

# Mesoionic Carbene Cobalt Complexes as Multipurpose Catalyst Precursors for Hydrosilylation and Dihydropyrimidinone Synthesis

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Dedicated to *Peter E. Kündig* on the occasion of his 75th birthday

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Metalation of CH<sub>2</sub>OH-substituted triazolium salts with CoCl<sub>2</sub> under basic conditions affords C,O-bidentate chelating carbene Co(III) complexes (**3a**, **3b**), while analogous phenyl-substituted triazolium salts produce monodentate carbene Co(II) complexes (**3c**, **3d**). The distinct substituent-induced properties of the metal centers were demonstrated by electrochemical measurements and catalytic activities in two specific processes. The complexes showed appreciable activity in the reduction of C=O bonds through hydrosilylation, with methoxybenzene-functionalized triazolylidene Co(III) complex **3a** achieving a high selectivity towards aldehydes vs. ketones with turnover frequencies (TOFs) up to 200 h<sup>-1</sup>. The C,O-chelate systems were also active catalysts in the *Biginelli* process, a one-step three-component reaction for efficient dihydropyrimidinone synthesis. Optimization of reaction conditions provides high activity with complex **3a**, reaching TOFs of 800 h<sup>-1</sup>, the highest activity known for cobalt NHC complexes to date.

**Keywords:** *Biginelli* reaction, cobalt, hydrosilylation, ligand tuning, N-heterocyclic carbene.

## Introduction

Recent years have seen an increasing interest in using molecularly defined cobalt complexes for catalytic application.<sup>[1]</sup> This interest has been sparked by the relatively easy accessibility of a wide variety of cobalt oxidation states,<sup>[2,3]</sup> and the high natural abundance of this metal.<sup>[4]</sup> Even though several well-defined cobalt systems have been reported for application in homogeneous catalysis,<sup>[5–11]</sup> progress has been limited due to the often paramagnetic nature of potentially reactive cobalt complexes, imparting difficulties in characterization, as well as the low coordinative stability of these complexes. Ligand design offers a reliable methodology to tackle this challenge and to enhance the stability of the complexes without compromising their reactivity.

Even though N-heterocyclic carbene (NHC) ligands have been employed highly successfully for enhancing the catalytic activity of a variety of transition metals in homogeneous processes,<sup>[12–21]</sup> their impact on base metals such as cobalt has been much more limited,<sup>[9,22–24]</sup> largely due to the hard-soft mismatch of higher-valent 3d metal centers with soft C-donor ligands.<sup>[25–30]</sup> This low compatibility can be alleviated by rational ligand design especially through functionalization of the NHC scaffold with a potentially chelating oxygen donor substituent, thus considering the oxyphilic character of base metals in high oxidation states.<sup>[31,32]</sup> In addition to an enhanced robustness of the carbene-metal unit in a putative catalytic process, such chelation often entails additional electronic and structural properties.<sup>[33,34]</sup> Inspired by these considerations, we have developed a new synthetic approach to cobalt complexes containing mesoionic triazole-derived NHC ligands,<sup>[35–38]</sup> both with and without O-donor functionalization. The presence of the oxygen donor group has a marked

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influence on the stability of different cobalt oxidation states and greatly enhances the catalytic activity of the triazolylidene cobalt complexes as demonstrated here for hydrosilylation and the *Biginelli* 3-component condensation leading to dihydropyrimidinones.

## Results and Discussion

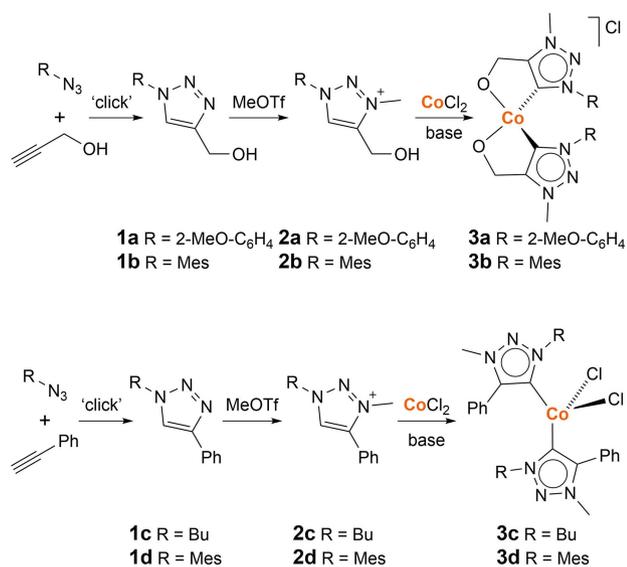
### Synthesis and Characterization of Triazolylidene Cobalt Complexes

The new OH-functionalized triazole ligand precursors **1a** and **1b** were accessible by copper-catalyzed 'click' cycloaddition reaction of the appropriate azide and propargyl alcohol (Scheme 1). The same synthetic route with terminal alkynes afforded triazoles **1c** and **1d**. Their subsequent methylation with MeOTf yielded triazolium salts **2a–2d** in high yields. This synthetic procedure is fully compatible with the alcohol functionality and does not require any particular precaution or protection. The triazolium salts were metallated under mild conditions (KO<sup>t</sup>Bu, r.t.) using CoCl<sub>2</sub> as simple metal precursor to give complex **3a–3d** in high yields (> 70%) as air-stable blue solids.

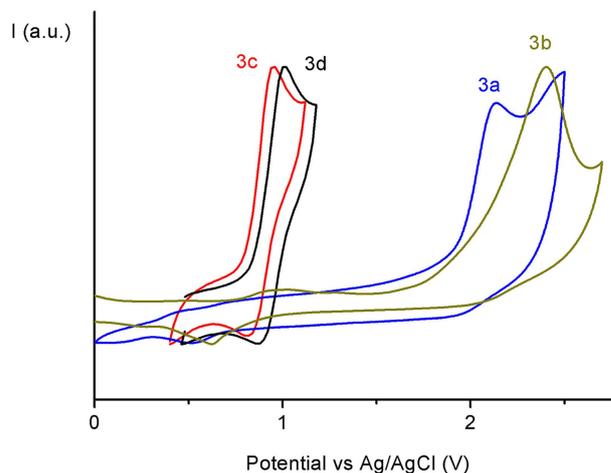
All the complexes are paramagnetic at room temperature (CD<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>CN solution). Magnetic susceptibility measurements in CD<sub>2</sub>Cl<sub>2</sub> solution indicated a significantly smaller magnetic moment for complexes **3a** and **3b** ( $\mu_{\text{eff}} = 3.1 \mu_{\text{B}}$ ) when compared to **3c** and **3d** ( $\mu_{\text{eff}} = 3.8 \mu_{\text{B}}$ ), consistent with different cobalt oxidation states. The magnetic moment for

complexes **3c** and **3d** is in line with previously reported data for cobalt(II) species<sup>[39]</sup> and suggests a pseudotetrahedral geometry of cobalt with  $S = 3/2$ . In contrast, the lower magnetic moment of complexes **3a** and **3b** suggests a cobalt(III) center in a rather rare<sup>[40]</sup> pseudotetrahedral geometry, which accounts for two unpaired electrons and  $S = 1$ . Within the two subclasses of complexes no substantial difference in the magnetic moment was observed ( $\mu_{\text{eff}} = 3.1(4)$  and  $3.1(2)$  for **3a** and **3b**, respectively;  $\mu_{\text{eff}} = 3.8(4)$  and  $3.8(2)$  for **3c** and **3d**, resp.), suggesting that carbene wingtip variation affects the total magnetic moment only marginally. Oxidation of the metal center in complexes **3a** and **3b** to cobalt(III) may have occurred spontaneously by traces of fortuitous air during the reaction and may be promoted by the presence of hard oxygen donors on the carbene ligand. Similar behavior has been observed with P,O-chelated Co(III) complexes.<sup>[41]</sup>

Further confirmation of the different oxidation states in the series of complexes **3a–3d** was obtained from electrochemical measurements (Figure 1). The profiles for complexes **3a** and **3b** drastically differ from those of complexes **3c** and **3d** and show an irreversible oxidation above 2 V, while the latter feature a partially reversible redox process around 0.8 V vs. Ag/AgCl (Table 1). These distinct oxidation potentials clearly indicate different electron densities at the metal centers, consistent with lower cobalt oxidation state in **3c** and **3d** vs. **3a** and **3b**. In addition, the oxidation potential of complexes **3c** and **3d** is similar to that of known cobalt(II) complexes with imidazolylidene ligands.<sup>[39]</sup> The 100 mV shift in oxidation potential



**Scheme 1.** Synthesis of NHC cobalt(III) complexes **3a** and **3b** and cobalt(II) complexes **3c** and **3d**.



**Figure 1.** Electrochemical profile of the Co NHC complexes **3a–3d**.

**Table 1.** Oxidation potentials for complexes **3a–3d**.<sup>[a]</sup>

Entry	Complex	$E_{1/2}$
1	<b>3a</b>	2.13 <sup>[b]</sup>
2	<b>3b</b>	2.40 <sup>[b]</sup>
3	<b>3c</b>	0.79
4	<b>3d</b>	0.88

<sup>[a]</sup> 1 mM solution of Co complex in MeCN using 1 mM Co complex, 0.1 M (NBu<sub>4</sub>)PF<sub>6</sub> as supporting electrolyte, 250 mV s<sup>-1</sup> scan rate, Fc<sup>+</sup>/Fc as internal standard  $E_{1/2}$  = 0.46 V vs. Ag/AgCl; <sup>[b]</sup>  $E_{pa}$  of irreversible oxidation.

between complex **3c** and **3d** is rationalized with the stronger donor properties of a N-alkyl vs. a N-aryl substituent, implying a direct influence of the N-substituent on the donor properties of the triazolylidene ligand. The irreversible oxidation observed with complexes **3a** and **3b** suggests a chemical modification of the coordination sphere upon metal oxidation, which may involve the non-coordinating chloride or the potentially hemilabile O-chelation of the triazolylidene ligand. In addition, the lower oxidation potential for **3a** compared to **3b** (2.13 and 2.40 V vs. Ag/AgCl) indicates that ligand design allows for tailoring the electron density at the metal center. Of note, the Hammett parameter for the MeO group in complex **3b** ( $\sigma_{OMe} = -0.39$ ) is lower than the sum of the three Me substituents in the mesityl substituent in **3a** ( $\sigma_{Tot} = -0.51$ ),<sup>[42,43]</sup> which should lead to a lower oxidation potential for **3b**. Stereoelectronic effects are therefore assumed to affect the redox potential of the cationic Co<sup>III</sup> center more substantially than the inductive effects of the triazolylidene substituents in particular in orienting the carbene heterocycle with respect to the metal coordination plane.<sup>[44]</sup> Specifically, the bulkier methoxy substituent might induce a distorted metal-ligand orbital overlap due to the mutual steric congestion between these triazolylidene substituents in a presumed pseudo-tetrahedral complex geometry, which prevents any  $\pi$  back-donation to the carbene ligand and therefore increases the electron density at the metal center.

### Catalytic Hydrosilylation

Reduction of carbonyl compounds by hydrosilylation is a fundamental process in organic chemistry, however, to date most reported catalysts are based on precious metal such as iridium,<sup>[45]</sup> ruthenium,<sup>[46]</sup> platinum,<sup>[47]</sup> or gold.<sup>[48]</sup> As an alternative, systems based on Earth-abundant metals including Cu,<sup>[49]</sup> Ni,<sup>[50]</sup>

and Fe<sup>[51]</sup> have recently been explored in carbonyl hydrosilylation and showed promising results. Remarkably, processes based on well-defined cobalt systems for selective hydrosilylation remain quite scarce.<sup>[52,53]</sup>

Complexes **3a–3d** were therefore evaluated as catalyst precursors for the hydrosilylation of carbonyl groups. In a first screening aimed to identify suitable reaction conditions, 4-methylbenzaldehyde was used as model substrate in presence of 2 mol-% of complex **3a** (Table 2). Hydrosilylation with PhSiH<sub>3</sub> over 24 h in 1,2-dichloroethane gave moderate conversion at room temperature (60%, Entry 1). For analytical purposes, the hydrosilylation product was subsequently converted into the corresponding benzyl alcohol by treatment with a methanolic NaOH solution (1 M) for 16 h at room temperature, which provided yields of the corresponding alcohol products for each reaction. Increasing the temperature to 40 °C significantly enhanced catalytic activity and afforded full conversion within 4 h (Entry 2). Changing the silane to Ph<sub>2</sub>SiH<sub>2</sub> or Et<sub>3</sub>SiH lowered activity considerably (Entries 3 and 4), while modifying the solvent from dichloroethane to CH<sub>2</sub>Cl<sub>2</sub> reduced the activity only slightly (82% conversion in 4 h, Entry 5). A blank experiment, using the best conditions but in absence of the cobalt complex gave no detectable product even over extended reaction times (Entry 6), indicating the essential role of the complex as catalyst precursor.

Under these optimized conditions, all cobalt complexes **3a–3d** showed catalytic activity and converted

**Table 2.** Hydrosilylation of 4-methylbenzaldehyde with complex **3a**.<sup>[a]</sup>

Entry	Solvent	Silane	T [°C]	Time [h]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[c]</sup>
1	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	PhSiH <sub>3</sub>	25	24	60	56
2	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	PhSiH <sub>3</sub>	40	4	99	96
3	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	Ph <sub>2</sub> SiH <sub>2</sub>	40	4	11	n.d.
4	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	Et <sub>3</sub> SiH	40	4	< 1	n.d.
5	CH <sub>2</sub> Cl <sub>2</sub>	PhSiH <sub>3</sub>	40	4	82	76
6 <sup>[d]</sup>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	PhSiH <sub>3</sub>	40	24	< 1	n.d.

<sup>[a]</sup> General conditions: 4-Me-benzaldehyde (0.5 mmol), PhSiH<sub>3</sub> (0.6 mmol) and complex **3a** (2 mol-%) in the indicated solvent (0.4 mL) with C<sub>6</sub>Me<sub>6</sub> (0.05 mmol, internal standard). <sup>[b]</sup> Conversions determined by <sup>1</sup>H-NMR spectroscopy. <sup>[c]</sup> Yields determined by <sup>1</sup>H-NMR spectroscopy after treatment with NaOH (1 M) in MeOH, n.d. = not determined. <sup>[d]</sup> Reaction performed in the absence of **3a**.

3-methyl-benzaldehyde completely within less than 16 h (Table 3, Entries 1–4). Complex **3a** and **3b** performed considerably better than complexes **3c** and **3d** and reached essentially full conversion within 4 h. The difference in activity is in agreement with two fundamentally different cobalt centers in complexes **3a** and **3b** vs. **3c** and **3d**, supporting the different oxidation states of the complexes deduced from electrochemical and magnetic measurements. Accordingly, cationic cobalt(III) centers containing a C,O-bidentate chelating NHC ligand induce much higher hydrosilylation activity than neutral Co(II) complexes. This is in line with the notion that higher-valent base metals with enhanced Lewis acidic character are beneficial for carbonyl hydrosilylation, e.g. for Ni and Mo-based systems.<sup>[50,54]</sup> Moreover, the O-donor moiety may serve as hemilabile site or engage in metal-ligand cooperativity to cleave the Si–H bond across the O–Co fragment.

Only small differences are observed when comparing the Co<sup>III</sup> complexes **3a** and **3b** with differently substituted triazolylidene ligands (Entries 1 and 2). The methoxyphenyl group of **3a** induces slightly higher activity than the mesityl substituent in complex **3b** (58 vs. 46% in 1 h). Complexes **3c** and **3d** display essentially identical activity, suggesting no effect of the N-bound substituent (butyl vs. mesityl). These data indicate that substituent variation does not offer much opportunity for tailoring the catalytic activity of the cobalt center, an effect that has been observed previously for NHC iron-catalyzed hydrosilylation.<sup>[44]</sup> We note that simple CoCl<sub>2</sub> as precatalyst did not lead to any detectable conversion (Entry 5), suggesting that

the triazolylidene ligand is crucial for imparting catalytic activity. In addition, catalytic runs at different loadings of complex **3a** suggest first order kinetics in cobalt complex (Figures S13 and S14), thus supporting a molecularly well-defined catalytically active species.

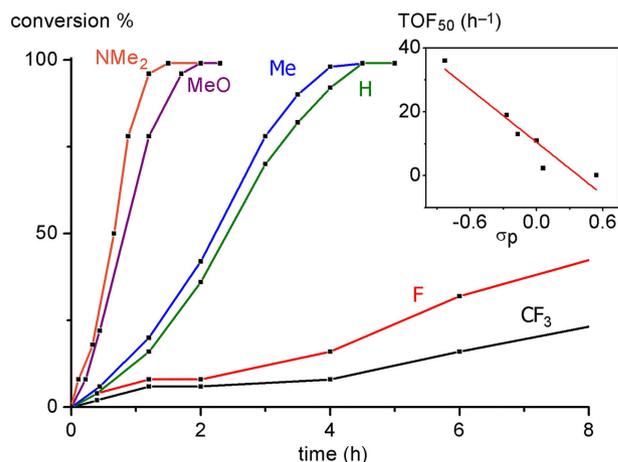
Hydrosilylation of a variety of differently substituted benzaldehydes revealed a high tolerance of the cobalt complex **3a** to various functional groups. Aldehydes with electron-donating substituents (R=NMe<sub>2</sub>, OMe, Me) as well as with electron-withdrawing substituents (R=F, CF<sub>3</sub>) are fully converted (Figure 2 and Table S2). The observed reaction rates show an inverse Hammett correlation, with higher  $\sigma_p$  parameter imparting slower rates (inset Figure 2) and indicate a strong effect of the substituent on the catalytic activity of the complex. Moreover, the inverse correlation implies the build-up of positive charge during the turnover limiting step. As an extreme case, 4-nitrobenzaldehyde ( $\sigma_p=0.78$ ) is only poorly converted (15% after 24 h), suggesting the occurrence of side reactions that deactivate the catalyst with this substrate. Remarkably, acetophenone is not hydrosilylated at all under these conditions even after prolonged reaction time (48 h), indicating no activity towards ketone reduction and thus a high selectivity towards aldehyde conversion.

The catalytic capacity of complex **3a** as the most active system was probed with 4-anisaldehyde as a substrate (Table 4). Decreasing the catalyst loading from 2 to 1 mol-% results in slower conversion and 3 h rather than 2 h were required to complete the reaction (Entries 1 and 2). Increasing the temperature to 60 °C

**Table 3.** Hydrosilylation of 4-methylbenzaldehyde with complexes **3a–3d**.<sup>[a]</sup>

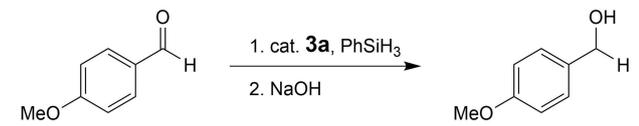
Entry	[Co]	Time [h]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[c]</sup>
1	<b>3a</b>	1 (4)	58 (99)	54 (96)
2	<b>3b</b>	1 (4)	46 (94)	37 (88)
3	<b>3c</b>	4 (16)	42 (96)	33 (92)
4	<b>3d</b>	4 (16)	38 (92)	32 (86)
5	CoCl <sub>2</sub>	24	< 1	n.d.

<sup>[a]</sup> General conditions: 4-Me-benzaldehyde (0.5 mmol), PhSiH<sub>3</sub> (0.6 mmol), Co complex (2 mol-%), 1,2-dichloroethane (0.4 mL), C<sub>6</sub>Me<sub>6</sub> (0.05 mmol, internal standard), 40 °C. <sup>[b]</sup> Conversions determined by <sup>1</sup>H-NMR spectroscopy. <sup>[c]</sup> Yields determined by <sup>1</sup>H-NMR spectroscopy after treatment with NaOH (1 M) in MeOH, n.d. = not determined.



**Figure 2.** Catalytic hydrosilylation of benzaldehydes with different *para*-substituents using Co(III) complex **3a**; inset: correlation of the turnover frequency at 50% conversion (TOF<sub>50</sub>) with Hammett parameter ( $\sigma_p$ ) is linear ( $R^2=0.90$ ).

**Table 4.** Hydrosilylation of anisaldehyde with complexes **3a**.<sup>[a]</sup>



Entry	<b>3a</b> [mol-%]	T [°C]	Time [min]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[c]</sup>	TON	TOF <sub>50</sub> [h <sup>-1</sup> ]
1	2	40	120	99	96	48	27
2	1	40	180	98	95	96	38
3	2	60	50	99	95	48	57
4	1	60	56	97	95	96	100
5	0.5	60	60	98	96	192	190
6	0.25	60	150	97	95	384	180

<sup>[a]</sup> General conditions: 4-anisaldehyde (0.5 mmol), PhSiH<sub>3</sub> (0.6 mmol), complex **3a** (2 mol-%), 1,2-dichloroethane (0.4 mL), C<sub>6</sub>Me<sub>6</sub> (0.05 mmol, internal standard), 40 °C. <sup>[b]</sup> Conversions determined by <sup>1</sup>H-NMR spectroscopy. <sup>[c]</sup> Yields determined by <sup>1</sup>H-NMR spectroscopy after treatment with NaOH (1 M) in MeOH.

increased the activity and complete conversion was reached in 50 min at 2 mol-% cobalt complex (*Entry 3*). Gradual decreasing of the pre-catalyst loading to 0.5% under the same conditions did not compromise the reaction time significantly to achieve full conversion (*Entries 3–5*), establishing a TOF<sub>50</sub> = 190 h<sup>-1</sup>. Further decrease of the catalyst loading to 0.25 mol-% did not affect the turnover frequency but enhanced the turnover number to almost 400 (*Entry 6*). While these complexes constitute the first examples of Co–NHC complex that are catalytically active in aldehyde hydrosilylation, it should be noted that the TOF reached by complex **3a** is some two orders of magnitude lower than the most active iron<sup>[55]</sup> or manganese<sup>[56]</sup> complexes reported for this transformation.

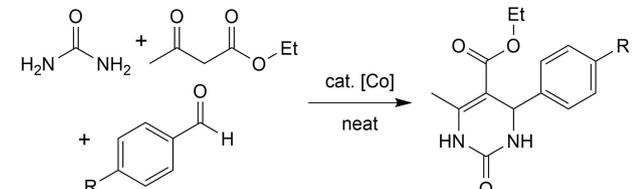
Mechanistic conclusions are difficult to draw based on the data available, and while it is tempting to attribute the higher catalytic activity of **3a** and **3b** to the higher Lewis acidity of the cationic Co(III) center when compared to the neutral Co(II) center in **3c** and **3d**, also the presence of the potentially reactive Co–O bond in **3a** and **3b** and the substitutional lability difference of Co(II) vs. Co(III) may play decisive roles. Distinction of these effects is not possible due to the synthetic selectivity of complex formation (*cf. Scheme 1*). Despite numerous attempts, no cobalt(II) product could be obtained when starting from the hydroxy-functionalized triazolium salts **2a** and **2b**. A wide variety of mechanisms have been discussed in

literature for the hydrosilylation of olefins and carbonyl compounds.<sup>[49,57,58]</sup> Based on the difficulty of 3d metals to undergo two-electron oxidations and reductions, which is a distinct feature compared to precious metals, Si–H bond oxidative addition to the Co center, for example as invoked by the *Chalk–Harrod* mechanism,<sup>[59]</sup> seems less probable. A plausible pathway involves the direct activation of the carbonyl group through coordination to the Co center to form an active species which then undergoes a facile hydrosilylation to form the silylether.

### *Biginelli One-Step 3-Component Reaction to Dihydropyrimidones*

The *Biginelli* reaction, *i.e.* the one-pot three component condensation of an aryl halide, a β-ketoester and urea,<sup>[60]</sup> is an attractive methodology to prepare 3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs), a class of compounds with versatile biological activity such as calcium channel blocking, anti-hypertension, anti-inflammation, anti-viral effects.<sup>[61–65]</sup> It provides an interesting entry for the construction of pharmaceutically relevant compounds from small and inexpensive molecules starting materials,<sup>[66,67]</sup> and has therefore been improved considerably since its discovery. Process optimization has included the use of *Brønsted* and *Lewis* acids,<sup>[68]</sup> ionic liquids,<sup>[69]</sup> and magnetic nanoparticles<sup>[70]</sup> as catalysts. Within this context, we were interested in probing complexes **3a–3d** as *Biginelli* reaction catalysts that are less toxic and based on an Earth-abundant metals.

An initial set of experiments aimed at optimizing the reaction conditions was performed with complex **3a** as precatalyst (0.5 mol-%), and using ethyl acetoacetate, benzaldehyde and urea as the three-component mix for DHPM synthesis. While at room temperature, yields are negligible after 3 h, they are moderate at 40 °C (35%) and essentially quantitative at 100 °C already after 1 h (*Table S3*). Blank experiments in the absence of the cobalt complex or in the presence of simple CoCl<sub>2</sub> did not give significant conversion (< 15% yield after 4 h), supporting the beneficial role of the triazolylidene Co system in this transformation. All four complexes **3a–3d** show appreciable activity under these conditions (*Table 5, Figure S9*). Complex **3a** performed considerably better than complexes **3b–3d**, demonstrated by the higher TOF<sub>50</sub> of 200 h<sup>-1</sup> vs. 80 h<sup>-1</sup>, and the longer reaction time required with complexes **3b–3d** to reach full conversion (*Entries 1–4*). The high activity of the Co(III) complex **3a** is rationalized, in parts, by its high Lewis acidity (*cf.*

**Table 5.** *Biginelli* three-components reaction catalyzed with complexes **3a–3d**.<sup>[a]</sup>


Entry	[Co]	R	Time [min]	Yield [%] <sup>[b]</sup>	TOF <sub>50</sub> [h <sup>-1</sup> ]
1	<b>3a</b>	H	60	99	200
2	<b>3b</b>	H	120	96	82
3	<b>3c</b>	H	360	95	80
4	<b>3d</b>	H	280	98	80
5	<b>3a</b>	OMe	90	98	130
6	<b>3a</b>	CF <sub>3</sub>	15	99	780
7	<b>3a</b>	NO <sub>2</sub>	60	11	24

<sup>[a]</sup> General reaction conditions: benzaldehyde (0.5 mmol), EtOAcAc (0.5 mmol), urea (0.5 mmol), Co complex (0.5 mol-%), 1,3,5-trimethoxybenzene (0.05 mmol; internal standard), neat, 100 °C. <sup>[b]</sup> Yields determined by <sup>1</sup>H-NMR spectroscopy.

electrochemical analysis), which is well-known in the *Biginelli* reaction to accelerate the rate-limiting first C–N bond formation by urea activation.<sup>[71,72]</sup> Specifically, *Lewis* acids promote urea activation through coordination, as well as the formation of the iminium intermediate.<sup>[71,72]</sup> The similar initial activity of complexes **3b–3d** suggests that the *Biginelli* reaction conditions lead to rapid oxidation of the Co(II) center in complexes **3c** and **3d**. In contrast to **3b**, oxidized **3c** and **3d** lack supporting stabilization of the Co<sup>III</sup>–C<sub>carbene</sub> bond through chelation, and this fact may rationalize the erosion of catalytic activity at later stages of the reaction, leading to considerably longer reaction times with these two complexes to reach completion. These results underline the relevance of supporting the M–C<sub>carbene</sub> bond for the design of robust catalysts with base metals.

Complex **3a** was used to incorporate differently substituted benzaldehydes. The catalyst is compatible with electron withdrawing and donating groups such as –OMe and –CF<sub>3</sub> functionalities (Table 5, Entries 5 and 6), though nitro groups are not tolerated, and yields are only poor when using nitrobenzaldehyde as a substrate (11 %, Entry 7). This same functional group limitation was observed in hydrosilylation, strongly suggesting that the cobalt complex is quenched by the nitro group. The observed reaction rates for the other substituents suggest a direct *Hammett* correlation with higher  $\sigma$  parameters inducing higher rates. A similar trend has been reported previously,<sup>[72]</sup> and it is

in agreement with the mechanistic role of the metal center in acting as a *Lewis* acid to promote the nucleophilic addition of urea to benzaldehyde and concomitant build-up of negative charge density in the rate-limiting step. Hence, electron-poor carbonyl groups undergo a more facile addition to urea, as observed here in a very small series of substrates. Notably, the turnover frequencies and numbers observed with catalyst **3a** and 4-CF<sub>3</sub>-benzaldehyde are the best values reported for cobalt complexes in this condensation reaction and very similar to the best iron<sup>[73]</sup> and copper<sup>[74]</sup> catalysts reported thus far.

## Conclusions

A synthetic approach to neutral cobalt(II) and cationic cobalt(III) complexes with mesoionic triazolyidene ligands was developed. In order to investigate the effect on the metal center, subtle variations of the substituents of the triazolyidene scaffold were introduced. The use of *O*-donor functionalized ligands afforded complexes in higher oxidation states than in the absence of any potential chelation. Distinct electrochemical properties suggested different structures for the two classes of complexes. The cobalt complexes are suitable precatalysts with good activity and selectivity for the hydrosilylation of aldehydes and excellent activities for the components *Biginelli* reaction to synthesize dihydropyrimidones. Our results show that the cobalt(III) complex **3a** with a chelating alkoxy-triazolyidene ligand is the most efficient in both catalytic reactions and reaches appreciable turnover frequencies of 200 and 800 h<sup>-1</sup>, respectively. The complex is tolerant to a variety of functional groups, is air-stable and readily prepared in few synthetic steps from cheap precursors. These features demonstrate the potential of combining *O*-donor functionalized mesoionic carbenes with base metals as catalyst precursors that are competitive to systems based on precious metals.

## Experimental Section

### General

Azidomesitylene, 2-azidomethoxybenzene and triazolium salts **2c** and **2d** were synthesized following procedures reported in literature.<sup>[44,75,76]</sup> All other reagents were commercially available and used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C with *Bruker* spectrometers

operating at 300 or 400 MHz ( $^1\text{H-NMR}$ ), and 100 MHz ( $^{13}\text{C-NMR}$ ), respectively. Chemical shifts ( $\delta$  in ppm, coupling constants  $J$  in Hz) were referenced to residual solvent signals ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and are reported downfield from  $\text{SiMe}_4$ . Assignments are based on homo- and heteronuclear shift correlation spectroscopy. The purity of bulk samples of the complexes has been established by NMR spectroscopy, and by elemental analysis, which were performed at the University of Bern Microanalytic Laboratory by using a *Thermo Scientific Flash 2000 CHNS-O* elemental analyzer. High-resolution mass spectrometry was carried out with a *Thermo Scientific LTQ Orbitrap XL* (ESI-TOF).

Cyclic voltammetry measurements were carried out using a *Metrohm Autolab Model PGSTAT101* potentiostat employing a gastight three electrode cell under an argon atmosphere. A platinum disk with 3.0 mm<sup>2</sup> surface area was used as the working electrode and polished before each measurement. The reference electrode was  $\text{Ag/AgCl}$ ; the counter electrode was Pt foil.  $\text{Bu}_4\text{NPF}_6$  (0.1 M) in dry  $\text{CH}_2\text{Cl}_2$  was used as supporting electrolyte with analyte concentrations of approximately 1 mM. The ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) redox couple was used as an internal reference ( $E_{1/2} = 0.46$  V vs.  $\text{Ag/AgCl}$ ).<sup>[77]</sup>

Solution magnetic susceptibility measurements were determined at 25 °C by the *Evans* method in  $\text{CD}_2\text{Cl}_2$  using reported diamagnetic corrections.<sup>[78–80]</sup>

**[1-(2-Methoxyphenyl)-1H-1,2,3-triazol-4-yl]-methanol (1a).** To a solution of 1-azido-2-methoxybenzene (1.10 g, 7.36 mmol) and propargyl alcohol (0.50 g, 8.83 mmol) in THF (15 mL),  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  (0.37 g, 1.47 mmol), sodium ascorbate (1.46 g, 7.36 mmol) and  $\text{H}_2\text{O}$  (15 mL) were added, and the mixture was stirred at 70 °C for 16 h. After this time, the THF was removed *in vacuo* and the solid redissolved in  $\text{CH}_2\text{Cl}_2$ . The organic solution was washed with dilute  $\text{NH}_4\text{OH}$  solution (4 × 15 mL),  $\text{H}_2\text{O}$  (20 mL) and brine (15 mL) and dried over  $\text{MgSO}_4$ . The solution filtered through a short pad of silica and eluted with  $\text{CH}_2\text{Cl}_2$ . All volatiles were removed under reduced pressure to afford **1a** as an off-white solid (1.20 g; 76%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 8.07 (s, 1 H,  $\text{H}_{\text{Trz}}$ ); 7.71 (d, 1 H,  $J = 8.2$ ,  $\text{H}_{\text{Ph}}$ ); 7.39 (t,  $J = 8.2$ , 1 H,  $\text{H}_{\text{Ph}}$ ); 7.08–7.03 (m, 2 H, 2  $\text{H}_{\text{Ph}}$ ); 3.84 (s, 3 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz,  $\text{CDCl}_3$ ): 151.30 ( $\text{C}_{\text{Ph-O}}$ ); 130.28 ( $\text{C}_{\text{Ph}}$ ); 126.38 ( $\text{C}_{\text{Ph-N}}$ ); 125.63 ( $\text{C}_{\text{Trz-H}}$ ); 124.20 ( $\text{C}_{\text{Trz-CH}_2}$ ); 121.32 ( $\text{C}_{\text{Ph}}$ ); 112.37 ( $\text{C}_{\text{Ph}}$ ); 56.64 ( $\text{CH}_2\text{-O}$ ); 56.07

( $\text{CH}_3\text{-O}$ ). HR-ESI-MS: 206.0920 ( $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2^+$ ,  $[\text{M} + \text{H}]^+$ ; calc. 206.0924).

**4-(Hydroxymethyl)-1-(2-methoxyphenyl)-3-methyl-1H-1,2,3-triazol-3-ium Trifluoromethanesulfonate Salt (2a).** To a solution of triazole **1a** (300 mg, 1.46 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added MeOTf (0.21 mL, 1.10 mmol). The mixture was stirred for 3 h at room temperature, after which time the solvents were removed *in vacuo*. The oil was then washed with  $\text{Et}_2\text{O}$  to afford **2a** as a white waxy solid (400 mg; 74%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CD}_3\text{CN}$ ): 8.72 (s, 1 H,  $\text{H}_{\text{Trz}}$ ); 7.70–7.66 (m, 2 H, 2  $\text{H}_{\text{Ph}}$ ); 7.34 (d,  $J = 8.2$ , 1 H,  $\text{H}_{\text{Ph}}$ ); 7.22 (t,  $J = 8.2$ , 1 H,  $\text{H}_{\text{Ph}}$ ); 4.88 (d,  $J = 2.2$ , 2 H,  $\text{CH}_2$ ); 4.39 (t,  $J = 2.2$ , 1 H, OH); 4.32 (s, 3 H,  $\text{CH}_3$ ); 3.95 (s, 3 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz,  $\text{CD}_3\text{CN}$ ): 153.18 ( $\text{C}_{\text{Ph-O}}$ ); 144.37 ( $\text{C}_{\text{Ph-N}}$ ); 134.48 ( $\text{C}_{\text{Ph}}$ ); 131.41 ( $\text{C}_{\text{Trz-H}}$ ); 126.63 ( $\text{C}_{\text{Ph}}$ ); 124.62 ( $\text{C}_{\text{Trz-CH}_2}$ ); 122.32 ( $\text{C}_{\text{Ph}}$ ); 114.52 ( $\text{C}_{\text{Ph}}$ ); 57.41 ( $\text{CH}_2\text{-O}$ ); 53.22 ( $\text{CH}_3\text{-O}$ ); 39.56 ( $\text{CH}_3\text{-N}$ ). HR-ESI-MS: 369.0613 ( $\text{C}_{12}\text{H}_{14}\text{F}_3\text{N}_3\text{O}_5\text{S}^+$ ,  $[\text{M-OTf}]^+$ ; calc. 369.0606).

**[1-(2,4,6-Trimethylphenyl)-1H-1,2,3-triazol-4-yl]-methanol (1b).** Azidomesitylene (1.19 g, 7.36 mmol), propargyl alcohol (0.50 g, 8.83 mmol),  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  (0.37 g, 1.47 mmol) and sodium ascorbate (1.46 g, 7.36 mmol) were suspended in a 1:1:1 v/v/v  $^t\text{BuOH/THF/H}_2\text{O}$  solvent mixture (12 mL). The pale yellow solution was stirred for 16 h at r.t. All volatiles were removed *in vacuo* and the solid was extracted with MeOH (3 × 30 mL). The extracts were evaporated to dryness and the residue was purified by column chromatography ( $\text{Al}_2\text{O}_3$ ;  $\text{CH}_3\text{CN/CH}_2\text{Cl}_2$  1:2) to yield the triazole **1b** as an off-white powder (1.10 g, 88%).  $^1\text{H-NMR}$  (400 MHz,  $(\text{D}_6)\text{DMSO}$ ): 8.14 (s, 1 H,  $\text{H}_{\text{Trz}}$ ); 7.08 (s, 2 H,  $\text{H}_{\text{Mes}}$ ); 5.27 (t,  $J = 2.1$ , 1 H, OH); 4.61 (d,  $J = 2.1$ , 2 H,  $\text{CH}_2$ ); 2.32 (s, 3 H,  $\text{CH}_3$ ); 1.88 (s, 6 H, 2  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz,  $(\text{D}_6)\text{DMSO}$ ): 147.97 ( $\text{C}_{\text{Trz-C}_{\text{Mes}}}$ ); 139.27 ( $\text{C}_{\text{Mes}}$ ); 134.48 ( $\text{C}_{\text{Mes}}$ ); 133.59 ( $\text{C}_{\text{Mes}}$ ); 128.78 ( $\text{C}_{\text{Mes}}$ ); 124.60 ( $\text{C}_{\text{Trz-H}}$ ); 54.99 ( $\text{C-H}_2$ ); 20.60 ( $\text{CH}_3$ ); 16.82 ( $\text{CH}_3$ ). HR-ESI-MS: 218.1287 ( $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}^+$ ,  $[\text{M} + \text{H}]^+$ ; calc. 218.1288).

**4-(Hydroxymethyl)-3-methyl-1-(2,4,6-trimethylphenyl)-1H-1,2,3-triazol-3-ium Trifluoromethanesulfonate Salt (2b).** To a solution of triazole **1b** (300 mg, 1.38 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added MeOTf (0.19 mL, 1.76 mmol). The mixture was stirred for 5 h at room temperature, after which time the solvents were removed *in vacuo*. The oil was then washed with  $\text{Et}_2\text{O}$  to afford **2b** as a white waxy solid (420 mg; 80%).  $^1\text{H-NMR}$  (400 MHz,  $(\text{D}_6)\text{DMSO}$ ): 9.14 (s, 1 H,  $\text{H}_{\text{Trz}}$ ); 7.21 (s, 2 H,  $\text{H}_{\text{Mes}}$ ); 6.10 (br., 1 H, OH); 4.85 (s,

2 H, CH<sub>2</sub>); 4.35 (s, 3 H, CH<sub>3</sub>); 2.36 (s, 3 H, CH<sub>3</sub>); 2.02 (s, 6 H, 2 CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (101 MHz, (D<sub>6</sub>)DMSO): 144.80 (C<sub>Mes</sub>); 141.73 (C<sub>Trz</sub>-C<sub>Mes</sub>); 134.27 (C<sub>Mes</sub>); 131.29 (C<sub>Mes</sub>); 130.81 (C<sub>Mes</sub>); 129.40 (C<sub>Trz</sub>-H); 52.58 (CH<sub>2</sub>); 38.52 (CH<sub>3</sub>-N); 20.66 (CH<sub>3</sub>); 16.65 (CH<sub>3</sub>). HR-ESI-MS: 232.1440 (C<sub>14</sub>H<sub>18</sub>F<sub>3</sub>N<sub>3</sub>O<sub>4</sub>S<sup>+</sup>, [M-OTf]<sup>+</sup>; calc. 232.1444).

### General Procedure for the Synthesis of the Cobalt Complexes

The corresponding triazolium salt and KO<sup>t</sup>Bu were dissolved in THF (10 mL) under inert atmosphere and stirred for 30 min. The mixture was cannulated to a suspension of CoCl<sub>2</sub> in THF (5 mL). The mixture was stirred for 8 h at room temperature. All volatiles were then removed *in vacuo*. CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added to the residue and the suspension was filtrated through a short pad of *Celite*. Evaporation of all solvent afforded a dark blue solid, which was purified by precipitation to obtain the desired complex in high purity.

**Complex 3a.** Following the *General Procedure* starting from triazolium salt **2a** (200 mg, 0.54 mmol), KO<sup>t</sup>Bu (123 mg, 1.1 mmol), and CoCl<sub>2</sub> (39 mg, 0.30 mmol). Precipitation from Et<sub>2</sub>O afforded complex **3a** as a light blue powder (230 mg, 72%). μ<sub>eff</sub> = 3.1(5) μ<sub>B</sub>. HR-ESI-MS: 495.1188 (C<sub>22</sub>H<sub>24</sub>ClCoN<sub>6</sub>O<sub>4</sub><sup>+</sup>, [M-Cl]<sup>+</sup>; calc. 495.1186). Anal. calc. for C<sub>22</sub>H<sub>24</sub>ClCoN<sub>6</sub>O<sub>4</sub> (594.02): C 49.78, H 4.56, N 15.83; found: C 50.05, H 4.45, N 15.88.

**Complex 3b.** Following the *General Procedure* starting from triazolium salt **2b** (200 mg, 0.52 mmol), KO<sup>t</sup>Bu (123 mg, 1.1 mmol), and CoCl<sub>2</sub> (38 mg, 0.29 mmol). Precipitation from Et<sub>2</sub>O gave complex **3b** as a dark blue powder (230 mg, 80%). μ<sub>eff</sub> = 3.1(2) μ<sub>B</sub>. HR-ESI-MS: 519.1910 (C<sub>26</sub>H<sub>32</sub>ClCoN<sub>6</sub>O<sub>2</sub><sup>+</sup>, [M-Cl]<sup>+</sup>; calc. 519.1913). Anal. calc. for C<sub>26</sub>H<sub>32</sub>ClCoN<sub>6</sub>O<sub>2</sub> (554.96): C 56.27, H 5.81, N 15.14; found: C 56.16, H 5.72, N 14.98.

**Complex 3c.** Following the *General Procedure* starting from triazolium salt **2c** (200 mg, 0.55 mmol), KO<sup>t</sup>Bu (62 mg, 0.65 mmol), and CoCl<sub>2</sub> (39 mg, 0.30 mmol). Precipitation from hexane afforded complex **3c** as a blue powder (250 mg, 81%). μ<sub>eff</sub> = 3.8(4) μ<sub>B</sub>. HR-ESI-MS: 524.1856 (C<sub>26</sub>H<sub>34</sub>Cl<sub>2</sub>CoN<sub>6</sub><sup>+</sup>, [M-Cl]<sup>+</sup>; calc. 524.1860). Anal. calc. for C<sub>26</sub>H<sub>34</sub>Cl<sub>2</sub>CoN<sub>6</sub> (560.43): C 55.72, H 6.12, N 15.00; found: C 55.35, H 6.16, N 14.88.

**Complex 3d.** Following the *General Procedure* starting from triazolium salt **2d** (200 mg, 0.47 mmol) and KO<sup>t</sup>Bu (62 mg, 0.65 mmol), and CoCl<sub>2</sub> (36 mg, 0.28 mmol). Precipitation from hexane yielded com-

plex **3d** as a blue powder (240 mg, 76%). μ<sub>eff</sub> = 3.8(2) μ<sub>B</sub>. HR-ESI-MS: 648.2168 (C<sub>36</sub>H<sub>38</sub>Cl<sub>2</sub>CoN<sub>6</sub><sup>+</sup>, [M-Cl]<sup>+</sup>; calc. 648.2173). Anal. calc. for C<sub>36</sub>H<sub>38</sub>Cl<sub>2</sub>CoN<sub>6</sub> (684.57): C 63.16, H 5.60, N 12.28; found: C 62.96, H 5.66, N 12.08.

### General Procedure for Hydrosilylation Catalysis

Hexamethylbenzene (0.05 mmol, 8.1 mg, internal standard) was added to an oven-dried vial equipped with a stirring bar. The vial was purged with nitrogen and charged with the appropriate cobalt complex in 1,2-dichloroethane (0.4 mL). Subsequently, PhSiH<sub>3</sub> (0.60 mmol) and aldehyde (0.50 mmol) were added and the mixture stirred at 40 °C. The reaction was monitored periodically by analyzing an aliquot by <sup>1</sup>H-NMR spectroscopy (CDCl<sub>3</sub>, 298 K, 300 MHz). Once the reaction was complete, indicated by the disappearance of the aldehyde proton, the mixture was treated with a solution of NaOH in MeOH (1 M) at room temperature for 16 h. The solvent was removed under vacuum, and the product was extracted into Et<sub>2</sub>O (5 mL). This solution was filtered through silica and the filtrate was concentrated under vacuum. Conversions and yields were determined by comparison of NMR integrals of starting material and product, respectively, with those of the internal standard.

### General Procedure for Catalytic Biginelli Three-Component Condensation

1,3,5-Trimethoxybenzene (0.05 mmol, internal standard) was added to an oven-dried vial equipped with a stirring bar. The vial was purged with N<sub>2</sub> and charged with the appropriate cobalt complex. Subsequently, EtOAcAc (0.50 mmol) and aldehyde (0.50 mmol) were added and the mixture stirred at the desired temperature. The reaction was monitored periodically by analyzing an aliquot by <sup>1</sup>H-NMR spectroscopy ((D<sub>6</sub>)DMSO, 293 K, 300 MHz) and yields were determined by comparison of NMR integrals of product with those of the internal standard. Once the reaction was complete, the reaction mixture was dissolved in the minimum amount of MeOH (1 mL) and then the product was precipitated with water.

## Supplementary Material

NMR Spectra of ligands, metal complexes and catalytic products as well as supplementary catalytic data are

available on the WWW under <https://doi.org/10.1002/hlca.202100181>.

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## Author Contribution Statement

S. B. performed the experiments. S. B. and M. A. designed the experiments, analyzed the data and wrote the article.

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