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Cobalt Induced Tandem C−H Activation/Decarbonylation of Various Aromatic Aldehydes and Related Benzylic Alcohols Forming Mononuclear Aryl Monocarbonyl Complexes

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Reactions between $Co(CH_3)(PMe_3)_4$ and various ortho-substituted aromatic aldehydes ($Ar(R_1,R_2)CHO$) and related benzylic alcohols ($Ar(R_1,R_2)CH_2OH$) proceed with high selectivity to give the mono carbonyl complexes $Aryl(R_1,R_2)(PMe_3)_3Co(CO)$: $R_1 = H$, $R_2 = CH_3$ (**1**), R_1= H, R_2 = ethyl (**2**), $R_1 = CH_3$, $R_2 = CH_3$ (**3**), $R_1 = H$, $R_2 = NH_2$ (**4**), $R_1 = F$, $R_2 = F$ (**5**), $R_1 = H$, $R_2 = CF_3$ (**6**), and $R_1 = H$, R_2 = benzo (**7**). This tandem C−H bond activation/decarbonylation reaction provides easy and rapid access under mild conditions (−70 °C) to the first isolated trimethylphosphine stabilized aryl-monocarbonyl complexes of cobalt. X-ray diffraction studies were performed on ortho-amino substituted complex **4**, ortho-trifluormethyl **6**, and naphthyl derivative **7**.

Introduction

Stoichiometric and catalytic transformations involving C−H activation are of present interest due to the synthetic utility that the facile functionalization of unreactive C−H bonds would provide.[1] The relatively low cost of cobalt complexes, as compared to their more expensive 4d and 5d congeners, provides an impetus for their utilization in catalytic or stoichiometric transformations that proceed through C−H bond activation.[2]

Recently, we studied the activation of aromatic, vinylic, and aliphatic C−H bonds and its high selectivity with $CoCH_3(PMe_3)_4$ assisted by nitrogen[3] and phosphorus[4] donor functions. The activation of the C−H bond of aldehydes is a reaction of great interest due to its connection with the catalytic decarbonylation of these substrates and its importance in organometallic and organic synthesis.

The activation of aldehyde C−H bonds has been investigated by other research groups with iron(0),[5] ruthenium(0),[6,7] ruthenium(II),[8] osmium(VI, IV, 0),[9−11] rhodium(I),[12−18] rhodium(III),[19] iridium(I),[18,20−25] iridium(III),[19]

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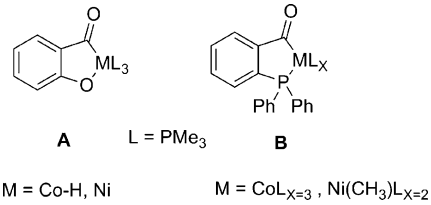
Scheme 1. Five-Membered Nickel and Cobalt Acyl Metallacycles



and platinum(0).[26] In some cases, the C−H activation step is followed by decarbonylation which results in a R−M−CO derivative,[7,8,19−22,26] while in other examples, a stable acyl−metal−hydride is formed.[9,10,18,26]

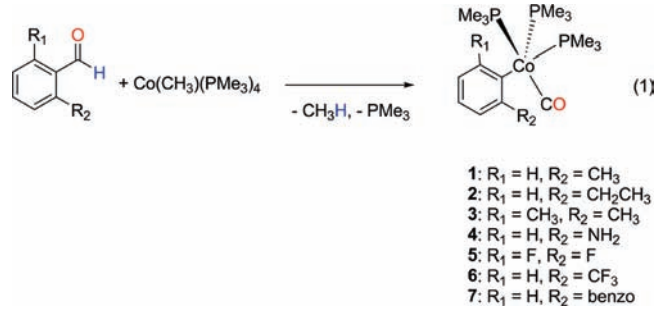
The majority of research studies centering on aldehyde decarbonylation have utilized Rh(I) complexes, which have been found to be the most efficient catalysts.[27−35] Activity has also been reported for cobalt(I) systems[36] and for a cobalt-protoporphyrin complex,[37] but no information has been given for intermediates. In a related study of aldehydic C−H bond activation with a pentamethylcyclopentadiene supported Co(I) center, Brookhart et al. described the intermolecular hydroacylation of vinylsilanes with a variety of alkyl aldehydes.[38]

We have previously reported on the activation of OC(R)−H bonds of salicylaldehyde derivatives (**A**),[39,40] 2-diphenylphosphinobenzaldehyde (**B**),[41] with trimethylphosphine supported methyl nickel, and methyl cobalt complexes, where thermally stable acyl complexes were observed with five-membered metallacycles (Scheme 1).

In this report, we describe the synthesis of stable ortho-aryl-substituted cobalt complexes with one terminal carbonyl group. With various aromatic aldehydes, the reaction of $CoCH_3(PMe_3)_4$ follows, regioselectively, a tandem C−H activation/carbonyl migration deinsertion pathway. The same reaction products are observed with related benzylic alcohols in fair yields.

Results and Discussion

The reaction of aromatic aldehydes with $CoCH_3(PMe_3)_4$ proceeds at −70 °C through C−H activation followed by a decarbonylation step according to eq 1. During warm up, the evolution of gas (CH_4) is detected, and the color changes from dark red to orange-yellow.



This method provides high yields and appears to be widely applicable by tolerating different functional groups in ortho positions of the starting aldehydes, with the formation of aryl carbonyl complexes [Aryl(R_1,R_2)$(PMe_3)_3$Co(CO)]: R_1 = H, R_2 = CH_3 (**1**), R_1 = H, R_2 = ethyl (**2**), R_1 = CH_3, R_2 = CH_3 (**3**), R_1 = H, R_2 = NH_2 (**4**), R_1 = F, R_2 = F (**5**), R_1 = H, R_2 = CF_3 (**6**), and R_1 = H, R_2 = benzo (**7**) (eq 1). All products crystallize from pentane or diethyl ether as orange rhombic crystals in 58−79% yield.

When the reactions were all carried out in pentane, without crystallization of a product, just by filtering and washing with ice-cold pentane, a light yellow powder was obtained in almost quantitative yields, according NMR data.

The complexes (**1**−**7**) show similar ^{1}H, ^{13}C(^{1}H), and ^{31}P(^{1}H) NMR spectra and absorption regions in the infrared (IR) for the ν(C≡O) stretching frequencies. In the ^{1}H NMR spectra of **1**−**7**, the resonances for the trimethylphosphine ligands appear at 1.18−1.30 ppm as broad singlets, except for **1**, which appears at 1.23 ppm as a doublet ($^2J_{P,H}$ = 6.1 Hz). The metallated carbon resonances (Co−*C*) in the ^{13}C(^{1}H) NMR are observed as expected with a low field shift for complexes **1**−**7** from 166 to 180 ppm as broad multiplets (cobalt: I = 7/2). The ^{31}P(^{1}H) NMR resonances of complexes **1**−**7** exhibit at δ = 8.2−10.3 ppm broad singlets, which are assigned for a trigonal bipyramidal coordination sphere with dynamic ligand behavior (Berry type pseudorotation and ligand dissociation). In addition, when cooling down the NMR samples to −80 °C, no P,P-coupling of the different phosphorus nuclei was observed. In the IR, these complexes absorb at 1850−1886 cm^{-1} ν(C≡O) in their IR spectra, which are typical stretching frequencies for terminal carbon monoxide ligands.[42] To the best of our knowledge, **1**−**7** represent the first examples of simple aryl monocarbonyl cobalt complexes.

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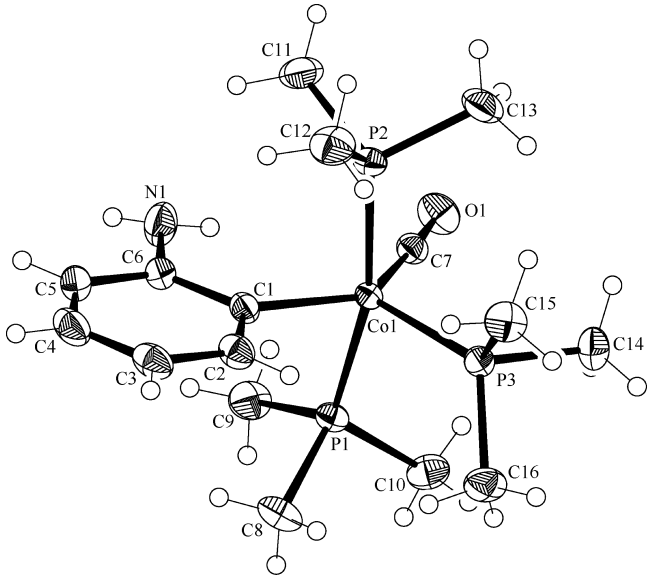

Figure 1. Molecular structure of **4**; selected bond lengths [Å] and angles [deg]: Co1−C1 2.016(1), Co1−C7 1.709(1), Co1−P1 2.1709(4), Co1−P2 2.1620(4), Co1−P3 2.2369(5), C7−O1 1.158(2), C1−C6 1.425(2), N1−H···Co 2.76(2), C6−N1 1.379(2), C7−Co1−C1 137.37(6), P1−Co1−P2 164.57(2), C1−Co1−P3 110.89(4), C7−Co1−P3 111.74(4), P1−Co1−P3 97.27(2), P2−Co1−P3 97.57(2), C6−C1−Co1 123.99(10), N1−C6−C1 120.66(12).

A single-crystal X-ray diffraction study was performed on the ortho-amino-substituted complex **4**. Dark orange rhombic crystals were grown through the cooling of ether solutions of **4** to −27 °C.

The molecular structure of **4** is shown in Figure 1. The cobalt atom resides in the center of a trigonal bipyramid of donor atoms, where the carbon atom of the phenyl group, a trimethylphosphine ligand, and the carbonyl group occupy equatorial positions. The two remaining PMe_3 ligands reside in axial positions. The main axis connecting apical positions (P2−Co1−P1 = 164.57(2)°) is slightly bent from idealized geometry (180°) and the angles from the equatorial (P3) to the axial phosphorus atoms are similar to 97.57(2)° for P2 and 97.27(2)° for P1, respectively. The sum of inner ligand angles in the equatorial plane (358°) is in accord with a cobalt atom centered in the trigonal plane. The Co−P bond lengths (2.1709(4) Å and 2.1620(4) Å) fall in a range also observed for other cobalt complexes containing aryl and carbonyl groups.[43] The Co1−P3 distance (2.2369(5) Å) is elongated due to the *trans* influence of the C1 atom of the phenyl group. The complex contains two different Co−C bonds: a shorter one connected to the carbonyl ligand (Co1−C7 = 1.709(1) Å) and a longer one connected to the phenyl group (Co1−C1 = 2.016(1) Å), which is typical for (sp, sp^2) hybridized carbon atoms.[43]

The bond distance between the protons of the ortho amino group and the cobalt atom is relatively short (N−H···Co = 2.76(2) Å). However, no spectroscopic evidence was found for agostic or anagostic interactions, which was reported by Brammer et al.,[44] for a cobaltate anion containing a metal contact (N−H···Co = 2.613 Å).

In a reverse reaction pathway, a stable five-membered 2-aminoacyl palladium metallacycle was reported when carbon monoxide inserts into the palladium aryl bond.[45] In the cobalt case, the balance of the hard NH_2-donor and the remaining soft trimethylphosphine ligands is not suitable for stabilizing such a five-membered aminoacyl cobaltacycle.

Only when a soft donor atom in the ortho position of 2-diphenylphosphinobenzaldehyde is present does the reaction with $CoCH_3(PMe_3)_4$ afford stable acyl complexes as aforementioned, by the insertion of carbon monoxide observed with a phenyltris((*tert*-butylthio)methyl)borate cobalt complex,[46] or by hydrolysis of a CF_2-group in a [Cp] stabilized cobalt complex.[47]

The well-established and related nucleophilic reaction pathway is observed when the carbonyl−metalate complex reacts with the corresponding benzoylchloride derivatives forming stable acyl complexes,[48] which can readily decarbonylate.[49] This is also reported for the anion $[Co(CO)_4]^-$.[50] Typically, these complexes have a central equatorial *tris*-carbonyl motif $[Co(CO)_3]$ in common.[51] To the best of our knowledge, an initial aldehyde−C−H activation reaction at cobalt centers has not been reported before. We were able to extend its scope with aryl aldehyde derivatives. The reaction pathway allows the synthesis of aryl−cobalt (monocarbonyl) complexes, which cannot be prepared easily by other routes. So far, only when π-acceptor substituents are present (e.g., allyl- or diphenylphosphino chelating substituents) were mononuclear complexes with an [Ar−Co−CO] *monocarbonyl* unit described.[52,53]

Under similar reaction conditions, complex **6** was synthesized (eq 1). Its spectroscopic data are very similar to that of complex **4** (see Experimental Method section). The molecular structure of **6** (Figure 2)shows a distorted trigonal bipyramidal coordination environment of cobalt(I), with two trimethylphosphine ligands in apical positions. The aryl ligand that lies in a plane containing the carbonyl group and

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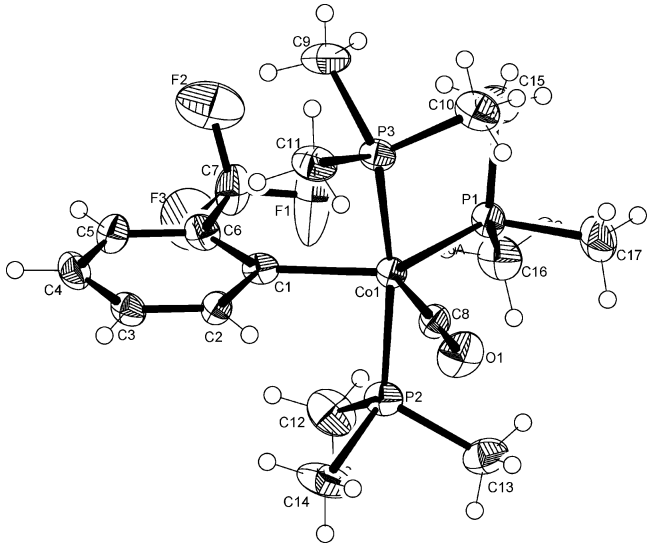
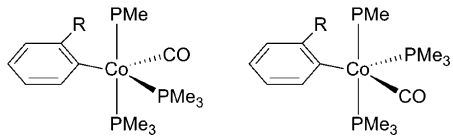


Figure 2. Molecular structure of **6**; selected bond lengths [Å] and angles [deg]: Co1−C1 2.048(6), Co1−C8 1.733(6), Co1−P1 2.2465(15), Co1−P2 2.1793(19), Co1−P3 2.1783(18), C8−O1 1.178(7), C1−C6 1.416(8), C6−C7 1.511(8), C7−F1 1.285(8), C7−F2 1.354(9), C7−F3 1.356(9), C8−Co1−C1 118.4(2), P3−Co1−P2 168.88(6), C1−Co1−P3 85.49(17), C8−Co1−P3 88.5(2), P1−Co1−P2 95.38(7), P1−Co1−P3 95.58(6), C6−C1−Co1 134.9(4).

Scheme 2. *Syn*- and *Anti*-Conformation of the Ar(R)−Co−CO Unit in **4**, **6**, and **7** in Solid State



R = NH_2, Benzo R = CF_3

syn-(**4**, **7**) *anti*-(**6**)

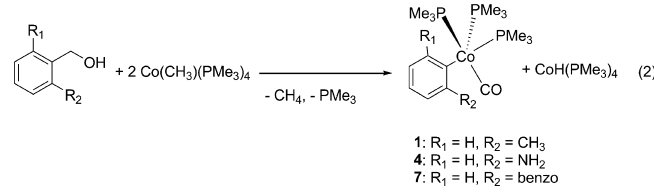
the third trimethylphosphine ligand occupy the equatorial positions.

The Co−C and Co−P bond distances and angles closely resemble those for the related complex **4**. The most interesting feature in the molecular structure is the *anti*-conformation of the carbonyl ligand and the trifluoromethyl group in the ortho position of **6** in a solid state (Scheme 2). Geometrical parameters as well as the unresolved disorder of the CF_3 group suffer from rather bad data quality and should be understood as proof of connectivity only.

Interestingly, in **6**, the steric demand of the trimethylphosphine ligand is oriented toward the trifluoromethyl substituent, and the smaller carbonyl group is pointing away. An opposite arrangement would be expected with the bulky CF_3-substituent.

Alternative Reaction Pathway. An alternative reaction pathway occurs with benzylic alcohols (2-methylbenzylalcohol, 2-aminobenzylacohol, and 1-naphthalenemethanol). When combining $CoCH_3(PMe_3)_4$ with the related alcohol in diethyl ether, a slow color change from red to yellow is observed after between 24 and 48 h has passed (eq 2).

With a reaction yield of 29−44%, the same products as aforementioned (eq 1) for selected benzaldehydes were achieved with the related benzylic alcohols, and additionally,



$CoH(PMe_3)_4$ is formed, identified by IR spectra ν(Co−H) = 1935 cm^{-1}. Ostensibly, in a prevailing side reaction, the hydrido-cobalt side product (Scheme 3) attacks the benzene system, observed in a raw product ^{1}H NMR spectrum of **7**, which exhibits proton resonances in typical olefinic area range between 5.3−5.8 ppm and other resonances of unidentified byproducts. Unfortunately, we have not been able to isolate those olefinic products.

However, again, the complexes (**1**, **4**, and **7**) crystallize as orange-yellow rhombic crystals from pentane and diethyl ether solutions. The predicted structure of **7** (similar to that of **4** and **6**) derived from NMR data in solution was confirmed by X-ray diffraction (Figure 3). The Co−P and P−C bond lengths are close to the average reported mean values of bond lengths.[54] In complex **7**, the orientation of the carbonyl ligand exhibits a *syn* orientation to the condensed aryl-ring in the ortho position. The distance between the cobalt atom and the neighboring hydrogen atom in the 8-position of the naphthyl ring (H1···Co1 = 2.888 Å) is relatively short, similar to that in complex **4**, but, again, without spectroscopic evidence for agostic or anagostic interactions.[55]

All spectral data obtained from solutions are consistent with the results of the three X-ray diffraction experiments. Selected structural and NMR data for **4** and **7** are summarized in Table 1.

Proposed Reaction Mechanism. The proposed reaction mechanism for the formation of complexes **1**−**7** is initiated by dissociation of a trimethylphosphine ligand from the starting complex $[Co(CH_3)(PMe_3)_4]$ (18 VE). The tetracoordinated $[Co(CH_3)(PMe_3)_3]$ intermediate (16 VE) proceeds in reaction with the aromatic aldehyde by an aldehydic C−H bond activation when the hexacoordinated acyl cobalt complex is formed (Scheme 1). A stable acyl cobalt complex has been isolated in a previous study, when a diphenylphosphino group was introduced into the ortho position of the aldehyde.[41] Without a phosphorus donor atom in the ortho position, the hydrido−methyl−Co(III) intermediate is unstable (release of CH_4) and a decarbonylation step occurs by insertion of the cobalt fragment into the aryl−acyl bond, generating a terminal carbonyl Co(I) complex. A similar tandem C−H activation/decarbonylation reaction of highly hindered tertiary aliphatic aldehydes with iridium complexes has been previously described by Alaimo et al.[56]

An alternative route starts from the related alcohol, which proceeds through elimination of methane, producing an

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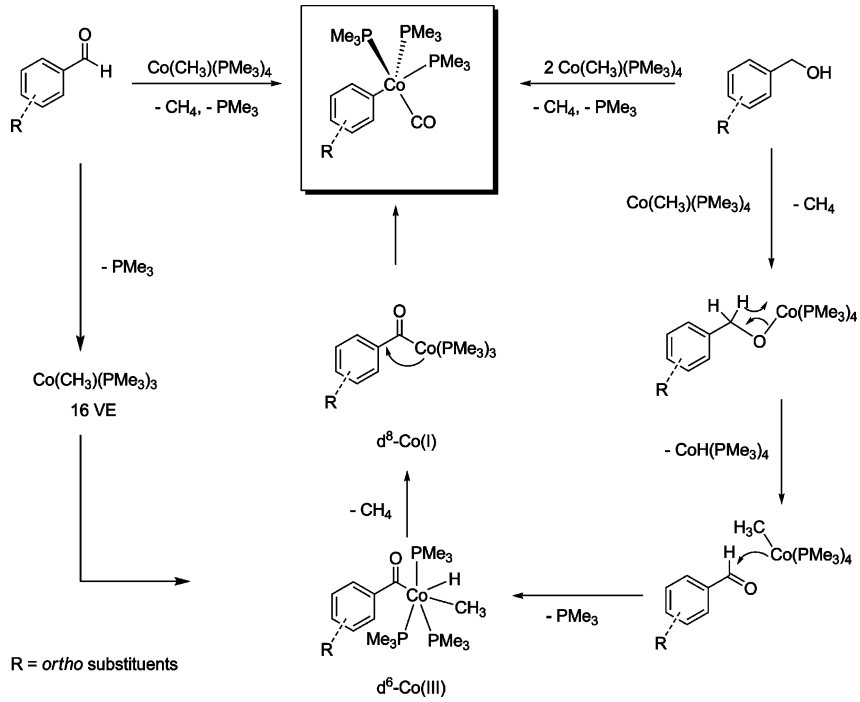
Scheme 3. Proposed Reaction Pathway of $Co(CH_3)(PMe_3)_4$ with Aromatic Aldehydes and Benzylic Alcohol Derivatives



alcoholate cobalt complex (Scheme 3). β-Hydrogen elimination releases the in situ generated aldehyde and a stable hydrido−cobalt(I) complex (NMR). Afterward, still present $CoCH_3(PMe_3)_4$ in solution reacts with the new formed aldehyde, which might also explain the rather low yield (<50%). Half of the initial complex $[Co(CH_3)(PMe_3)_4]$ is used to generate the aldehyde, and the other half is used to take the aldehyde to the final product. After the elimination of methane from the hydrido−methyl d^6-cobalt(III) species, the d^8-cobalt(I) acyl complex is formed, and the reaction sequence ends up in the same pathway as described with the related aldehydes.

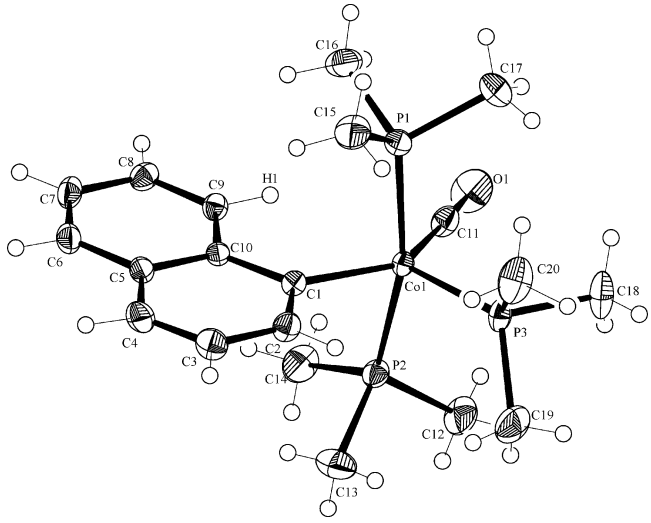


Figure 3. Molecular structure of **7**; selected bond lengths [Å] and angles [deg]: Co1−C1 2.0170(17), Co1−C11 1.7261(18), Co1−P1 2.1842(6), Co1−P2 2.1745(5), Co1−P3 2.2436(6), C11−O1 1.179(2), C1−C10 1.454(2), C9−C10 1.430(2), H1···Co1 2.888(1), C1−Co1−C11 140.22(8), P2−Co1−P1 163.82(2), C1−Co1−P3 109.45(5), C11−Co1−P3 110.33(6), P1−Co1−P3 97.44(2), P2−Co1−P3 98.22(2), C10−C1−Co1 124.32(12).

Conclusion

The cobalt-induced tandem C−H activation/carbonyl migratory deinsertion reaction described in this work has provided easy and rapid access to mononuclear complexes, with an Ar−Co−CO fragment as the general constituent. The reaction pathway allows the preparation of monocarbonyl cobalt complexes, which cannot be easily prepared by other routes. All new complexes (**1**−**7**) could be synthesized under mild conditions (−70 °C) in high yield starting from the benzaldehyde derivative or in fair yield from the corresponding alcohol. The reaction proceeds regioselectively with the aldehydic or alcoholic functional group, with spectroscopic evidence for neither activation nor interaction with the other substituents in the ortho position (N−H/C−H/C−F bonds) of the aromatic backbone or even other available aromatic C−H bonds.

Experimental Section

General Procedures and Materials. All air-sensitive and volatile materials were handled using standard vacuum techniques and were kept under argon. Microanalyses: Kolbe Microanalytical Laboratory, Mülheim/Ruhr, Germany. Melting points/decomposition tempera-

Table 1. Selected Structural and Spectroscopic Data of Aryl−Co(I)−CO Complexes **4** and **7**

	4	**7**
aryl(C)−Co [Å]	2.016(1)	2.0170(17)
Co−P [Å]	2.16−2.23	2.17−2.24
Co−*C*O [Å]	1.709	1.726
C≡O [Å]	1.158	1.179
ortho H···Co [Å]	2.762	2.888
$P_{(ax)}$−Co−$P_{(ax)}$ [deg]	164.57	163.82
C_{aryl}−Co−CO [deg]	137.37	140.22
^{1}H NMR δ P*Me*$_3$	1.28 s(br)	1.18 s(br)
^{13}C(^{1}H) NMR δ *C*−Co	180.3 m	171.5 m
^{31}P(^{1}H) NMR δ *P*Me$_3$	9.5 m	7.8 m
IR ν (C≡O) cm^{-1}	1850	1872

Table 2. Crystal Data and Refinement Details for Compounds **4**, **6**, and **7**

	4	**6**	**7**
empirical formula	$C_{16}H_{33}CoNOP_3$	$C_{17}H_{31}CoF_3OP_3$	$C_{20}H_{34}CoOP_3$
molecular mass	407.3	460.3	442.3
crystal size [mm]	0.45 × 0.40 × 0.25	0.35 × 0.31 × 0.23	0.44 × 0.35 × 0.22
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [Å]	8.6624(12)	8.6290(12)	12.9194(12)
b [Å]	9.0674(13)	9.7981(14)	13.3931(12)
c [Å]	14.291(2)	26.151(4)	13.7459(14)
α [deg]	80.705(11)	90.0	90.0
β [deg]	76.995(11)	91.910(12)	100.45(2)
γ [deg]	69.557(10)	90.0	90.0
V [Å^3]	1020.6(2)	2209.8(5)	2339.0(4)
Z	2	4	4
D_{calcd} [g/cm^3]	1.325	1.383	1.256
μ(Mo Kα) [mm^{-1}]	1.077	1.021	0.945
temperature [K]	150(2)	150(2)	150(2)
Θ − limits [deg]	1.47 − 26.37	2.22 − 27.88	1.99 − 26.94
h	$-10 \le h \le 10$	$-11 \le h \le 11$	$-16 \le h \le 16$
k	$-11 \le k \le 11$	$-12 \le k \le 12$	$-16 \le k \le 17$
l	$-17 \le l \le 17$	$-34 \le l \le 34$	$-17 \le l \le 17$
reflns measured	14959	15396	34196
unique data	4107 [R_{int} = 0.090]	4503 [R_{int} = 0.105]	5013 [R_{int} = 0.056]
parameters/restraints	216/2	236/0	236/0
absorption corr.	semiempirical	semiempirical	semiempirical
max and min transmn.	0.7745 and 0.6428	0.8141 and 0.7163	0.8191 and 0.6813
GOF on F^2	1.052	1.245	1.081
$R1$ [$I \ge 2\sigma(I)$]	0.0242	0.0794	0.0344
$wR2$ (all data)	0.0637	0.1820	0.0856
largest diff. peak/hole	0.369 and −0.275 e·Å^{-3}	0.632 and −0.798 e·Å^{-3}	0.705 and −0.588 e·Å^{-3}

tures: sealed capillaries, uncorrected values. Chemicals (Acros/Merck) were used as purchased. Literature methods were followed in the preparation of $CoCH_3(PMe_3)_4$[57] and 2-aminobenzaldehyde.[58] IR: Nujol mulls between KBR discs, Bruker spectrophotometer type FRA 106. ^{1}H, ^{13}C(^{1}H) NMR and ^{31}P(^{1}H) NMR spectra were recorded with a Bruker DRX-500 spectrometer.

Experimental Method. Solutions of the cobalt complex in tetrahydrofuran (THF) on a scale of about 1−4 mmol were combined with equimolar amounts of the aldehyde (Method A) in the same solvent or in diethyl ether for the related benzylic alcohol derivatives (Method B) and stirred at −70 °C. The reaction mixture was allowed to warm to 20 °C and stirred for maximum 3 h at 20 °C (Method B: 24 h). The volatiles were removed in vacuo, and the residue was extracted with fresh pentane and/or diethyl ether and filtered over a glass-sinter disk (G3). When the solution was cooled, crystals formed. The solution was decanted off, and the crystals were washed with cold pentane and dried in vacuo to afford analytically pure materials **1**−**7**.

Carbonyl[2-(methylphenyl)-C]tris(trimethylphosphine)cobalt(I) (1). Method A: 2-Methylbenzaldehyde (695 mg, 5.78 mmol) was combined at −70 °C with $CoMe(PMe_3)_4$ (2.18 g, 5.78 mmol) to afford an orange, waxy solid of **1**. Yield 1.52 g (65%). Method B: 2-Methylbenzylalcohol (210 mg, 1.71 mmol) was combined at 20 °C with $CoMe(PMe_3)_4$ (650 mg, 1.71 mmol) to afford yellow crystals. Yield 307 mg (44%). Mp 104−106 °C (dec). IR (Nujol): $\tilde{\nu}$ = 1881 s (ν C═O); 1574 m (ν C═C) cm^{-1}. ^{1}H NMR (500 MHz, [D$_8$]THF, 293 K, ppm): δ = 1.23 (d, $^2J_{P,H}$ = 6.1 Hz, 27H, PCH_3); 2.34 (s, 3H, CH_3); 6.56 (t, $^3J_{H,H}$ = 6.9 Hz, 1H, Ar−H); 6.66 (dd, $^3J_{H,H}$ = 6.3 Hz, $^4J_{H,H}$ = 0.8 Hz, 1H, Ar−H); 6.85 (d, $^3J_{H,H}$ = 7.1 Hz, 1H, Ar−H); 7.29 (d, $^3J_{H,H}$ = 7.2 Hz, 1H, Ar−H). ^{13}C(^{1}H) NMR (125 MHz, [D$_8$]THF, 293 K, ppm): δ = 19.5 (d, $^1J_{P,C}$ = 21.0 Hz, PCH_3); 28.2 (s, CH_3); 120.4 (s, CH); 120.6 (s, CH); 125.6 (s, CH); 146.3 (s, CH); 147.4 (s, C); 166.9 (m, Co−C). ^{31}P(^{1}H) NMR (202 MHz, [D$_8$]THF, 293 K, ppm): δ = 8.8 (m(br), 3P, PCH_3) ppm. Anal. Calcd for $C_{17}H_{34}CoOP_3$ (406.3): C, 50.25; H, 8.43; P, 22.87. Found: C, 49.82; H, 8.93; P, 22.62.

Carbonyl[2-(ethylphenyl)-C]tris(trimethylphosphine)cobalt(I) (2). Method A: 2-Ethylbenzaldehyde (338 mg, 2.51 mmol) was combined at −70 °C with a solution of $CoMe(PMe_3)_4$ (952 mg, 2.51 mmol) to afford orange-yellow crystals. Yield 762 mg (72%). Mp 103−105 °C (dec). IR (Nujol): $\tilde{\nu}$ = 1882 s (ν C═O); 1575 m (ν C═C) cm^{-1}. ^{1}H NMR (500 MHz, [D$_8$]THF, 293 K, ppm): δ = 0.91 (dt, $^3J_{H,H}$ = 7.5 Hz, $^6J_{P,H}$ = 5.7 Hz, 1H, CH_3); 1.24 (s(br), 27H, PCH_3); 2.63 (q, $^3J_{H,H}$ = 7.5 Hz, 2H, CH_2); 6.57 (dt, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, Ar−H); 6.74 (dt, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, Ar−H); 6.89 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H, Ar−H); 7.40 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, Ar−H). ^{13}C(^{1}H) NMR (125 MHz, [D$_8$]THF, 293 K, ppm): δ = 10.9 (dt, $^5J_{P,C}$ = 28.8 Hz, $^5J_{P,C}$ = 14.7 Hz, CH_3); 19.3 (m, PCH_3); 32.4 (s, CH_2); 120.1 (s, CH); 120.6 (s, CH); 123.1 (s, CH); 146.6 (s, CH); 153.4 (s, C); 166.8 (m, C). ^{31}P(^{1}H) NMR (202 MHz, [D$_8$]THF, 293 K, ppm): δ = 10.3 (s(br), 3P, PCH_3) ppm. Anal. Calcd for $C_{18}H_{36}CoOP_3$ (420.3): C, 51.43; H, 8.63; P, 22.11. Found: C, 50.95; H, 8.94; P, 21.88.

Carbonyl[2,6-(dimethylphenyl)-C]tris(trimethylphosphine)cobalt(I) (3). Method A: 2,6-Dimethylbenzaldehyde (230 mg, 1.71 mmol) was combined with $CoMe(PMe_3)_4$ (648 mg, 1.71 mmol) at −70 °C to afford a yellow powder of **3**. Yield 482 mg (67%). Mp 114−116 °C (dec). IR (Nujol): $\tilde{\nu}$ = 1886 s (ν C═O); 1574 m (ν C═C) cm^{-1}. ^{1}H NMR (500 MHz, [D$_8$]THF, 293 K, ppm): δ = 1.30 (s(br), 27H, PCH_3); 2.14 (s, 6H, CH_3); 6.46−6.55 (m, 3H, Ar−H). ^{13}C(^{1}H) NMR (125 MHz, [D$_8$]THF, 293 K, ppm): δ = 15.6 (m, PCH_3); 23.7 (s, CH_3); 121.2 (s, CH); 122.7 (s, CH); 140.2 (s, CH); 143.1 (s, C); 166.3 (m, Co−C). ^{31}P(^{1}H) NMR (202 MHz,

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[D_8]THF, 293 K, ppm): δ = 9.0 (m(br), 3P, PCH_3) ppm. Anal. Calcd for $C_{18}H_{36}CoOP_3$ (420.3): C, 51.43; H, 8.63. Found: C, 51.22; H, 8.63.

Carbonyl[2-(aminophenyl)-C]tris(trimethylphosphine)cobalt(I) (4). Method A: $CoMe(PMe_3)_4$ (850 mg, 2.24 mmol) was combined with 2-aminobenzaldehyde (272 mg, 2.24 mmol) at −70 °C to afford after cooling to 4 °C orange crystals of **4** suitable for X-ray diffraction. Yield 650 mg (71%). Method B: 2-Aminobenzylalcohol (340 mg, 2.76 mmol) in diethyl ether was combined at 20 °C with $CoMe(PMe_3)_4$ (1.04 g, 2.76 mmol) to afford yellow crystals. Yield 425 mg (38%). Mp 123−127 °C (dec). IR (Nujol): $\tilde{\nu}$ = 1850 s (ν C═O); 1577 m (ν C═C) cm^{-1}. ^{1}H NMR (500 MHz, [D_8]THF, 293 K, ppm): δ = 1.28 (s(br), 27H, PCH_3); 4.29 (s(br), 2H, NH_2); 6.25 (m, 2H, Ar−H); 6.56 (m, 1H, Ar−H); 6.82 (m, 1H, Ar−H). ^{13}C(^{1}H) NMR (125 MHz, [D_8]THF, 293 K, ppm): δ = 20.0 (m, PCH_3); 108.8 (s, CH); 115.7 (s, CH); 121.5 (s, CH); 144.7 (s, CH); 156.7 (s, C); 180.3 (m, Co−C); 207.6 (m, Co−*C*O). ^{31}P(^{1}H) NMR (202 MHz, [D_8]THF, 293 K, ppm): δ = 9.5 (m(br), 3P, PCH_3) ppm. Anal. Calcd for $C_{16}H_{33}CoNOP_3$ (407.3): C, 47.42; H, 7.71; N, 3.46; P, 22.93. Found: C, 47.11; H, 8.49; N, 3.40; P, 22.75.

Carbonyl[2,6-(difluorophenyl)-C]tris(trimethylphosphine)cobalt(I) (5). Method A: 2,6-Difluorbenzaldehyde (220 mg, 1.54 mmol) was combined at −70 °C with $CoMe(PMe_3)_4$ (585 mg, 1.54 mmol) to afford yellow crystals. Yield 437 mg (66%). Mp 108−110 °C (dec). IR (Nujol): $\tilde{\nu}$ = 1878 s (ν C═O); 1577 m (ν C═C) cm^{-1}. ^{1}H NMR (500 MHz, [D_8]THF, 293 K, ppm): δ = 1.24 (s(br), 27H, PCH_3); 6.51 (dd, $^3J_{H,H}$ = 6.6 Hz,$^3J_{H,H}$ = 6.0 Hz, 2H, Ar−H); 6.79 (dd, $^3J_{H,H}$ = 7.4 Hz,$^3J_{H,H}$ = 6.9 Hz, 1H, Ar−H). ^{13}C(^{1}H) NMR (125 MHz, [D_8]THF, 293 K, ppm): δ = 19.5 (m, PCH_3); 107.4 (d,$^2J_{C,F}$ = 35.0 Hz, CH); 122.8 (t,$^3J_{C,F}$ = 9.0 Hz, CH); 169.1 (m, CoC); 172.4 (dd,$^1J_{C,F}$ = 222.0 Hz,$^3J_{C,F}$ = 21.0 Hz, CF). ^{31}P(^{1}H) NMR (202 MHz, [D_8]THF, 293 K, ppm): δ = 8.2 (m(br), 3P, PCH_3) ppm. Anal. Calcd for $C_{16}H_{30}CoF_2OP_3$ (428.3): C, 44.87; H, 7.06. Found: C, 44.95; H, 7.37.

Carbonyl[2-(trifluoromethylphenyl)-C]tris(trimethylphosphine)cobalt(I) (6). Method A: 2-Trifluoromethylbenzaldehyde (720 mg, 4.13 mmol) was combined at −70 °C with $CoMe(PMe_3)_4$ (1.560 mg, 4.13 mmol) to afford deep red octahedral crystals of **6**, which were suitable for X-ray diffraction. Yield 1.10 g (58%). Mp 115−118 °C (dec). IR (Nujol): $\tilde{\nu}$ = 1866 s (ν C═O); 1578 m (ν C═C) cm^{-1}. ^{1}H NMR (500 MHz, [D_8]THF, 293 K, ppm): δ = 1.21 (s(br), 27H, PCH_3); 6.84 (s, 2H, Ar−H); 7.28 (s, 1H, Ar−H); 7.57 (s, 1H, Ar−H). ^{13}C(^{1}H) NMR (125 MHz, [D_8]THF, 300 K, ppm): δ = 19.7−20.1 (m, PCH_3); 122.5 (s, CH); 126.9 (s, CH); 127.0 (s, CH); 129.1 (m, CF_3); 146.2 (m, CH); 174.3 (m, Co−C); 204.6 (m, Co-CO). ^{31}P(^{1}H) NMR (202 MHz, [D_8]THF, 293 K, ppm): δ = 10.3 (m(br), 3P, PCH_3) ppm. Anal. Calcd for $C_{17}H_{31}CoF_3OP_3$ (460.3): C, 44.36; H, 6.79; P, 20.19. Found: C, 44.29; H, 6.70; P, 20.20.

Carbonyl[1-(naphthyl)-C]tris(trimethylphosphine)cobalt(I) (7). Method A: 1-Naphthaldehyde (338 mg, 2.16 mmol) was combined at −70 °C with a solution of $CoMe(PMe_3)_4$ (820 mg, 2.16 mmol) to afford orange rhombic crystals, which were suitable for X-ray diffraction. Yield 757 mg (79%). Method B: 1-Naphthalenemethanol (270 mg, 1.71 mmol) was combined at 20 °C with $CoMe(PMe_3)_4$ (645 mg, 1.71 mmol) in diethyl ether to afford yellow crystals at −27 °C. Yield 219 mg (29%). Mp 122−124 °C (dec). IR (Nujol): $\tilde{\nu}$ = 1872 s (ν C═O); 1578 m (ν C═C) cm^{-1}. ^{1}H NMR (500 MHz, [D_8]THF, 293 K, ppm): δ = 1.18 (s(br), 27H, PCH_3); 6.91 (t, $^3J_{H,H}$ = 7.1 Hz, 1H, Ar−H); 7.17 (s(br), 2H, Ar−H); 7.24 (d, $^3J_{H,H}$ = 7.7 Hz, 1H, Ar−H); 7.34 (d, $^3J_{H,H}$ = 6.5 Hz, 1H, Ar−H); 7.53 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, Ar−H); 8.56 (d, $^3J_{H,H}$ = 7.1 Hz, 1H, Ar−H). ^{13}C(^{1}H) NMR (125 MHz, [D_8]THF, 293 K, ppm): δ = 22.3 (d, $^1J_{P,C}$ = 18.8 Hz, PCH_3); 117.9 (s, CH); 118.0 (s, CH); 120.4 (s, CH); 120.5 (s, CH); 124.7 (s, CH); 130.6 (s, C); 135.9 (s, CH); 138.8 (s, CH); 140.6 (s, C); 171.5 (m, C); 201.1 (m, Co−C). ^{31}P(^{1}H) NMR (202 MHz, [D_8]THF, 293 K, ppm): δ = 7.8 (m(br), 3P, PCH_3) ppm. Anal. Calcd for $C_{20}H_{34}CoOP_3$ (442.3): C, 54.31; H, 7.75; P, 21.01. Found: C, 54.38; H, 7.85; P, 21.10.

In Situ Observation of Aldehydes/Co-hydride. In an NMR Schlenk tube, $CoCH_3(PMe_3)_4$ (7.52 mg, 0.0198 mmol) was combined with 1-naphthalenemethanol (2.65 mg, 0.0198 mmol) in 0.8 mL THF-d_8 condensed to the starting materials. Under vacuum, the solution was frozen to −196 °C, and the reaction tube was sealed. The reaction was immediately monitored at room temperature by ^{1}H NMR spectroscopy. Within 30 min, resonances were observed for free 1-naphthaldehyde (δ = 10.41 ppm, s(br), Ar−C*H*O), and these resonances continued to increase for about 2 h. Other resonances were observed for CH_4, and in the high-field region (−23.9 ppm) it was indicated that the Co-hydride species [Co*H*(PMe_3)$_4$][59] was the byproduct. Finally, after 4 h, a ^{13}C(^{1}H) NMR spectrum of the reaction mixture was recorded and the *C*HO-carbon resonance of 1-naphthaldehyde identified at 193.3 ppm. Other resonances were also observed in the spectra including multiplets at δ = 5.80, 5.57, and 5.32, and resonances for carbonyl[1-(naphthyl)-*C*]tris(trimethylphosphine)cobalt(I) (**7**) are present in low intensity. For the in situ experiment with equimolar amounts of 2-methylbenzylalcohol (5.23 mg, 0.0428 mmol) with $CoCH_3(PMe_3)_4$ (16.1 mg, 0.0428 mmol) under same conditions, 2-methylbenzylaldehyde was identified: (-^{1}H NMR, 500 MHz, 296 K): δ = 10.28 ppm (s(br) Ar−C*H*O); (^{13}C(^{1}H) NMR, 125 MHz, 296 K): δ = 192.12 ppm (s, Ar−*C*HO).

X-ray Structure Determinations. Data collection was performed on a STOE IPDSII image plate detector using Mo Kα radiation (λ = 0.71019 Å). Details of the crystal structure are given in Table 2. Data collection: Stoe XAREA.[60] Cell refinement: Stoe X-AREA.[60] Data reduction: Stoe X-RED.[60] The structure was solved by direct methods using SHELXS-97,[61] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97.[61] The hydrogen atoms were observed or calculated and refined riding on the bonded carbon atoms. For **6**: It was not possible to model the apparent disorder of the $C(7)F_3$ group accordingly, so the large a.d.p.'s (anisotropic displacement parameters) of F1−F3 have no physical relevance. The structure is of marginal quality and should be understood as proof of connectivity only [$R1 = 0.0794$ ($I \geq 2\sigma(I)$)].

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Supporting Information Available: Tables containing full X-ray crystallographic data for **4**, **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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