Synthesis, Characterization, and Catalytic Reactivity of {CoNO}₈ PCP Pincer Complexes

Jan Pecak, Wolfgang Eder, Berthold Stöger, Sara Realista, Paulo N. Martinho, Maria José Calhorda, Wolfgang Linert, and Karl Kirchner*

ABSTRACT: The reaction of coordinatively unsaturated Co(II) PCP pincer complexes with nitric oxide leads to the formation of new, air-stable, diamagnetic mono nitrosyl compounds. The synthesis and characterization of five- and four-coordinate Co(III) and Co(I) nitrosyl pincer complexes based on three different ligand scaffolds is described. Passing NO through a solution of [Co(PCPNO-iPr)Cl]₂, [Co(PCP-iPr)Cl] or [Co(PCPCH₂-iPr)Br] led to the formation of the low-spin complex [Co(PCP-iPr)(NO)]⁻ with a strongly bent NO ligand. Treatment of the latter species with (X = Cl, Br) AgBF₄ led to chloride abstraction and formation of cationic square-planar Co(I) complexes of the type [Co(PCPNMe-iPr)Cl(NO)]⁺ featuring a linear NO group. This reaction could be viewed as a formal two electron reduction of the metal center by the NO radical from Co(III) to Co(I), if NO is counted as NO⁺. Hence, these systems can be described as {CoNO}₈ according to the Enemark-Feltham convention. X-ray structures, spectroscopic and electrochemical data of all nitrosyl complexes are presented. Preliminary studies show that [Co(PCPNO-iPr)(NO)]⁺ catalyzes efficiently the reductive hydroboration of nitriles with pinacolborane (HBpin) forming an intermediate {CoNO}₈ hydride species.

INTRODUCTION

The investigation of pincer ligands and their transition metal complexes has received significant attention during the past decades.¹ Their adjustable steric and electronic properties enable the stabilization of various chemical systems and thus allow for the investigation of fundamental reactivity and for the design of innovative catalysts. Since their introduction by Moulton and Shaw in 1976, no pincer ligand has retained as much attention as the PCP scaffold based on the phosphino-methylated benzene.² Related pincer ligands that feature an aromatic anionic benzene backbone connected to phosphine donors via CH₂, O, or NR (R = H, alkyl or aryl)linkers provide for a very attractive class of ligands that are simple to prepare and modify. With respect to first-row transition metals, the chemistry of nickel PCP complexes is already quite comprehensive, but studies of cobalt, iron, manganese and chromium PCP pincer complexes are exceedingly rare. This may be attributed to the failure of many simple metal salts to cleave the C–H bonds of the arene moiety of the pincer ligands and/or the thermodynamic instability of the resulting complexes. Another important ancillary ligand in coordination chemistry is the nitrosyl (NO) ligand.³ Transition metal nitrosyl compounds often play an important role in enzymatic reactions but are relatively unexplored yet in homogeneous catalysis. Indeed, the redox noninnocent character of this ligand is one of its basic and eminent features. It can bind to a metal center in various bonding modes, i.e., the linear and the bent mode, and can be treated as either NO⁺ (nitrosonium), NO⁺ (neutral radical), or NO⁻ (nitrosyl). This could enable the stabilization of intermediates in catalytic cycles by supplying or detracting electron density or generating vacant coordination sites. Since different binding modes can lead to different formal oxidation states, Enemark and Feltham proposed a simple notation, {MNO}ⁿ⁺ (n = metal d + NO-π* electrons) to describe metal NO complexes unambiguously and ease their theoretical comparison.⁴ Surprisingly, as cobalt is concerned, no PCP pincer nitrosyl complexes featuring a direct cobalt–carbon single bond have been reported in the literature. An overview of existing group 9 nitrosyl complexes being supported by pincer type ligands is depicted in Chart 1.⁵–⁷ Recently our group reported a series of chromium, manganese, and iron nitrosyl complexes supported by aromatic PCP and PNP pincer ligands.⁸ In this account, we describe a series of well-defined four- and five-coordinate low-spin {CoNO}₈ nitrosyl PCP pincer...
Chart 1. Examples of Group 9 Nitrosyl Pincer Complexes

![Chart 1](image)

Figure 1. Structural view of 1b showing 50% displacement ellipsoids (H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Co1–C1 1.9131(9), Co1–Cl 2.2258(4), Co1–P1 2.1879(4), Co1–P2 2.1898(3), P1–Co1–P2 162.90(1), P1–Co1–C1 178.88(5).

Figure 2. Structural view of 1c showing 50% displacement ellipsoids (H atoms and a second independent complex omitted for clarity). Selected bond lengths [Å] and angles [°]: Co1–C1 1.955(1), Co1–Br1 2.3764(2), Co1–P1 2.2077(4), Co1–P2 2.2124(4), P1–Co1–P2 169.39(2), C1–Co1–Br1 177.49(4).

Selected metrical parameters are provided in the figure captions. The molecular structures of these compounds show the metal in a typical slightly distorted-square planar conformation with the PCP ligands coordinated to the metal center in a tridentate mode. In both complexes the C1–Co1–C1 and C1–Co1–Br1 angles deviate slightly from linearity being 178.88(5)° and 177.49(4)°, respectively. The P1–M–P2 angles are 162.90(1) and 169.39(2)°, respectively. The Co1–C1 bond distances are 1.9131(9) and 1.955(1), respectively.

Direct nitrosylation of complexes 1a–1c with nitric oxide at ambient pressure afforded the five-coordinate, green colored, diamagnetic compounds 2a–2c in 91–98% isolated yield (Scheme 1). All three complexes were fully characterized by a combination of 1H, 13C{1H}, and 31P{1H} NMR spectroscopy, ATR-IR spectroscopy, and HR-MS analysis. In the proton decoupled 31P spectrum the compounds exhibit broad resonances at 139.1, 198.9, and 77.4 ppm, respectively, for the N, O, or CH2 linked systems. Moreover, one single strong absorption band for the characteristic NO stretching mode is detected at 1643, 1650, and 1639 cm⁻¹, respectively, in the IR spectrum for 2a–2c. These values are indicative for NO in a bent coordination mode and therefore advocate for a formal interpretation as NO⁻ anion and the assignment of the oxidation state +II for the cobalt center. In addition, they underline the different donor strengths (CH2 ≈ NR > O) of the ligands in use expressed via NO π-back-bonding, according to the series of Telman’s electronic parameters.12

In order to unequivocally establish the ligand arrangement around the metal centers, the solid-state structures of complexes 2a and 2b were determined by X-ray diffraction. Suitable single crystals were grown for this purpose from saturated pentane solutions kept at −20 °C. A view of the molecular structures is depicted in Figures 3 and 4 with selected bond distances and angles reported in captions. Both complexes adopt a slightly distorted square pyramidal geometry (τ ≈ 0.1)13 with the metal center surrounded by three meridionally placed donor atoms of the PCP ligand and the nitrosyl group occupying the apical position.

The N–O bond distances are 1.164(3) and 1.176(2) Å for 2a and 2b, respectively. The Co–N–O angles of 140.1(2) and 140.2(1)° are in the range expected for a bent configuration. Gaviglio et al. reported a N–O bond distance of 1.184(4) Å and a Rh–N–O angle of 127.4(3)° for the iso electronic {RhNO}₈ pincer complex [RhIII(PCP-iBu)(NO)Cl]₂¹⁴.
Cyclic voltammetry studies were conducted for compound 2a to gain a deeper insight into the electronic structure and properties. The cyclic voltammogram exhibits a strong redox process at $E_{1/2} = 0.11$ V in dichloromethane, and two consecutive reductions at $E_{1/2} = -1.21$ and $-1.64$ V (see Supporting Information). The reduction at $-1.21$ V is an irreversible process and probably metal based. In order to assign the redox processes involved in solution, spectro-electrochemical infrared (SEC-IR, Figure 5) experiments were carried out, and changes in the N-O stretching frequency were monitored.

After applying a voltage of 1.00 V, the absorption at 1654 cm$^{-1}$, typical for a bent NO alignment, gradually shifts to a new resonance at 1771 cm$^{-1}$ typical of a linear NO coordination mode (OCP = Open Circuit Potential).

Figure 3. Structural view of 2a showing 50% displacement ellipsoids (H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Co1–Cl1 2.2947(12), Co1–Cl1 1.959(2), Co1–P1 2.227(1), Co1–P2 2.236(1), Co1–N3 1.736(2), N3–O1 1.164(3), P1–Co1–P2 155.88(2), C1–Co1–Cl1 151.25(6), Co1–N3–O1 140.1(2).

Figure 4. Structural view of 2b showing 50% displacement ellipsoids (H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Co1–Cl1 2.2823(5), Co1–Cl1 1.939(2), Co1–P1 2.2298(5), Co1–P2 2.2070(5), Co1–N1 1.726(1), N1–O3 1.176(2), P2–Co1–P1 154.58(2), C1–Co1–Cl1 150.69(5), Co1–N1–O3 140.2(1).

Figure 5. SEC-IR experiments with [Co(PCP**NMe**-Pr)(NO)] (2a, 5 mM in CH2Cl2) at 1.00 V vs Ag pseudoreference electrode. The absorption at 1654 cm$^{-1}$, typical for a bent NO alignment, gradually shifts to a new resonance at 1771 cm$^{-1}$ typical of a linear NO coordination mode (OCP = Open Circuit Potential).

Figure 6. HOMO of [Co(PCP**NMe**-Pr)(NO)] (2a, left) and the calculated spin density in open-shell [Co(PCP**NMe**-Pr)(NO)]$^+$ obtained after electrochemical oxidation (right).

coordinate nitrosyls are in general very likely to bend when the basal ligands are strong σ- or π-donors. Since the assignment of an oxidation is not trivial owing to the delocalization of the HOMO, [Co(PCPNMe3-Pr)(NO)]$^+$ is best described as (CoNO)$^+$ using the Enemark–Feltham notation.

One electron reduction of 2a, on the other side, leads to a loss of the halide ligand (optimized Co–Cl distance 5.41 Å) and formation of a nearly linear NO moiety (calc. Co–N–O angle 176.8°). The Co–NO π bonding and antibonding orbitals are strongly involved in both processes.

Treatment of 2a and 2b with halogen scavengers such as AgBF$_4$ or TIPF$_6$ in CH$_2$Cl$_2$ afforded the square planar, diamagnetic cationic complexes 3a and 3b in 75 to 88% yield (Scheme 2). In the IR spectrum both compounds exhibit strong bands at 1806 and 1861 cm$^{-1}$, which is a characteristic feature for a linear configuration of the NO moiety. In the $^3$P($^1$H) spectrum the associated resonances at 156.0 and 216.9 ppm are shifted downfield with respect to 2a and 2b.

Single crystals of 3a and 3b were successfully grown by slow diffusion of pentane into a saturated solution in THF and
analyzed by X-ray diffraction. A structural view is depicted in Figures 7 and 8 with selected bond distances and angles reported in captions. The molecular structures of both compounds show

**Figure 7.** Structural view of 3a showing 50% displacement ellipsoids (H atoms and counterion omitted for clarity). Selected bond lengths [Å] and angles [°]: Co1–C1 1.929(4), Co1–P1 2.2068(11), Co1–P2 2.202(1), Co1–N3 1.631(3), N3–O1 1.173(4), P2–Co1–P1 164.57(4), C1–Co1–N3 176.0(2), Co1–N3–O1 176.6(3).

**Figure 8.** Structural view of 3b showing 50% displacement ellipsoids (H atoms and counterion omitted for clarity). Selected bond lengths [Å] and angles [°]: Co1–C1 1.932(2), Co1–P1 2.2042(8), Co1–P2 2.2023(7), Co1–N1 1.635(2), N3–O1 1.162(2), P2–Co1–P1 159.68(3), C1–Co1–N1 175.1(1), Co1–N1–O3 177.3(2).

in captions. The molecular structures of both compounds show the metal center in a square planar coordination geometry (r_e < 0.1)\(^1\) with the N–O group located trans to the ipso carbon atom. The N–O bond distances are 1.173(4) and 1.162(2) Å for 3a and 3b, respectively. The Co–N–O angles are 176.6(3) and 177.3(2)° showing a small deviation from linearity probably as a result of strong σ-donation by the benzene ring. The C_\text{ipso}-Co bond length is also slightly shortened compared to their five-coordinate precursors.

In this sense, the abstraction of a halide atom leads to formation of a complex with a formal oxidation state of + I and an electronic isomerization between two \{CoNO\}\(^3\) complexes: Co\(^{III}\)–NO\(^+\) ↔ Co\(^{IV}\)–NO\(^-\). It is therefore reasonable to compare these compounds to already literature known Co(I) PCP pincer complexes. Murugesan et al. reported on the synthesis of low-spin complexes \[\text{Co}^I(\text{PCP}^{\text{NMMe}}\cdot\text{iPr})(\text{iBuNC})_2\] and \[\text{Co}^I(\text{PCP}^{\text{NMMe}}\cdot\text{iPr})(\text{CO})_2\] with very similar shifts in the \(^{31}\text{P}([H])\) spectrum (164.6 and 170.6 ppm, respectively) as compared to 3a (156.0 ppm).\(^1\) An alternative and effective approach to cationic 3a is therefore utilizing a simple and fast ligand exchange reaction starting from \[\text{Co}^I(\text{PCP}^{\text{NMMe}}\cdot\text{iPr})(\text{CO})_2\] (4a, vide supra) and NOBF\(_4\) in dichloromethane (Scheme 3). Complex 3a readily reacts with CO in solution to afford the five-coordinate adduct \[\text{Co}^I(\text{PCP}^{\text{NMMe}}\cdot\text{iPr})(\text{CO})_2\cdot\text{NOBF}_4\]

### Scheme 3. Alternative Synthesis of Complex 3a

\[\text{Co}^I(\text{PCP}^{\text{NMMe}}\cdot\text{iPr})(\text{CO})_2\cdot\text{NOBF}_4\] (5) similar to the Rh complexes reported by Milstein and co-workers.\(^5\) In the IR spectrum this complex gives rise to strong bands at 2025 (\(\nu_{\text{CO}}\)) and 1732 (\(\nu_{\text{NO}}\)) cm\(^{-1}\). The latter may suggest a linear NO moiety coordinated in the equatorial position trans to the C_\text{ipso} carbon atom. Compound 5 is inherently unstable and decomposes to 3a instantaneously when exposed to air or a vacuum.

The cyclic voltammogram of cationic 3a exhibits reox processes at 0.68 V and two consecutive reductions at -1.14 V and -1.35 V. The first oxidation wave at 0.68 V can tentatively be assigned to oxidation of the PCP ligand moiety. DFT calculations show that the HOMO of 3a is a delocalized \(\pi\) orbital on the pincer ligand.

Scan rate experiments show that the reduction peak at -1.14 V is an irreversible process, whereas the peak at -1.35 V is associated with a quasi-reversible reduction. DFT calculations reveal that the LUMO and LUMO+1 are both antibonding between Co and NO, and the reduction product has an elongated Co–NO bond. The loss of the NO ligand is thus likely to happen in the first irreversible step, and the second reduction wave might result from a secondary product.

Reaction of 3a with LiCl in MeOH-\(d_4\) leads to formation of 2a in quantitative yield. It must be mentioned that putative 3c can be prepared in the same manner as 3a and 3b, but it proved to be very difficult to afford an analytically pure compound (approximately 75% yield, \(\nu_{\text{NO}} = 1823\) cm\(^{-1}\)).

Since various cobalt species including PNN and NNN pincer type complexes were shown to be catalytically active for the reductive hydroboration of ketones and nitriles, we began preliminary studies on the potential of the nitrosyl Co(I) complex 3a for this type of transformation.\(^{17a-19}\) Complex 3a (4 mol %) reacted with both aromatic and aliphatic nitriles and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) in benzene at 25 °C (Table 1). After filtration and workup with HCl in dry diethyl ether all amines were isolated as ammonium salts and characterized by \(^1\)H and \(^{13}\)C\(^{[\text{H}]\}) NMR spectroscopy. Monitoring of the reaction by \(^1\)H NMR spectroscopy revealed the formation of a hydride intermediate giving rise to a triplet resonance at -9.3 ppm (\(J_{\text{HP}} = 57\) Hz), which may be involved in the catalytic cycle. This species prevails throughout the experiment and may be structurally related to the pyrrole-based hydride complex described by Tonzetich and co-workers.\(^6\)

### CONCLUSION

In sum we have prepared a series of cobalt nitrosyl complexes supported by PCP pincer ligands that are connected via NMe, O, or CH\(_2\) spacers to an aromatic backbone and fully characterized them by a combination of X-ray, NMR, CV, and FT-IR techniques. Five coordinate Co(III) complexes of the type \[\text{Co}^I(\text{PCP})(\text{NO})X\] (X = Cl or Br) can easily be prepared by direct nitrosylation of the related 15e Co(II) precursors \[\text{Co}^I(\text{PCP})X\] (1a–1c) using nitric oxide. Treatment of these compounds with halide scavengers (AgBF\(_4\) or TIPF\(_4\)) leads to the formation of square planar cationic Co(I) complexes of the type \[\text{Co}^I(\text{PCP})(\text{NO})\] in good yields. Alternatively, \[\text{Co}^I(\text{PCP})(\text{NO})\] was also obtained by reacting the
Table 1. Reductive Hydroboration of Nitriles Catalyzed by 3a

| Product | Yield (%) |
|---------|-----------|
| ![Image](image1.png) | 89 |
| ![Image](image2.png) | 76 |
| ![Image](image3.png) | 95 |
| ![Image](image4.png) | 71 |
| ![Image](image5.png) | 86 |
| ![Image](image6.png) | 88 |

Reactivity conditions: 0.33 mmol substrate, 0.72 mmol HBpin (2.2 equiv), 3a (4 mol %), 1 mL of benzene. Isolated yields as hydrochloride. Conversion determined by $^{19}$F($^1$H) NMR spectroscopy.

literature known dicarbonyl complex [Co(PCPNO$_2$-iPr)Cl] with NOBF$_4$. Structural characterization by means of X-ray diffraction supports the IR measurements that show that the NO moiety is strongly bent in the Co(III) species (approximately 140°) and nearly linear for the Co(I) systems. Both classes of compounds are stable low-spin diamagnetic compounds that can be unambiguously described as {Co(NO)$_2$} systems according to the Enemark–Feltham convention. Preliminary studies showed that [Co(PCPNO$_2$-iPr)(NO)]$^+$ (3a) efficiently catalyzes the reductive hydroboration of nitriles with HBpin at room temperature, presumably via a hydride intermediate. These observations warrant further investigations of the catalytic activity of cobalt nitrosyl pincer complexes.

**EXPERIMENTAL SECTION**

*General Information.* All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in an MBraun inert-gas glovebox. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. Nitric oxide (NO 2.5%) was purchased from MESSER GmbH (Gumpoldskirchen, Austria). The synthesis of 2-bromo-1,3-phenylene)bis(methylene)bis-(dipropylphosphane) (P(C–Br)[P(CH$_2$-iPr)$_2$]).$^{11}$ [Co(PCPNMe$_3$-iPr)Cl] (1a),$^{13}$ [Co(PCP$_3$-iPr)Cl] (1b),$^{11}$ and [Co(PCPNMe$_3$-iPr)(CO)$_2$] (4a)$^{14}$ was carried out according to the literature. $^1$H, $^13$C($^1$H) NMR spectra were referenced internally to residual protiosolvent and solvent resonances, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). $^3$P($^1$H) NMR spectra were referenced externally to H$_3$PO$_4$ (85%) (δ = 0 ppm). Infrared spectra were recorded in attenuated total reflection (ATR) mode on a PerkinElmer Spectrum Two FT-IR spectrometer.

High resolution-accurate mass spectra were recorded on a hybrid Maxis Qq-TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) fitted with an ESI source. Measured accurate mass data of the [M]+ ions for confirming calculated elemental compositions were typically within ± 5 ppm accuracy. The mass calibration was done with a commercial mixture of perfluorinated trialkyl-triazines (ES Tuning Mix, Agilent Technologies, Santa Clara, CA, USA).

Cyclic voltammograms were recorded in a three-electrode system single-compartment electrochemical cell with glassy carbon (3 mm diameter, CHI Instruments) and platinum wire as working and counter electrodes, respectively. The reference electrode used was a saturated Calomel electrode (SCE, 0.241 V vs. NHE); however, all potentials are referenced to the Fc'/Fc couple (0.44 V vs. SCE). One mM solutions of the complexes in dichloromethane were used and TBAPF$_6$ (0.2 M) as supporting electrolyte. All experiments were accomplished using an Autolab PGSTAT128N potentiostat (Metrohm GmbH) controlled by NOVA software. SEC-IR experiments were performed using a cell acquired from LabOmak. This cell has two platinum grids as working and counter electrodes and an Ag wire as the pseudoreference electrode. A 5% saturated MeCN solution with 5 mM of complex and 0.2 M of TBAPF$_6$ was injected in the SEC-IR cell. A linear voltammogram was performed using a scan rate of 10 mV s$^{-1}$ to reach the suitable potential (+1.0 vs Ag pseudoreference) after the first oxidation peak. The IR spectra were obtained using a Nicolet Nexus 6700 FTIR spectrophotometer with a resolution of 4 cm$^{-1}$ with 16 scans between 2200 and 1500 cm$^{-1}$. The background spectrum was recorded with the sample at the open circuit potential.

**Synthesis.** [Co(PCP$_3$-iPr)(NO)]Cl (1c). To a solution of P(C–Br)[P(CH$_2$-iPr)$_2$], iPr (100 mg, 0.24 mmol) in THF (10 mL), n-BuLi (0.32 mL, 1.6 M, 0.48 mmol) was slowly added at −78 °C and then stirred for 1 h. After allowing to warm to room temperature a suspension of anhydrous CoBr$_2$ (55 mg, 0.25 mmol) in THF (5 mL) was added in dropwise fashion. The reaction mixture was stirred for 0.5 h and all volatiles were allowed to warm to room temperature a suspension of anhydrous CoBr$_2$ (55 mg, 0.25 mmol) in THF (5 mL) was added in dropwise fashion. The reaction mixture was stirred for 0.5 h and all volatiles were removed under reduced pressure. The remaining brownish solid was extracted into n-pentane and the yellow extract was filtered through a plug of Celite. The solvent was partially removed under a vacuum and the solution was placed in a freezer at −20 °C to obtain a yellow crystalline solid. Yield: 74 mg (65%). $^3$P($^1$H) NMR (162 MHz, C$_6$D$_4$Cl$_2$) δ = 2.9 Hz), 17.2 (t, $J$ = 5.7 Hz), 32.5 (s), 18.3 (s), 17.4 (t, $J$ = 2.9 Hz), 17.2 (t, $J$ = 3.9 Hz), 16.9 (s). $^1$H HR-MS (ESI$^+$, C$_6$H$_3$OH) m/z calculated for C$_{20}$H$_{37}$CoN$_3$OP$_2$ [M$^+$] 475.0729 found 475.0728.

[Co(PCP$_3$-iPr)(NO)]Cl (2a). A solution of [Co(PCP$_3$-iPr)(Cl)] (1a) (100 mg, 0.21 mmol) in THF (5 mL) was stirred for 15 min under a NO gas atmosphere (1 bar) whereupon the solution turned from red to green. Insoluble materials were removed by filtration through a plug of Celite. The solvent was partially removed under a vacuum and the solution was placed in a freezer at −20 °C to obtain a yellow crystalline solid. Yield: 74 mg (65%). $^3$P($^1$H) NMR (162 MHz, C$_6$D$_4$Cl$_2$) δ = 169.1 (1H, Br) ppm. $^1$H HR-MS (ESI$^+$, C$_6$H$_3$OH) m/z calculated for C$_{20}$H$_{37}$CoBr$_2$ [M$^+$] 475.0729 found 475.0728.
vacuum. Yield: 75 mg (85%).

red solid was washed twice with pentane (3 mL) and dried under a vacuum. Yield: 39 mg (88%).

reduced pressure; the product was washed with pentane (3 mL) and filtered via syringe filter.

Yield: 41 mg (75%).

reaction mixture was stirred at room temperature for 24 h. The reaction mixture was then filtered through a PTFE syringe filter, diluted with Et2O (4 mL), and a solution of HCl in Et2O was added dropwise until the precipitation of the hydrochloride was complete. The obtained ammonium salts were washed with Et2O, dried under vacuum, and analyzed by H NMR spectroscopy.

X-ray Structure Determination. X-ray diffraction data for 1a, 1c, 2a, 2b, 3a, and 3b (CCDC 1953233 (1a), 1959138 (1c), 1953234–1953237 (2a, 3a, 3b)) were collected at T = 100 or 150 K in a dry stream of nitrogen on a Bruker Kappa APEX II diffractometer system using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) and fine sliced q- and ω-scans. Data were reduced to intensity values with SAINT and an absorption correction was applied with the multiscan approach implemented in SADABS. The structures were solved by the dual space method implemented in SHELT1 and refined against F2 with SHELXL. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. The Co–N and N–O distances of the minor (3%) orientation of a disordered NO ligand were restrained to 1.74(2) and 1.16(2) Å, respectively. Molecular graphics were generated with the program MERCURY.

Computational Details. The Amsterdam Density Functional program (ADF) was used in the Density Functional Theory calculations. Geometries were optimized without symmetry constraints, considering solvent (acetonitrile), with gradient correction, using the Vosko–Wilk–Nusair Local Density Approximation of the correlation energy and the Generalized Gradient Approximation with Becke’s exchange23 and Perdew’s correlation functions. Unrestricted calculations were carried out for open shell complexes. The solvent correction was taken into account using the COSMO approach implemented in ADF. Relativistic effects were treated with the ZORA approximation. Triple ζ Slater-type orbitals (STO) were used to describe all the valence electrons of H, C, B, and N, augmented with a set of two polarization functions (H, single ζ 2s, 2p, C and N, 3s, 3p, O, and P single ζ 3d, 4f, and Co single ζ 4p, 4f) and with a frozen core (1ς) for C, O, N, and P, and for Co (1ς 2p). Orbitals and three-dimensional structures were drawn with Chemcraft.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00167.

H, 13C{1H} and 31P{1H} NMR spectra of all complexes and organic products (PDF)

Optimized Cartesian coordinates for DFT-calculated structures (XYZ)

Accession Codes
CCDC 1953233–1953237 and 1959138 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author
Karl Kirchner — Institute of Applied Synthetic Chemistry, Vienna University of Technology, A-1060 Vienna, Austria; orcid.org/0000-0003-0872-6159; Email: karl.kirchner@tuwien.ac.at

Authors
Jan Peck — Institute of Applied Synthetic Chemistry, Vienna University of Technology, A-1060 Vienna, Austria

Wolfgang Eder — Institute of Applied Synthetic Chemistry, Vienna University of Technology, A-1060 Vienna, Austria
Berthold Stöger – X-Ray Center, Vienna University of Technology, A-1060 Vienna, Austria
Sara Realista – Instituto de Tecnologia Química e Biológica António Xavier, ITQB NOVA, Universidade Nova de Lisboa, 2780-157 Oeiras, Portugal
Paulo N. Martinho – BioISI – Biosystems and Integrative Sciences Institute, DQB, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal; orcid.org/0000-0003-2552-6263
Maria José Calhorda – BioISI – Biosystems and Integrative Sciences Institute, DQB, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal; orcid.org/0000-0002-6872-3569
Wolfgang Linert – Institute of Applied Synthetic Chemistry, Vienna University of Technology, A-1060 Vienna, Austria; orcid.org/0000-0002-7177-0163

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00167

Notes
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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on April 24, 2020, with several incorrect structures. In Scheme 1, compounds 1c and 2c should include Br instead of Cl. In Table 1, the bottom two structures should be benzyl amines. The corrected version was reposted on May 19, 2020.