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Electronic Effects of Ligands on the Cobalt(II)–Porphyrin-Catalyzed Direct C–H Arylation of Benzene

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The electronic effects of the porphyrin ligand on the cobalt(II)-porphyrin-catalyzed direct C–H arylation of benzene with 4-iodotoluene were explored. The investigation was facilitated by the easy preparation of various substituted porphyrin ligands. The reaction rates were found to be dependent on the electron richness of the cobalt(II)–porphyrins. Such effects are consistent with the electronic influences on the rate-determining aryl iodide bond cleavage.

Introduction

Utilization of ligands in homogeneous transition-metal-catalyzed reactions is essential. The ligands form transition-metal complexes with the inorganic metal salts, providing solubility and stability. However, the manner in which the ligands modify the reactivity of ligated metal centres through electronic effects is far more important to a reaction system. A demonstrative example is the successful oxidative addition of Pd complexes to strong C–Cl bonds of aryl chlorides with the use of electron-rich $PtBu_3$ or PCy_3 ligands,[1] but it fails for the more commonly available PPh_3 ligand. The underlying principle involves the enhanced nucleophilicity of the Pd centre in the presence of very strong σ-donor ligands. Therefore, the Pd centre more readily attacks the σ* orbital of a C–Cl bond, facilitating the oxidative addition.[2] This shows that a suitable choice of ligand with varying electronic effects greatly facilitates the rate of the fundamental reaction step and makes reactions more facile.[3] The issue is particularly true when reaction pathways are ionic in nature or sensitive to electronic environments.

Therefore, finding the best ligand for a reaction system is crucial to optimization. Initial ligand screening is generally a random approach. Several readily available ligands are selected on the basis of their denticities, binding atoms, cone angles, hardness/softness or donor/acceptor properties. Although distinctive experimental results can be obtained, the commercially available ligands for preliminary studies may not be a final choice for maximum optimization when the scope of the reaction is broadened, such as the cross coupling of aryl chloride with C–Cl bond cleavage.[1] Moreover, a systematic evaluation of ligand electronic effects on the reaction will be a useful tool for mechanistic investigations.

The realization of ligand control can be accomplished by installing different substituents to tune the electronic factors, while keeping the steric environment minimally altered. Indeed, Busacca et al. discovered the ligand electronic dependence of stereoselectivity in asymmetric Heck reactions.[4] Very recently, Sanford et al. achieved the regioselective α-arylation of naphthalene through the systematic modulation of ligand substituent electronics.[5]

The macrocyclic porphyrin ligand is attractive for its thermal stability and easily tunable substituents at both the *meso* and β positions. Many porphyrin derivatives can be prepared from readily available aldehydes and pyrroles to meet the electronic requirements.[6] Therefore, the use of first-row transition-metal metalloporphyrins as catalysts, such as cobalt(II)–porphyrins, is attractive for the ease of ligand modulability and as a cheap metal source. Zhang et al. have extensively studied the chemistry of cobalt(II)–porphyrins on C–H amination,[7] cyclopropanation[8] and aziridination.[9] The studies revealed that the electronic factor of the porphyrin ligands is critical to the reaction outcome. Similarly, Sharghi et al. discovered that the electronics of cobalt(II)–porphyrins affect the reaction yields as well as the reaction rates in the thiocyanation of epoxides, because of the different formation constants for thiocyanate complexation.[10]

Aryl–aryl bond formations from two aromatics are of fundamental importance, and the search is always on for more user-friendly approaches.[11] Obtaining biaryls through direct C–H arylation is desirable.[12] Recently, we

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have reported the cobalt(II)–porphyrin-catalyzed direct C–H arylation of unactivated arenes with aryl halides.[13] In view of the easily tunable porphyrin ligands and thus its electronic effects on reaction systems, we report on the influences of electron-rich and -poor cobalt(II)–porphyrins on the direct C–H arylation of benzene. The axial ligand effects will also be discussed.

Results and Discussion

With the successful discovery of the direct C–H arylation of benzene with 4-iodotoluene catalyzed by $Co^{II}(t_{4\text{-OMe}}pp)$,[13] we further examined the porphyrin electronic effect by employing $Co^{II}(tpp)$, $Co^{II}(ttp)$, $Co^{II}(t_{4\text{-Cl}}pp)$, $Co^{II}(t_{4\text{-CF3}}pp)$ and $Co^{II}(tmp)$ as the catalysts (Figure 1). These cobalt(II)–porphyrins were easily prepared by condensation of the corresponding substituted aldehydes with pyrrole, followed by metallation with $Co(OAc)_2{\cdot}4H_2O$.[14c] Electron-donating and -withdrawing *meso*-aryl substituents were installed with reference to $Co^{II}(tpp)$.

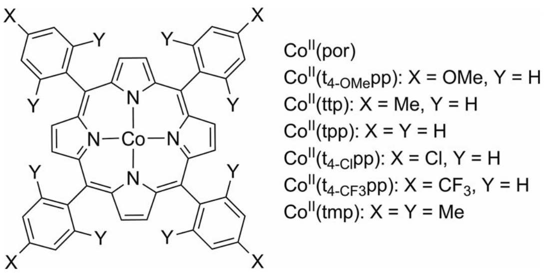
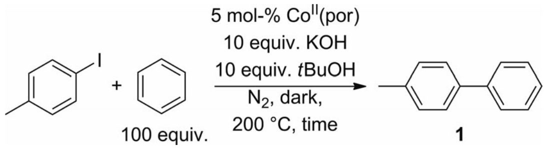


Figure 1. Structures of cobalt(II)–porphyrin complexes.

To our delight, we observed that the rate of direct C–H arylation increased with the electron richness of the $Co^{II}(por)$ catalysts (Table 1). Electron-donating porphyrin $Co^{II}(t_{4\text{-OMe}}pp)$ resulted in the fastest C–H arylation in 2 h to give 79% of 4-methylbiphenyl (Table 1, Entry 1). A slightly longer reaction time was needed when less electron-rich $Co^{II}(ttp)$ was used (Table 1, Entry 2). However, electron-poor cobalt(II)–porphyrins, such as $Co^{II}(t_{4\text{-Cl}}pp)$ and $Co^{II}(t_{4\text{-CF3}}pp)$, decreased the reaction rates significantly compared with other porphyrin ligands (Table 1, Entries 4 and 5). The poor solubility of $Co^{II}(t_{4\text{-CF3}}pp)$ in the reaction mixture also accounts for its lower performance. Interestingly, the reaction-rate enhancement was not observed when electron-rich and sterically hindered $Co^{II}(tmp)$ was employed (Table 1, Entry 6). This is likely attributed to the offset of the electronic effect by bulky mesityl substituents. Meanwhile, reduction of 4-iodotoluene occurred in all cases as toluene was detected from the GC–MS analysis of the reaction mixtures. Therefore, cobalt(II)–porphyrins bearing electron-donating *meso*-aryl substituents increased the rate of direct C–H arylation of benzene.

Table 1. Electronic effects of porphyrins on the direct C–H arylation of benzene with 4-iodotoluene.



Entry	$Co^{II}(por)$	Time [h]	Yield of **1** [%][a]
1	$Co^{II}(t_{4\text{–OMe}}pp)$	2	79
2	$Co^{II}(ttp)$	3.5	88
3	$Co^{II}(tpp)$	4	70
4	$Co^{II}(t_{4\text{–Cl}}pp)$	8	78
5	$Co^{II}(t_{4\text{–CF3}}pp)$	20	66
6	$Co^{II}(tmp)$	4	84

[a] GC yield.

To obtain a quantitative comparison of the cobalt(II)–porphyrin electronic effect, the reactions of 4-iodotoluene with benzene catalyzed by various $Co^{II}(por)$ complexes at 200 °C were monitored by withdrawing aliquots from the reaction mixtures for GC–MS analyses. The consumptions of 4-iodotoluene were plotted against reaction times. The plots fit well with a first-order exponential decay function (Figure 2) and confirmed the first-order dependence on 4-iodotoluene. The rate law can be expressed as rate $\propto k_{obs}$[4-iodotoluene]. The initial concentrations of benzene, $Co^{II}(por)$ and 4-iodotoluene were 10.1 M, 5.07 mM and 101 mM, respectively.

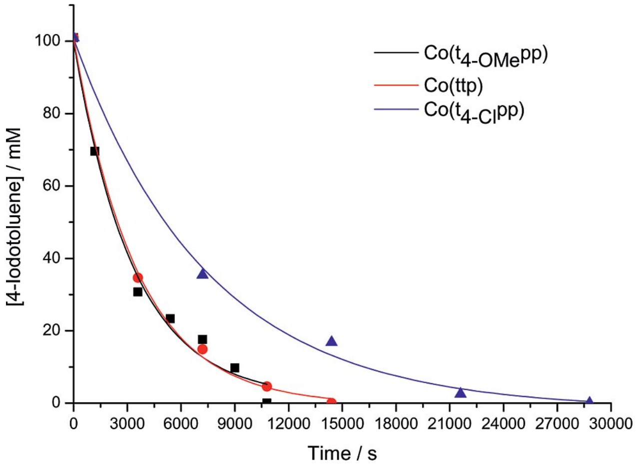


Figure 2. Reaction time profile of 4-iodotoluene.

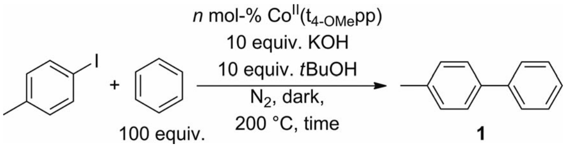
The k_{obs} values for the $Co^{II}(t_{4\text{-OMe}}pp)$- $Co^{II}(ttp)$- and $Co^{II}(t_{4\text{-Cl}}pp)$-catalyzed direct C–H arylation were measured to be $2.1 \times 10^{-4}\,s^{-1}$, $2.0 \times 10^{-4}\,s^{-1}$ and $9.2 \times 10^{-5}\,s^{-1}$ at 200 °C, respectively (Table 2). Hence, the rate of consumption of 4-iodotoluene in the reaction with benzene catalyzed by $Co^{II}(por)$ follows the order: $Co^{II}(t_{4\text{-OMe}}pp) > Co^{II}(ttp) > Co^{II}(t_{4\text{-Cl}}pp)$.

Table 2. Observed rate constants of the $Co^{II}(por)$-catalyzed direct C–H arylation at 200 °C.

Entry	$Co^{II}(por)$	k_{obs} [s^{-1}]	Relative rate
1	$Co^{II}(t_{4\text{–OMe}}pp)$	2.1×10^{-4}	2.3
2	$Co^{II}(ttp)$	2.0×10^{-4}	2.2
3	$Co^{II}(t_{4\text{–Cl}}pp)$	9.2×10^{-5}	1.0

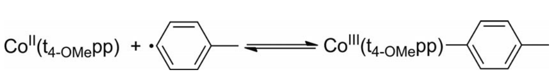
We then examined the catalyst loading effects where 2.5, 5, 10 and 20 mol-% of $Co^{II}(t_{4\text{-}OMe}pp)$ catalyst was employed. Reducing the catalyst loading from 5 to 2.5 mol-% increased the reaction time without affecting the yield of **1** (Table 3, Entry 1). This is in line with the rate-determining formal iodine atom abstraction step with $Co^{II}(t_{4\text{-}OMe}pp)$, since the decreased concentration of $Co^{II}(t_{4\text{-}OMe}pp)$ reduces the rate of aryl radical generation.[13] However, when the catalyst loading was increased to 10 mol-%, the reaction was slower compared with that of 5 mol-% (Table 3, Entries 2 and 3), but there was a small increase in the reaction yield. This observation is interesting as the reaction rate did not increase with catalyst loading or attained saturation. Therefore, we then studied the catalytic arylation with 20 mol-% of $Co^{II}(t_{4\text{-}OMe}pp)$ loading. The catalysis required an unexpectedly long reaction time of 17 h, with only 41 % of **1** formed. The low yield of **1** was accounted for by the possible formation of $Co^{III}(t_{4\text{-}OMe}pp)$(4-tolyl) from the trapping of the 4-tolyl radical with $Co^{II}(t_{4\text{-}OMe}pp)$ (Scheme 1).

Table 3. Catalyst loading effects on the direct C–H arylation of benzene with 4-iodotoluene.



Entry	Catalyst loading [mol-%]	Time [h]	Yield of **1** [%][a]
1	2.5	4	77
2	5	2	79
3	10	4	81
4	20	17	41

[a] GC yield.



Scheme 1. Formation of $Co^{III}(t_{4\text{-}OMe}pp)$(4-tolyl) from $Co^{II}(t_{4\text{-}OMe}pp)$ and the 4-tolyl radical.

A higher catalyst loading should have resulted in faster 4-tolyl radical generation, a more rapid homolytic substitution of benzene and a faster catalytic direct C–H arylation.[13] However, instead of only being a catalyst for iodine atom abstraction, $Co^{II}(t_{4\text{-}OMe}pp)$ can also act as an aryl radical trap in the reaction mixture. Relatively high concentrations of 4-tolyl radical and $Co^{II}(t_{4\text{-}OMe}pp)$ combine to give $Co^{III}(t_{4\text{-}OMe}pp)$(4-tolyl) (Scheme 1) since the combination rate constants of various Co^{II} species with alkyl radicals are fast and some are close to diffusion-controlled.[15] Some examples of combination rate constants of Co^{II} complexes with alkyl radicals are illustrated in Scheme 2.[15] This process competes with the homolytic substitution for direct C–H arylation. Therefore, the rate of the 4-tolyl radical attack on benzene is reduced, leading to even slower reaction rates.

$$Co^{II}(CN)_5^{3-} + \cdot C_2H_5 \xrightarrow{k = 10^8\ \text{M}^{-1}\ \text{s}^{-1}} C_2H_5\text{-}Co^{III}(CN)_5^{3-}$$

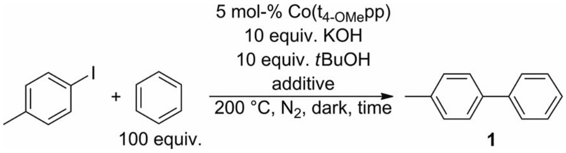
$$B_{12r} + \cdot CH_3 \xrightarrow{k = 2 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}} CH_3\text{-}B_{12}$$

$$Co^{II}(DMG)_2 + \cdot CH_3 \xrightarrow{k = 5 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}} Co^{III}(DMG)_2CH_3$$

Scheme 2. Combination rate constants of some Co^{II} complexes with alkyl radicals. B_{12r} = cobalamin; $Co^{II}(DMG)_2$ = bis(dimethylglyoximato)cobalt(II).

In addition to the enhanced effect of the electron-donating porphyrin ligand on the rate of direct C–H arylation of benzene with 4-iodotoluene, the axial ligand effect was investigated. It has been reported that in the presence of σ-donor ligands, the energy level of the singly occupied d_{z^2} orbital of Co^{II}(por) rises, enriching the metalloradical character.[16] Pyridine and PPh_3 were thus added to form the more reactive LCo^{II}(por) (L = pyridine or PPh_3) in situ, hoping to facilitate the iodine atom abstraction step. However, both pyridine and PPh_3 were inefficient as longer reaction times were required (Table 4, Entries 2 and 5). The formation constant of the 1:1 adduct $(py)Co^{II}(t_{4\text{-}OMe}pp)$ at 200 °C was estimated to be 49.1 M^{-1},[17] indicating that about 87% of the added $Co^{II}(t_{4\text{-}OMe}pp)$ exists as $(py)Co^{II}(t_{4\text{-}OMe}pp)$ in solution. The reduction of vacant sites on $Co^{II}(t_{4\text{-}OMe}pp)$ from two to one could account for the lower reactivity but is less reasonable. A rate enhancement should still have occurred. We favour the existence of a disproportionation equilibrium of axially ligated $Co^{II}(t_{4\text{-}OMe}pp)$ in the presence of L (L = OH^-, pyridine or PPh_3) to give $Co^{I}(t_{4\text{-}OMe}pp)^-$ and $L_nCo^{III}(t_{4\text{-}OMe}pp)^+$ (n = 1,2) at high temperatures (Scheme 3).[2b,18] This side reaction decreases the effective concentration of $Co^{II}(t_{4\text{-}OMe}pp)$ and, hence, the rate of iodine atom abstraction. Thus, the electronic effect of the porphyrin on the rate is unique.

Table 4. σ-Donor ligand effects on direct C–H arylation of benzene with 4-iodotoluene.



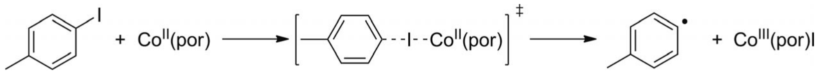
Entry	Additive	Loading [mol-%][a]	Time [h]	Yield of **1** [%][b]
1	none	–	2	79
2	pyridine	5	6	62
3	PPh_3	5	8	78
4	PPh_3	0.5	8	58
5	PPh_3	0.25	8	60

[a] With reference to 4-iodotoluene. [b] GC yield.

$$2\ Co^{II}(t_{4\text{-}OMe}pp) + n\,L \rightleftharpoons Co^{I}(t_{4\text{-}OMe}pp)^- + L_nCo^{III}(t_{4\text{-}OMe}pp)^+$$

L = OH^-, py or PPh_3
n = 1 or 2

Scheme 3. Disproportionation of $Co^{II}(t_{4\text{-}OMe}pp)$ promoted by axial ligands.



Scheme 4. Formal iodine atom abstraction as the rate-determining step.

From the above findings and the reaction mechanism proposed previously,[13] we conclude that the formal iodine atom abstraction is rate-determining (Scheme 4). The second-order rate constant for the formal iodine atom abstraction of 2-iodopyridine with $Co(CN)_5^{3-}$ at 25 °C is ca. 10^{-3} M^{-1} s^{-1}.[19] The nucleophilic radical nature of Co^{II}(por) is enhanced by electron-donating porphyrin ligands to facilitate the Ar–I bond cleavage.

Conclusions

The electronic effects of porphyrin ligands on the Co^{II}(por)-catalyzed direct C–H arylation are presented. The systematic modulation of ligand substituent electronics offers improved reactivity of economical first-row transition-metal catalysts. This provides another approach for reaction optimizations and mechanistic studies. Application of this concept to expand the scope of the ligand and substrate is ongoing.

Experimental Section

General: All reagents were purchased from commercial suppliers and used without further purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Thin layer chromatography was performed on precoated silica gel 60 F254 plates. Silica gel (Merck, 230–400 mesh) was used for column chromatography in air. Melting points were measured with a Reichert apparatus. ^{1}H NMR spectra were recorded with a Bruker Avance III 400 (400 MHz) spectrometer. Spectra were referenced internally with tetramethylsilane (TMS; δ = 0.00 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (J) are reported in Hertz (Hz). GC–MS analyses were conducted with a GC–MS-QP2010 Plus system by using an Rtx-5MS column (30 m × 0.25 mm). Free-base porphyrins and corresponding cobalt(II)–porphyrins were prepared according to literature procedures.[14] All the reactions were carried out in the dark with Teflon-stoppered reaction tubes covered with aluminum foil. Unless otherwise stated, the reactions were duplicated, and the yields are the average yields. All the reactions were stopped once the starting materials were consumed to >95%.

General Procedure for the Various Co^{II}(por)-Catalyzed Direct C–H Arylations of Benzene with 4-Iodotoluene: Co^{II}(t$_{4\text{-OMe}}$pp) (8.9 mg, 0.011 mmol), 4-iodotoluene (48.9 mg, 0.224 mmol), KOH (126 mg, 2.24 mmol), *t*BuOH (213 µL, 2.24 mmol) were added in benzene (2.0 mL, 22.4 mmol). The mixture was degassed during three freeze-pump-thaw cycles, flushed with N_2 and heated at 200 °C. After a GC–MS analysis of the reaction mixture to confirm complete consumption of 4-iodotoluene, the solvent was removed by rotary evaporation. The crude residue was purified by column chromatography (silica gel; 230–400 mesh) eluting with hexane to afford 4-methylbiphenyl (**1**). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 7.24 (d, J = 7.9 Hz, 2 H), 7.31 (t, J = 7.3 Hz, 1 H), 7.42 (t, J = 7.6 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.57 (d, J = 7.4 Hz, 2 H) ppm. M.p. 42.7–44.2 °C.[13] The same procedures were employed for the other Co^{II}(por) complexes.

General Procedure for the Co^{II}(t$_{4\text{-OMe}}$pp)-Catalyzed Direct C–H Arylation of Benzene with 4-Iodotoluene with Various Catalyst Loadings: Co^{II}(t$_{4\text{-OMe}}$pp) (0.0055 mmol, 0.022 mmol and 0.044 mmol) was used in the same procedure as described above.

General Procedure for the Co^{II}(t$_{4\text{-OMe}}$pp)-Catalyzed Direct C–H Arylation of Benzene with 4-Iodotoluene with Various Additives: Pyridine (0.011 mmol) and PPh_3 were added. For 0.5 and 0.25 mol-% PPh_3, 0.56 mM and 0.28 mM standard solutions of PPh_3 (2 mL) in benzene were used as solvent, respectively.

Acknowledgments

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[1] G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555–1564.
[2] a) R. H. Crabtree in *The Organometallic Chemistry of the Transition Metals* 4th ed., John Wiley & Sons, Inc., Hoboken, New Jersey, **2005**, pp. 165–166; b) J. Halpern, *Acc. Chem. Res.* **1970**, *3*, 386–392; c) J. K. Stille, K. S. Y. Lau, *Acc. Chem. Res.* **1976**, *9*, 434–442.
[3] M. L. Clarke, J. J. R. Frew, *Organomet. Chem.* **2009**, *35*, 19–46.
[4] C. A. Busacca, D. Grossbach, R. C. So, E. M. O'Brien, E. M. Spinelli, *Org. Lett.* **2003**, *5*, 595–598.
[5] A. J. Hickman, M. S. Sanford, *ACS Catal.* **2011**, *1*, 170–174.
[6] K. M. Kadish, K. M. Smith, R. Guilard in *The Porphyrin Handbook* 1st Ed., Academic Press, San Diego, **2000**.
[7] a) J. D. Harden, J. V. Ruppel, G.-Y. Gao, X. P. Zhang, *Chem. Commun.* **2007**, 4644–4646; b) J. V. Ruppel, R. M. Kamble, X. P. Zhang, *Org. Lett.* **2007**, *9*, 4889–4892; c) V. Lyaskovskyy, A. I. O. Suarez, H. Lu, H. Jiang, X. P. Zhang, B. de Bruin, *J. Am. Chem. Soc.* **2011**, *133*, 12264–12273.
[8] a) L. Huang, Y. Chen, G.-Y. Gao, X. P. Zhang, *J. Org. Chem.* **2003**, *68*, 8179–8184; b) W. I. Dzik, X. Xu, X. P. Zhang, J. N. H. Reek, B. de Bruin, *J. Am. Chem. Soc.* **2010**, *132*, 10891–10902; c) H. Lu, W. I. Dzik, X. Xu, L. Wojtas, B. de Bruin, X. P. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8518–8521.
[9] a) G.-Y. Gao, J. D. Harden, X. P. Zhang, *Org. Lett.* **2005**, *7*, 3191–3193; b) A. I. O. Suarez, H. Jiang, X. P. Zhang, B. de Bruin, *Dalton Trans.* **2011**, *40*, 5697–5705.
[10] H. Sharghi, A. H. Nejad, M. A. Nasseri, *New J. Chem.* **2004**, *28*, 946–951.
[11] G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447–2464.
[12] For first-row transition-metal catalyzed examples, see: a) H.-Q. Do, R. M. K. Khan, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 15185–15192; b) F. Vallée, J. J. Mousseau, A. B. Charette, *J. Am. Chem. Soc.* **2010**, *132*, 1514–1516; c) W. Liu, H. Cao, A. Lei, *Angew. Chem.* **2010**, *122*, 2048; *Angew. Chem. Int. Ed.* **2010**, *49*, 2004–2008; d) G. Xie, T. Li, X. Qu, J. Mao, *J. Mol. Catal. A* **2011**, *340*, 48–52; e) W. Liu, H. Cao, J. Xin, L. Jin, A. Lei, *Chem. Eur. J.* **2011**, *17*, 3588–3592; f) H. Li, C.-L. Sun, M. Yu, D.-G. Yu, B.-J. Li, Z.-J. Shi, *Chem. Eur. J.* **2011**, *17*, 3593–3597; for transition-metal-free catalyzed examples, see: g)

W. Liu, H. Cao, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong, A. Lei, *J. Am. Chem. Soc.* **2010**, *132*, 16737–16740; h) E. Shirakawa, K. Itoh, T. Higashino, T. Hayashi, *J. Am. Chem. Soc.* **2010**, *132*, 15537–15539; i) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li, Z.-J. Shi, *Nat. Chem.* **2010**, *2*, 1044–1049; j) Y. Qiu, Y. Liu, K. Yang, W. Hong, Z. Li, Z. Wang, Z. Yao, S. Jiang, *Org. Lett.* **2011**, *13*, 3556–3559.

[13] C. T. To, T. L. Chan, B. Z. Li, Y. Y. Hui, T. Y. Kwok, S. Y. Lam, K. S. Chan, *Tetrahedron Lett.* **2011**, *52*, 1023–1026.

[14] a) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* **1967**, *32*, 476; b) R. W. Wagner, D. Lawrence, J. S. Lindsey, *Tetrahedron Lett.* **1987**, *28*, 3069–3070; c) A. D. Adler, F. R. Longo, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

[15] a) J. Halpern, *Polyhedron* **1988**, *7*, 1483–1490; b) J. F. Endicott, G. F. Ferraudi, *J. Am. Chem. Soc.* **1977**, *99*, 243–245.

[16] B. B. Wayland, A. E. Sherry, A. G. Bunn, *J. Am. Chem. Soc.* **1993**, *115*, 7675–7684.

[17] F. A. Walker, *J. Am. Chem. Soc.* **1973**, *95*, 1150–1153. The formation constant was estimated by using $\Delta G = -RT\ln K$, assuming ΔG remained constant over the temperature range 298–473 K.

[18] a) D. Lexa, J. M. Savéant, J. Zickler, *J. Am. Chem. Soc.* **1980**, *102*, 2654–2663; b) V. Grass, D. Lexa, M. Momenteau, J. M. Savéant, *J. Am. Chem. Soc.* **1997**, *119*, 3536–3542; c) P. B. Chock, R. B. K. Dewar, J. Halpern, L.-Y. Wong, *J. Am. Chem. Soc.* **1969**, *91*, 82–84; d) B. B. Wayland, K. J. Balkus Jr., M. D. Farnos, *Organometallics* **1989**, *8*, 950–955; e) $\mathrm{Co^{I}(t_{4\text{-}OMe}pp)^{-}}$, though more nucleophilic than $\mathrm{Co^{II}(t_{4\text{-}OMe}pp)}$, probably precipitates in benzene rendering its poor reactivity.

[19] J. Halpern, J. P. Maher, *J. Am. Chem. Soc.* **1965**, *87*, 5361–5366.

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