Mechanochemical insertion of cobalt into porphyrinoids using $Co_2(CO)_8$ as a cobalt source

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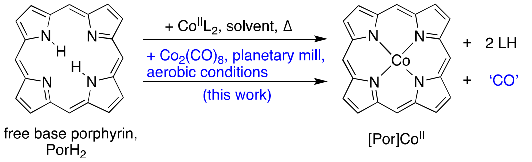
Cobalt porphyrinoids find broad use as catalysts or electrode materials. Traditional solution state cobalt insertion reactions into a free base porphyrinoid to generate the corresponding cobalt complexe generally require fairly harsh conditions, involving the heating of the reactants in high-boiling solvents for extended period of times. We report here an alternative method of cobalt insertion: A solvent-free (at least for the insertion step) mechanochemical method using a planetary ball mill with $Co_2(CO)_8$ as a cobalt source. The scope and limits of the reaction were investigated with respect to the porphyrinic substrate susceptible to the reaction conditions, the influences of different grinding aids, and bases added. While the mechanochemical method is, like other metal insertion methods into porphyrinoids, not universally suitable for all substrates tested, it is faster, milder, and greener for several others, when compared to established solution-based methods.

Introduction

Cobalt(II) porphyrins have long aroused interest for their ability to catalyze, e.g., benzylic C-H aminations,[1] oxidations,[2] carbene transfers,[3] alkene insertions,[4] including cyclopropanations,[5] electrochemical or photochemical CO_2 or oxygen reductions,[6, 7] and (enantioselective) radical cyclization reactions.[8] They have also been used, inter alia, as synthons in supramolecular assemblies,[9] in chemosensing materials,[10] as cathodes in microbial fuel cells,[11] as building blocks in biomedical applications,[12] or as a trap for azanone (HNO).[13] When complexed by porphyrins, cobalt(II) is the stable oxidation state of the metal at ambient, oxic conditions, though oxidation to cobalt(III) is facile.[2, 14, 15] The cobalt(II/III) complexes of the expanded porphyrins,[16] porphyrin isomers,[17] or carbaporphyrins[5, 18] are also known. Because of the relationship to the cobalt-containing co-factor vitamin B_{12},[19] there has also been a long-standing interest in cobalt corrins[20] and corroles.[21]

The central metal, cobalt, in the co-factor vitamin B_{12} is inserted by nature into a precursor porphyrin via a dedicated cobaltochelatase enzyme that distorts the porphyrin from planarity to accelerate the metal insertion step.[22] Metal insertion into synthetic cobalt porphyrinoids was near-exclusively achieved thermally via a metathesis reaction using the free base porphyrin and a cobalt(II) salt (acetate, chloride, acetylacetonate, etc.) at more or less elevated temperatures, ranging from reflux in MeOH (b.p. = 65 °C) to high-boiling solvents, like DMF (b.p. = 153°C) (Scheme 1).[23]



Scheme 1. Generalized thermal and mechanochemical cobalt(II) insertion reaction into porphyrins

Procedural improvements of the cobalt insertion step were published,[24] but the principle process has remained the same. On rare occasion, the macrocycle has been assembled at ambient temperature in the presence of the cobalt ion that may have acted as a template.[25]

Mechanochemistry broadly refers to chemical syntheses where activation is induced by mechanical force.[26] Possible advantages of solid state reactions employing mills over conventional solution-based reactions are access to different reaction pathways,[27, 28] the avoidance of a reaction solvent and decreased reaction times, although it is rare to have a single mechanochemical reaction encompass all advantages.[26, 29] Because milling processes require no reaction solvent, they circumvent the health or environmental hazards and energy costs associated with the handling, heating, cooling, and removal of solvents and, thusly, offer a greener alternative to solution-based reactions.[28] However, not all mechanochemical reactions entirely avoid all solvents when subsequent product isolation and purification steps are also considered, albeit some may.[30] Syntheses under mechanochemical conditions in ball mills have found applications in organic and inorganic syntheses,[26, 27, 29, 31, 32, 33] including the synthesis of porphyrins.[34]

Following a lead,[30] we recently reported on the use of a planetary ball mill in which the dry, solid reagents were intensely ground together to affect the mechanochemical

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Electronic Supplementary Information (ESI) available: Spectroscopic data identifying the known and novel cobalt porphyrinoids prepared. See DOI: 10.1039/x0xx00000x insertion of a number of metal ions (with focus on zinc(II), copper(II), and magnesium(II)) into a range of free base porphyrins.[32] However, insertion of cobalt(II) into *meso*-tetraphenylporphyrin (**TPP**) failed under the conditions chosen (2.5 equiv $CoCl_2 \cdot 6H_2O$ or $Co(OAc)_2 \cdot 4H_2O$, silica gel as grinding aid, 80 min grinding time) or were not satisfying using β-octaethylporphyrin (**OEP**) (50% conversion after 60 min milling time).[32]

The use of the transition metal carbonyl $Co_2(CO)_8$ as a metal source for the solution state synthesis of the cobalt complex of mesoporphyrin dimethyl ester has been reported (next to the uses of $V(CO)_6$, $Cr(CO)_6$, $Fe_3(CO)_{12}$, $Fe(CO)_5/I_2$, or $Ni(CO)_4$ for the formation of the corresponding vanadyl, chromium, iron, or nickel complexes).[35] However, high-boiling solvents, such as toluene (at 95 °C for 15 h), *n*-decane (at 170 °C for 1.5 h) or decalin (at 205 °C bath temperature), were needed for the formation of the cobalt(II) complex. Such harsh reaction conditions are presumably needed to thermally induce the break-up of the coordinatively saturated cobalt carbonyl cluster into species that have the ability to coordinate to the porphyrin nitrogen atoms. The harsh reaction conditions required likely prevented the routine use of $Co_2(CO)_8$ (or the other 3d metal carbonyls) as metal sources. More recent attempts at using $Ni(CO)_4$ as a nickel source, for example, failed to insert nickel into *meso*-tetrakis(C_6F_5)porphyrin (**T^FPP**), though another nickel(0) source, $Ni(COD)_2$, was successful.[36] The situation is also different for some 4d and 5d metals (ruthenium, rhenium, iridium, and osmium) with kinetically rather inert M(II) ions; here the use of the corresponding M(0) carbonyls as metal sources for the formation of the corresponding metallo-porphyrinoids offers distinct kinetic advantages and, therefore, have become standard practice.[23]

The use of the solid, non-volatile transition metal carbonyl $Co_2(CO)_8$ seems to be offering advantages as a cobalt source with respect to its ease of handling, broad availability, the lack of hard-to-remove anions or corresponding acids, and its potential atom economy. Moreover, work by the group of Friščić demonstrated the mechanochemical CO-to-halogen exchange of organometallic Re(I) complexes,[37] the mechanochemically activated oxidative cleavage of $M_2(CO)_{10}$ (M = Mn, Re),[38] as well as using $M(CO)_6$ (M = Cr, Mo, and W) for mechanochemical carbonylation reactions.[33] This supports the susceptibility of transition metal carbonyls to mechanochemical activation.

Thus, using the formation of cobalt porphyrinoids with $Co_2(CO)_8$ as a metal source as an example, we decided to test whether the evidently high activation energies needed to ‘crack’ the metal carbonyl can be overcome using mechanical force in a planetary mill. This report will reveal that it is indeed possible, leading to a milder and greener formation of some cobalt porphyrinoids in excellent yields. But as we will also detail here, we discovered that the mechanochemical insertion reaction is surprisingly complex and imbued with its unique scope and limits.

Results and discussion

Mechanochemical metal insertion reactions into porphyrins using a planetary mill are subject to a range of variables, including the mill parameters (such as rotational speed, vessel size, vessel material, milling time), the presence and nature of grinding aids that may enhance the mechanical energy transfer from the mill to the reagents, and additives that may change the acidity/basicity of the reaction media.[32] The grinding aids turned out to play mechanical as well as chemical roles in the outcome of the metal insertion reaction; in earlier work, we even found initially presumed inert grinding aids to lead to an accelerated decomposition of the (metallo)porphyrins.[32] The nature of the porphyrinoids also has a large influence on the rate and overall yield of the reaction, as expected based on the much varying basicity and conformational flexibility of the porphyrinoids.[23, 32] These many influences call for a testing of a wide variation of reaction conditions.

For simplicity, some parameters were nonetheless held constant in the experimental series presented here: the reaction temperature (ambient conditions, in a well-ventilated mill that provided sufficient air cooling to allow the reaction to not warm to any noticeable degree) and the metal source, $Co_2(CO)_8$. We approached our screening strategy in several phases. We first aimed to confirm that the cobalt insertion into **OEP** using $Co_2(CO)_8$ in a mill is indeed possible under mechanochemical control. Next, we screened the influences of the grinding aids and added bases on the cobalt insertion into **OEP**. From those experiments, we identified standard reaction conditions we used to screen a variety of other porphyrinic substrates, some for which the cobalt complexes were known, and others for which the corresponding cobalt complexes had previously not been reported.

Demonstration that the metal insertion reaction is under mechanochemical control.

Mere mixing of **OEP**, an archetype porphyrin known to readily insert cobalt using Co(II) salts, with $Co_2(CO)_8$ alone or with basic alumina does not affect any metal insertion reaction, even after left for days. However, milling the mixture with increasing energy input (increasing milling speed, time, or vessel size) affected the reaction as expected for a mechanochemical reaction (see ESI).

Equivalents of $Co_2(CO)_8$ as metal source needed

The use of $Co_2(CO)_8$ as the cobalt source (34.5% Co) is potentially an atom-economic way of delivering the metal ion, when compared to other standard (albeit less costly) cobalt salts ($Co(CH_3CO_2)_2 \cdot 4H_2O$, 23.6% Co; $CoCl_2 \cdot 6H_2O$, 24.8% Co), but not the anhydrous salt $CoCl_2$ (45.4% Co). Table 1 provides an overview over the number of equivalents of $Co_2(CO)_8$ needed for the insertion of cobalt into **OEP**. Thus, under the two conditions tested, at least a 1.5-fold excess of $Co_2(CO)_8$ is needed to drive the reaction essentially to completion within 60 min. Such a molar excess of metal is not unusual for classic metal insertion reactions.[23]

When $Co_2(CO)_8$ is milled on silica gel for 20 min in the absence of a porphyrin and the porphyrin is added subsequently, the reaction proceeds in the same speed and yield as if the carbonyl and porphyrin were directly combined, suggesting that $Co_2(CO)_8$ is not getting activated (or degraded) in the absence of the porphyrinic ligand.

Table 1. Effects of the use of varying equivalents of $Co_2(CO)_8$ on the outcome of the mechanochemical insertion of cobalt into **OEP** using a planetary mill.

Reaction	Equiv $Co_2(CO)_8$	Yield[a] at condition	
		A	B
$\underset{\text{(20 mg, 1 equiv)}}{\textbf{OEP}} \xrightarrow[\text{800 rpm, 50 mL agate vessel}]{\text{Co}_2\text{(CO)}_8\text{ (x equiv), Condition A: silica (0.5 g), No additive, 60 min; Condition B: basic Al}_2\text{O}_3\text{ (0.5 g), LiOH (50 mg), 35 min}} \underset{\text{(yield)}}{\textbf{[OEP]Co}}$	0.5	60%	70%
	1.0	85%	75%
	1.5	93%	92%
	2.5	93%	–
	5.0	97%	–

a Isolated yields.

Effects of grinding aids

The effects of the use of different grinding aids were tested (Table 2). Of those tested, the substrate Florisil (a synthetic magnesium silicate) was the least suitable. Notably, however, the adventitious Mg(II) insertion observed before with this grinding aid during zinc insertion reactions did not affect the cobalt insertion.[32] Generalized, at the same hardness, the more acidic alumina accelerated the cobalt insertion into **OEP** slightly more when compared to basic alumina. However, later experiments using other substrates, such as **TPP** or **T^{F}PP**, revealed that basic alumina held an edge over silica, even when a base was added (cf. also below), as well as other aluminas. Since we previously observed also significant substrate/product decomposition on silica gel over extended periods of time,[32] basic alumina was chosen as the preferred grinding aid. We therefore find again that the grinding aids affect the speed of the metal insertion reaction in ways that suggest their roles are well beyond acting as mere mechanical grinding aids.

Table 2. Effects of the use of different grinding aids (and one additive) on the outcome of the mechanochemical insertion of cobalt into **OEP** using $Co_2(CO)_8$ in a planetary mill.

Reaction	Grinding aid	Yield[a] after milling time
$\underset{\text{(20 mg, 1 equiv)}}{\textbf{OEP}} \xrightarrow[\text{800 rpm, time, 50 mL agate vessel}]{\text{Co}_2\text{(CO)}_8\text{ (65 mg, 5 equiv), grinding aid (0.5 g)}} \underset{\text{(yield after x time)}}{\textbf{[OEP]Co}}$	silica	90%, 50 min
	silica + Li_2CO_3 (100 mg)	75-85%, 75 min
	basic alumina	80%, 45 min
	neutral alumina	90-95%, 45 min
	acidic alumina	90%, 45 min
	Florisil	60-70%, 75 min

a Isolated yields.

Effects of bases added

The finding that more basic conditions accelerated the metal insertion reaction suggested the testing whether the addition of solid inorganic or organic Brønsted bases to the overall fastest grinding aid basic alumina would further accelerate the reaction (Table 33).

The effects of the added base varied widely, with two lithium salts standing out as being particularly beneficial, Li_2CO_3 and LiOH. Since the hydroxide had an edge on the carbonate, all subsequent experiments were performed under the optimized basic alumina/LiOH combination conditions. We cannot offer a mechanistic explanation as to advantages of the lithium bases over the corresponding bases of the other alkaline metals.

Table 3. Effects of different basic additives on the outcome of the mechanochemical insertion of cobalt into **OEP** using $Co_2(CO)_8$ in a planetary mill.

Reaction	Basic additive	Yield[a] after milling time
$\underset{\text{(20 mg, 1 equiv)}}{\textbf{OEP}} \xrightarrow[\text{800 rpm, time, 50 mL agate vessel}]{\text{Co}_2\text{(CO)}_8\text{ (65 mg, 5 equiv), basic alumina (0.5 g), additive (50 mg),}} \underset{\text{(yield after x time)}}{\textbf{[OEP]Co}}$	Li_2CO_3	90%, 45 min
	Na_2CO_3	70-75%, 50 min
	K_2CO_3	85%, 60 min
	LiOH	95%, 35 min
	NaOH	80%, 60 min
	2,2-bipyridine	(–), 50 min
	imidazole	50%, 70 min
	DABCO	40%, 60 min
	4-dimethyl-aminopyridine	(–), 70 min

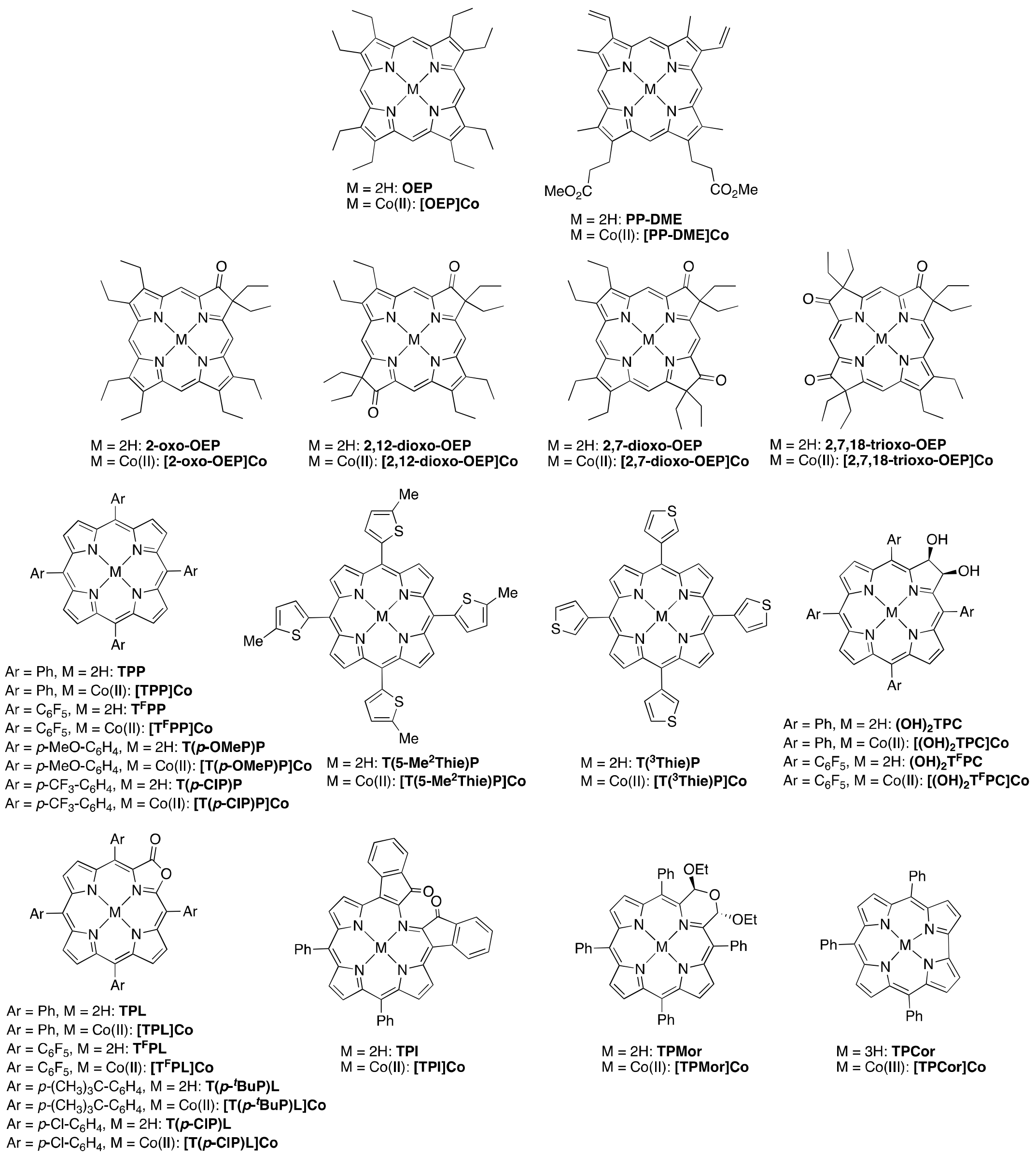
a Isolated yields in %; (++), (+), (–), (– –) refer to yields estimated visually by TLC, corresponding to > 80%, 80-60%, 60-30%, and < 30%, respectively.

The finding that basic reaction conditions are generally of benefit for the cobalt insertion is in contrast to the formation of zinc and copper porphyrins using M(II) salts under mechanochemical conditions that prefer slightly acidic media.[32] While the formal metathesis reaction requires the removal of the porphyrin NH protons, the affinity of the porphyrin for the metal ions is sufficiently large that the addition of base is not required for the formation of a wide range of transition metal porphyrins, cobalt included.[23] In fact, their formation can also take readily place in acidic media (such as hot acetic acid or phenol).[23] The addition of base is therefore primarily needed, at most, to shift the equilibrium to completion or to convert the corresponding acid of the metal salt to its more benign or more readily removable salt. However, the CO ligands delivering the cobalt are already volatile and perceivable innocuous. Thus, we cannot provide an explanation why the reaction benefits from the presence of a strong mineral base, including whether metallacarboxylate intermediates (as the product between a CO ligand and OH^-) play any mechanistic role in the mechanochemical formation of the porphyrin cobalt complexes using $Co_2(CO)_8$.

Influences of the porphyrinoid structure

To define the scopes and limits of the method, we screened a range of porphyrinoids of different degrees of saturation, stability, substituent patterns, and chromophore structures (Chart 1).

Chart 1. Molecular structures of the porphyrinoids used in this study.



M = 2H: **OEP**
M = Co(**II**): **[OEP]Co**

M = 2H: **PP-DME**
M = Co(II): **[PP-DME]Co**

M = 2H: **2-oxo-OEP**
M = Co(II): **[2-oxo-OEP]Co**

M = 2H: **2,12-dioxo-OEP**
M = Co(**II**): **[2,12-dioxo-OEP]Co**

M = 2H: **2,7-dioxo-OEP**
M = Co(II): **[2,7-dioxo-OEP]Co**

M = 2H: **2,7,18-trioxo-OEP**
M = Co(II): **[2,7,18-trioxo-OEP]Co**

Ar = Ph, M = 2H: **TPP**
Ar = Ph, M = Co(**II**): **[TPP]Co**
Ar = C_6F_5, M = 2H: **T^{F}PP**
Ar = C_6F_5, M = Co(II): **[T^{F}PP]Co**
Ar = *p*-MeO-C_6H_4, M = 2H: **T(*p*-OMeP)P**
Ar = *p*-MeO-C_6H_4, M = Co(II): **[T(*p*-OMeP)P]Co**
Ar = *p*-CF_3-C_6H_4, M = 2H: **T(*p*-ClP)P**
Ar = *p*-CF_3-C_6H_4, M = Co(II): **[T(*p*-ClP)P]Co**

M = 2H: **T(5-Me^{2}Thie)P**
M = Co(II): **[T(5-Me^{2}Thie)P]Co**

M = 2H: **T(^{3}Thie)P**
M = Co(II): **[T(^{3}Thie)P]Co**

Ar = Ph, M = 2H: **(OH)$_2$TPC**
Ar = Ph, M = Co(II): **[(OH)$_2$TPC]Co**
Ar = C_6F_5, M = 2H: **(OH)$_2$T^{F}PC**
Ar = C_6F_5, M = Co(**II**): **[(OH)$_2$T^{F}PC]Co**

Ar = Ph, M = 2H: **TPL**
Ar = Ph, M = Co(II): **[TPL]Co**
Ar = C_6F_5, M = 2H: **T^{F}PL**
Ar = C_6F_5, M = Co(**II**): **[T^{F}PL]Co**
Ar = *p*-$(CH_3)_3C$-C_6H_4, M = 2H: **T(*p*-^{t}BuP)L**
Ar = *p*-$(CH_3)_3C$-C_6H_4, M = Co(II): **[T(*p*-^{t}BuP)L]Co**
Ar = *p*-Cl-C_6H_4, M = 2H: **T(*p*-ClP)L**
Ar = *p*-Cl-C_6H_4, M = Co(**II**): **[T(*p*-ClP)L]Co**

M = 2H: **TPI**
M = Co(**II**): **[TPI]Co**

M = 2H: **TPMor**
M = Co(II): **[TPMor]Co**

M = 3H: **TPCor**
M = Co(**III**): **[TPCor]Co**

Table 4. Substrate scope of the outcome of the mechanochemical insertion of cobalt into diverse porphyrinoids using $Co_2(CO)_8$ in a planetary mill.

Reaction	Porphyrin	(Expected) Product	Yield[a] after milling time	Comments
Porphyrin (20 mg, 1 equiv) $\xrightarrow[\text{800 rpm, time; 50 mL agate vessel}]{Co_2(CO)_8 \text{ (65 mg, 5 equiv), basic alumina (0.5 g), LiOH (50 mg),}}$ [Porphyrinato]Co (yield after x time)	**OEP**	**[OEP]Co**	98% after 35 min	Clean reaction; **[OEP]Co** known[39]
	PP-DME	**[PP-DME]Co**	No expected product, after 40 min	Formation of products with a Co-porphyrin-type optical spectrum, not identical to that of genuine **[PP-DME]Co** known[40]; with increasing reaction time, formation of insoluble dark reddish (polymeric) solid, irrespective also whether LiOH was omitted or silica gel used as grinding agent
	2-oxo-OEP	**[2-oxo-OEP]Co**	90-95% after 35 min	Clean reaction; **[2-oxo-OEP]Co** this work, see also ESI
	2,7-dioxo-OEP	**[2,7-dioxo-OEP]Co**	90-95% after 35 min	Clean reaction; **[2,7-dioxo-OEP]Co** this work, see also ESI
	2,12-dioxo-OEP	**[2,12-dioxo-OEP]Co**	45-50% after 45 min	Some degradation of porphyrin/metalloporphyrin;[b] **[2,12-dioxo-OEP]Co** this work, see also ESI
	2,7,18-trioxo-OEP	**[2,7,18-trioxo-OEP]Co**	20-35% after 75 min	Incomplete reaction; some degradation;[b] **[2,7,18-trioxo-OEP]Co** this work, see also ESI
	TPP	**[TPP]Co**	90% after 35 min	Clean reaction; **[TPP]Co** known[39]
	T^{F}PP	**[T^{F}PP]Co**	85-90% after 40 min	Clean reaction; **[T^{F}PP]Co** known[41]
	T(*p*-OMeP)P	**[T(*p*-OMeP)P]Co**	(+) after 40 min	Minor degradation; **[T(*p*-OMeP)P]Co** known[42]
	T(*p*-ClP)P	**[T(*p*-ClP)P]Co**	50-60% after 50 min	Minor degradation; **[T(*p*-ClP)P]Co** known[42]
	$(OH)_2$TPC	**[$(OH)_2$TPC]Co**	(– –) after 40 min	Significant degradation; **[$(OH)_2$TPC]Co** known[15]
	$(OH)_2$T^{F}PC	**[$(OH)_2$T^{F}PC]Co**	40-45% after 40 min	Minor degradation; **[$(OH)_2$T^{F}PC]Co** this work, see also ESI
	TPL	**[TPL]Co**	(–) after 40 min	Instant onset of degradation; **[TPL]Co** known[15]
	T^{F}PL	**[T^{F}PL]Co**	50% after 40 min	Significant degradation after 20 min; **[T^{F}PL]Co** this work, see also ESI
	T(*p*-ClP)L	**[T(*p*-ClP)L]Co**	No product after 50 min	Significant degradation after 10 min; **[T(*p*-ClP)L]Co** this work, see also ESI
	T(*p*-^{t}Bu)PL	**[T(*p*-^{t}Bu)PL]Co**	(– –) after 40 min	Some degradation of porphyrin/metalloporphyrin[b]; **[T(*p*-^{t}Bu)PL]Co** this work, see also ESI
	T(^{3}Thie)P	**[T(^{3}Thie)P]Co**[7]	(++) after 40 min	Clean reaction; **[T(^{3}Thio)P]Co** known[7]
	T(5-Me^{2}Thie)P	**[T(5-Me^{2}Thie)P]Co**[7]	90% after 40 min	Clean reaction; **[T(5-Me^2)P]Co** known[7]
	TPCor	**[TPCor]Co**	50-65% after 35 min	No degradation, but incomplete reaction; **[TPCor]Co** known[43]
	TPMor	**[TPMor]Co**	45-60% after 40 min	Some degradation of porphyrin/metalloporphyrin;[b] **[TPM]Co** known[44]
	DPI	**[DPI]Co**	(– –)[c] after 50 min	Minor degradation; **[DPI]Co** known[44]

a Isolated yields in %; (++), (+), (–), (– –) refer to yields estimated visually by TLC, corresponding to > 80%, 80-60%, 60-30%, and < 30%, respectively.

b Decomposition is also often indicated by the formation of a grey, insoluble compound left on the alumina gel after extraction of the products.

c 10 mg scale.

We included the naturally derived porphyrin protoporphyrin dimethyl ester **PP-DME**,[45] the synthetic ß-octaalkylporphyrin **OEP**,[46] synthetic *meso*-tetraarylporphyrins carrying electron-rich (**TPP**,[47] **T(*p*-OMeP)P**,[48] **T(^{3}Thio)P**,[49] **T(5-Me^{2}Thio)P**[50]) or electron-poor (**T^{F}PP**,[51] **T(*p*-ClP)P**[48]) aryl groups, a series of ß-alkyl-oxo-porphyrinoids derived from **OEP**,[46] a chlorin (**2-oxo-OEP**),[52] a bacteriochlorin (**2,12-dioxo-OEP**),[52] an isobacteriochlorin (**2,7-dioxo-OEP**),[52] and a pyrrocorphin (**2,7,18-trioxo-OEP**)[52]. We incorporated here also *meso*-tetraarylchlorins (**$(OH)_2$TPC**[53] and **$(OH)_2$T^{F}PC**),[54] a *meso*-triphenylcorrole (**TPCor**)[55], a number of *meso*-arylporpholactones (**TPL**, **T^{F}PL**, **T(*p*-^{t}BuP)L**, and **T(*p*-CF_3P)L**)[56] and two further examples of porphyrinoids containing non-pyrrolic building blocks, the so-called pyrrole-modified porphyrins,[57] indaphyrin **TPI**[58] and morpholinochlorin **TPM**[59]. In many of the cases, their cobalt complexes were already literature-known (see Table 4).

The results of the cobalt insertion experiments using standardized conditions are listed in Table 4. The outcomes of the mechanochemical insertion of cobalt(II) using $Co_2(CO)_8$ vary widely with the porphyrinic substrates. The metal insertion into ß-octaalkylporphyrin **OEP** is excellent – fast and high yielding. The method is suitable for some, but not for all octaethyl-oxoderivatives: Chlorin **2-oxo-OEP** and isobacteriochlorin **2,7-dioxo-OEP** provided good results, but the much less basic bacteriochlorin derivative **2,12-dioxo-OEP**[60] and the even more electron-poor pyrrocorphin **2,7,18-trioxo-OEP** afforded only incomplete reactions, even after longer reaction times than the common 30-45 min, whereby the onset of decomposition over the longer time frames also became noticeable.

Somewhat surprising is the complete failure of the cobalt insertion reactions into protoporphyrin dimethyl ester (**PP-DME**). We suspect two reactions to contribute to our inability to isolate any of the expected cobalt complexes: The reactions of the vinyl- groups with $Co_2(CO)_8$ that possibly lead to polymerizations,[61] and the base-induced saponification of the dimethyl esters to generate the less soluble (in the solvents used for the chromatographic analysis or isolation) mono- or dicarboxylic acids, or both.

The most commonly used synthetic porphyrins, the electron-rich or -poor *meso*-tetraarylporphyrins, are equally suitable substrates for this cobalt insertion method. *meso*-Tetra(thienyl)porphyrins **T(^{3}Thie)P** and **T(5-Me^{2}Thie)P** behaved similarly to the other *meso*-tetraarylporphyrins in that they also showed a smooth and rapid conversion to the corresponding cobalt complexes, with no decomposition.

In contrast, the *meso*-tetraaryl-substituted diolchlorins (**(OH)$_2$TPC** and **(OH)$_2$T^{F}PC**) are too fragile. They are known to readily oxidize[62] or dehydrate,[53, 54] or (for **(OH)$_2$T^{F}PC**), loose HF to form intramolecular linkages under thermal or base-induced reaction conditions.[54] Both diol chlorins were previously shown to also not respond well to mechanochemical[32] or microwave-induced[63] metal insertion reactions using M(II) salts.

Porpholactones are considered to be robust, often even more robust than the corresponding porphyrin.[56] And yet, all four derivatives tested (**TPL**, **T^{F}PL**, **T(*p*-^{t}BuP)L**, and **T(*p*-ClP)L**) decomposed appreciably or even entirely under the cobalt insertion reactions. The lactone moiety in some porpholactones were shown to be susceptible to nucleophilic attack, albeit ring opening reaction were never observed.[64] While this reactivity might render these substrates unsuitable for metal insertion reactions in the presence of hydroxide, omission of LiOH also did not result in a considerably better outcome. Thus, we have to consider a yet unrecognized reactivity of the porpholactone with $Co_2(CO)_8$ (or a mechanochemically produced fragment). Other pyrrole-modified porphyrins, such as morpholinochlorin **TPMor** and indaphyrin **TPI** formed the corresponding cobalt complexes, but in less than satisfying yields. This again shows the mechanochemical insertion conditions are not inherently mild. The triphenylcorrole **TPCor** converted smoothly to the corresponding Co(II) complex.

Experimental

Materials

All solvents and reagents (Aldrich, Acros) were used as received. $Co_2(CO)_8$ was sourced from Strem (dark orange, moistened with 1-10% hexanes,) or Pfaltz and Bauer (dark purple, stabilized with 1-5% hexanes). *meso*-Arylporphyrins (**TPP**,[47] **T^{F}PP**,[51] **T(*p*-OMeP)P**,[48] **T(*p*-ClP)P**[48]) *meso*-thienylporphyrins (**T(^{3}Thie)P**,[49] **T(5-Me^{2}Thie)P**[50]), *meso*-arylchlorins (**(OH)$_2$TPC**[53], **(OH)$_2$T^{F}PC**[54]), porpholactones (**TPL**, **TFPL**, **T(*p*-^{t}BuP)L**, **T(*p*-ClP)L**),[56] octaalkylporphyrins (**OEP**[46], **PP-DME**[45]), β-oxohydroporphyrins (**2-oxo-OEP**, **2,7-dioxo-OEP**, **2,12-dioxo-OEP**, **2,7,18-trioxo-OEP**),[52] *meso*-triphenylcorrole **TPCor**,[55] morpholinochlorin **TPMor**[59], and indaphyrin **TPI**[58] were prepared as described in the literature, stemmed from commercial sources, or were gifted to us. The known metalloporphyrins that were used as comparison materials were prepared by cobalt insertions into the corresponding free base chromophores using classic solution-based methods.[23]

Analytical (aluminum backed, silica gel 60 Å, 250 μm thickness) and preparative (20 × 20 cm, glass backed, silica gel 60, 500 μm thickness) TLC plates, and standard grade, 60 Å, 32-63 μm flash column silica gel were used. Additives: silica gel (Sorbent Technologies, USA; particle size: 40 – 75 μm, surface area: 450 - 550 m^2/g, pH: 6.0 – 7.0); neutral alumina, Brock activity I (Sorbent Technologies, USA; particle size: 50 – 200 μm); basic alumina, Brock activity I (Sorbent Technologies, USA; particle size: 50 – 200 μm); acidic alumina, Brock activity I (M. Woelm, Germany); Florisil (Aldrich, USA; 100-200 mesh).

Safety note

$Co_2(CO)_8$ is potentially a volatile source of cobalt(0), can be pyrophoric and release carbon monoxide upon decomposition The NIOSH recommended maximum exposure limit for workers is 0.1 mg/m^3 over an eight-hour time-weighted average without the proper respiratory gear. The use of a fume hood, gloves and goggles are recommended when handling $Co_2(CO)_8$.

Instruments

Planetary ball mill. A Fritsch GmbH, Germany, planetary micro mill (Pulverisette 7 classic line) equipped with 2 grinding vessels was used in the milling experiments, with the main disc speeds ranging between 100 and 800 rpm. Small agate vessel A: Inner dimensions were 25 mm diameter, 49 mm height, volume ~12.5 mL, equipped with 5 agate balls (10 mm), total weight ~7.0 g. Large agate vessel B: Inner dimensions were 45 mm diameter, 37 mm height, volume ~50 mL, equipped with 5 agate balls (12 mm) with a total weight of ~13.6 g (for additional information, see ESI). Zirconia vessel: inner dimensions were 40 mm diameter, 40 mm height, volume ~44 mL, equipped with 5 zirconia balls (10 mm) with a total weight ~16.0 g,

Analytical Instrumentation. High-resolution mass spectra were recorded using an AB Sciex QStar Elite Quadrupole-TOF MS instruments. All UV-vis spectra were recorded on a Cary 50 UV-vis spectrometer (Varian).

Metal insertion procedures[‡]

[OEP]Co – General procedure for the mechanochemical insertion of cobalt(II) using a planetary ball mill and $Co_2(CO)_8$ as a metal source. Free base **OEP** (20 mg, 3.4 × 10^{-5} mol) was ground together with 2.5 equiv of $Co_2(CO)_8$ (34 mg, 8.5 × 10^{-5} mol) in a planetary ball mill using an agate vessel (50 mL) equipped with five agate balls (12 mm) at 800 rpm in the presence of the grinding aid basic alumina (500 mg) and LiOH (100 mg) as a base additive. The reaction was stopped in 10 min intervals to retrieve an aliquot of the dry mixture. It was placed into a pipette plugged with cotton, and extracted using small quantities of the TLC solvent. The extract was assessed with respect to the reaction progress by TLC and UV-vis spectroscopy. In reactions where the product was isolated, the solid mixture was loaded onto a silica gel column and the product extracted using the conditions listed.

[(OH)$_2$T^{F}PC]Co. Prepared from **(OH)$_2$T^{F}PC**[54] (50 mg, 5.0 × 10^{-5} mol) and $Co_2(CO)_8$ (42 mg, 1.23 × 10^{-4} mol) in 45% isolated yield (24 mg) using the general procedure. Chromatography conditions: acetone:hexanes-60:40 with 1% MeOH. R_f = 0.45 (silica, CH_2Cl_2); UV-vis (CH_2Cl_2) λ_{max} (log ε) 435 (1.69), 432 (4.20), 625 (3.52) nm; HR-MS (ESI+, 100% CH_3CN, TOF): *m/z* calc'd for $C_{44}H_{10}N_4O_2F_{20}Co$: 1064.9810 (for M^+); found: 1064.9748.

[T(p-^{t}BuP)L]Co. Prepared from **T(p-^{t}BuP)L**[56] (50 mg, 5.8 × 10^{-5} mol) and $Co_2(CO)_8$ (50 mg, 1.46 × 10^{-4} mol) in 20% isolated yield (11 mg) using the general procedure. Chromatography conditions: ethyl acetate:hexanes 60:40. R_f = 0.60 (silica, CH_2Cl_2); UV-vis (CH_2Cl_2) λ_{max} (log ε) 416 (4.90), 546 (4.43), 588 (4.76) nm; HR-MS (ESI+, 100% CH_3CN, TOF): *m/z* calc'd for $C_{59}H_{58}N_4O_2Co$: 913.3886 (for M^+); found: 913.4106.

[T^{F}PL]Co. Prepared from **T^{F}PL**[56] (80 mg, 8.1 × 10^{-5} mol) and $Co_2(CO)_8$ (69 mg, 2.02 × 10^{-4} mol) in 50% isolated yield (42 mg) using the general procedure. Chromatography conditions: ethyl acetate:hexanes-70:30. R_f = 0.30 (silica, CH_2Cl_2); UV-vis (CH_2Cl_2) λ_{max} (log ε) 405 (1.29), 551 (3.82), 592 (4.25) nm; HR-MS (ESI+, 100% CH_3CN, TOF): *m/z* calc'd for $C_{43}H_6N_4O_2F_{20}Co$: 1048.9497 (for M^+); found: 1048.9370.

[2-oxo-OEP]Co. Prepared from **2-oxo-OEP**[52] (20 mg, 3.63 × 10^{-5} mol) and $Co_2(CO)_8$ (31 mg, 9.07 × 10^{-5} mol) in 95% isolated yield (21 mg) using the general procedure. Chromatography conditions: 1% MeOH in ethyl acetate:hexanes 40:60. R_f = 0.73 (silica, CH_2Cl_2); UV-vis (CH_2Cl_2) λ_{max} (log ε) 321 (4.19), 369 (4.47), 410 (4.88), 568 (3.82), 616 (4.42) nm; HR-MS (ESI+, 100% CH_3CN, TOF): *m/z* calc'd for $C_{36}H_{44}N_4O_2Co$: 607.2847 (for M^+); found: 607.2842.

[2,7-dioxo-OEP]Co. Prepared from **2,7-dioxo-OEP**[52] (20 mg, 3.53 × 10^{-5} mol) and $Co_2(CO)_8$ (30 mg, 8.77 × 10^{-5} mol) in 95% isolated yield (21 mg) using the general procedure. Chromatography conditions: 1% MeOH in ethyl acetate:hexanes 50:50. R_f = 0.18 (silica, CH_2Cl_2), UV-vis (CH_2Cl_2) λ_{max} (log ε) 388 (4.36), 423 (4.30), 578 (3.80), 620 (4.26) nm; HR-MS (ESI+, 100% CH_3CN, TOF): *m/z* calc'd for $C_{36}H_{44}N_4O_2Co$: 623.2796 (for M^+); found: 623.2791.

[2,12-dioxo-OEP]Co. Prepared from **2,12-dioxo-OEP**[52] (20 mg, 3.53 × 10^{-5} mol) and $Co_2(CO)_8$ (30 mg, 8.77 × 10^{-5} mol) in 48% yield (11 mg) using the general procedure. Chromatography conditions: 1% MeOH in ethyl acetate:hexanes 50:50 R_f = 0.30 (silica, CH_2Cl_2); UV-vis (CH_2Cl_2) λ_{max} (log ε) 319 (4.39), 375 (4.44), 421 (4.76), 508 (3.50), 546 (3.38), 635 (3.71), 661 (3.92), 696 (4.92) nm; HR-MS (ESI+, 100% CH_3CN, TOF): *m/z* calc'd for $C_{36}H_{44}N_4O_2Co$: 623.2796 (for M^+); found: 623.2791

[2,7,18-trioxo-OEP]Co. Prepared from **2,7,18-trioxo-OEP**[52] (20 mg, 3.43 × 10^{-5} mol) and $Co_2(CO)_8$ (29 mg, 8.48 × 10^{-5} mol) in 35% yield (8 mg) using the general procedure. Chromatography conditions: 1 % MeOH in ethyl acetate:hexanes 70:30 R_f = 0.25 (silica, 1% acetone in CH_2Cl_2); UV-vis (CH_2Cl_2) λ_{max} (log ε) 324 (4.48), 423 (4.75), 660 (4.25), 706 (4.74) nm; HR-MS (ESI+, 100% CH_3CN, TOF): *m/z* calc'd for $C_{36}H_{44}N_4O_2Co$: 639.2745 (for M^+); found: 639.2740.

Conclusions

We can conclude that $Co_2(CO)_8$ is a suitable metal source for the preparation of a range of cobalt porphyrinoids under mechanochemical conditions in a planetary powder mill. The cobalt carbonyl offers advantages over cobalt(II) salts that failed to produce the porphyrinic cobalt(II) complexes under similar mechanochemical reaction conditions.[32] In stark contrast to the high-temperature conditions of the solution state reaction using $Co_2(CO)_8$,[35] the mechanochemical reaction takes place at or near ambient bulk temperature.[65] Even though the reaction is not offering significant advantages in terms of atom economy with respect to the metal source, the workup of the 'clean' reactions is a simple elution from the solid grinding mixture. Because of the absence of external sources of heat and solvent (at least for the metal insertion reaction, though not for the cobalt complex isolation and purification), the mechanochemical method can be identified as a greener method for the preparation of some cobalt porphyrinoids, when compared to traditional solution state methods. The reaction has the potential to be scaled. However, the mechanochemical cobalt insertion method is not general in that not all porphyrinoids are equally suitable for this reaction: While the method is particularly advantageous for the preparation of the cobalt(II) complexes of octaethylporphyrins, some octaethyl-β-oxoderivatives, tetraarylporphyrins, and corroles, much to our surprise, the porpholactones tested failed to provide good (or any) yields of the expected metallated products. Less surprising given their known fragility, the diol chlorins and some of the pyrrole-modified porphyrins tested also decomposed under the mechanochemical conditions and provided only marginal yields of the desired cobalt(II) complexes. Classic solution state methods delivered the cobalt complexes of these compound classes, but also in imperfect yields.[15, 44]

As discovered before for related mechanochemical zinc(II), copper(II), and Mg(II) insertion reactions,[32] the cobalt(II) insertion reaction is subject to strong influences by the grinding aid – that act beyond being merely mechanical aids – and other additives. Interestingly, the trends revealed are not always readily understood or predicted, likely as a result of a mechanistically complex reaction (involving the cracking of the carbonyl its coordination to the porphyrin, the exchange of further carbonyl ligands, and an oxidation reaction of the cobalt center). A fundamental difference of the use of the Co(0) carbonyl cluster as metal source for the formation of a [porphyrinato]M(II) complex is that it requires an (air) oxidation step. It is generally found that during the formation of metalloporphyrins carrying a metal ion in a higher oxidation state than that of the metal salt used to insert the metal ion, the oxidation step of the metal takes place after the insertion into the porphyrin.[23] However, our experimental design that did not allow the exclusion of air during the reaction or the capture of gaseous reaction products, did not allow us to glean any details of the oxidation process, including the fate of the CO ligands.

The study is highly encouraging of further work probing the use of mechanochemical metal insertion reactions into porphyrinoids, in general, and the use of transition metal carbonyls as metal sources, in particular.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ For a reproduction of the key spectra, see Supporting Information.

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