mindiola, R. Waterman, D.M. Jenkins, G.L. Hillhouse, Inorg. Chim. Acta 345 (2003) 299.
- [40] R. Beck, H. Sun, X. Li, S. Camadanli, H.-F. Klein, Eur. J. Inorg. Chem. (2008) 3253. [41] W. Wolfsberger, H. Schmidbaur, Syn. React. Inorg. Metal-Org. Chem. 4 (1974)
- 149.
- [42] H.H. Karsch, Chem. Ber. 110 (1977) 2699.
- [43] H.-F. Klein, H.H. Karsch, Chem. Ber. 108 (1975) 944.
- [44] H.-F. Klein, H.H. Karsch, Chem. Ber. 106 (1973) 1433.
- [45] Stoe & Cie, x-AREA (Version 1.18) and x-RED32 (Version 1.04). Stoe & Cie, Darmstadt Germany 2002
- [46] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Germany, 1997.