Cp$_2$TiCl$_2$-Catalyzed Carboxylation of Aryl Chlorides with Carbon Dioxide in the Presence of *n*-BuMgCl

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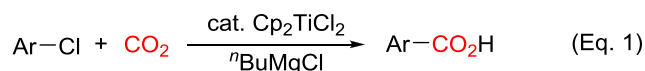
Ⓢ *Supporting Information*

ABSTRACT: Cp$_2$TiCl$_2$-catalyzed carboxylation of aryl chlorides with carbon dioxide to afford benzoic acids in good yields has been achieved in the presence of *n*-BuMgCl. The reaction proceeds by a sequential magnesium halide exchange reaction and carboxylation with CO$_2$ in a wide variety of aryl chlorides under mild conditions.

Ar−Cl + CO$_2$ (bubble) →[1) Cp$_2$TiCl$_2$ (5 mol %) *n*-BuMgCl (5 equiv.)][2) THF, rt, 2 h] Ar−CO$_2$H
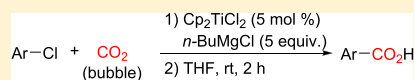
Carbon dioxide (CO$_2$) is an ideal carbon source that is cost-effective, sustainable, and inherently renewable.[1] In particular, carbon−carbon bond making reactions employing CO$_2$ are the most hopeful. Reactions using reactive Grignard, organolithium, and organosodium reagents reacting with CO$_2$ are essential for the carbon−carbon bond formation; however, the functional group compatibility with these reagents is limited.[2] In contrast, less reactive organoboranes,[3a−c] organozincs,[3d,e] organotins,[3f−i] organoaluminums,[3j,k] and organozirconiums[3l] were found to react with CO$_2$ with good functional group compatibility with transition metals as catalysts. Despite this, all of these organometallic reagents are mainly prepared from the corresponding aryl halides. Consequently, catalytic generation of the highly reactive organometallic species in situ from readily available substrates to react with CO$_2$ is more straightforward and efficient for the formation of carboxylic acids. Recently, several groups have independently reported Fe- or Ti-catalyzed carboxylation of alkenes with CO$_2$ in the presence of organomagnesium reagents to afford alkanecarboxylic acids with regioselectivity.[4,5] Likewise, catalytic generation of arylmetallic species in situ from aryl halides to react with CO$_2$ is also straightforward for the formation of benzoic acids, which are important motifs in a great number of natural and medicinal compounds.[6] Recently, transition-metal-catalyzed direct carboxylation of the aryl halides with CO$_2$ has attracted considerable attention and some reactions have been achieved using Pd,[7] Ni,[8] and Cu[9] catalysts. A method using early-transition-metal catalysts for the carboxylation of aryl halides with CO$_2$ under mild conditions remains to be studied, particularly using aryl chlorides, which are low-activity and pollutant perchlorinated compounds.[10] Influenced by this idea and as our ongoing project on CO$_2$ chemistry,[11] we wish to report herein the Cp$_2$TiCl$_2$-catalyzed synthesis of benzoic acids from aryl chlorides and CO$_2$ in the presence of *n*-butylmagnesium chloride (eq 1).

Titanium-catalyzed dechlorinations of halides with alkylmagnesium reagents have been reported.[12] We began our investigation with 4-chloroanisole (**1a**; 0.5 mmol) and 5 mol %

$$\text{Ar−Cl} + \text{CO}_2 \xrightarrow[{}^{n}\text{BuMgCl}]{\text{cat. Cp}_2\text{TiCl}_2} \text{Ar−CO}_2\text{H} \qquad \text{(Eq. 1)}$$

of Cp$_2$TiCl$_2$ in the presence of *n*-butylmagnesium chloride (*n*-BuMgCl; **2a**; 1.55 mmol, 0.78 mL, 2.0 M in THF solution) at 40 °C in ether for 6 h. Then, the reaction was bubbled with CO$_2$ at room temperature and the corresponding benzoic acid **3a** was observed in 39% NMR yield (Table 1, entry 1) along with 39% of the dechlorination product **4a** and 19% of the starting material **1a**. During the CO$_2$ gas bubbling, the reaction mixture became a mud and the syringe spiker was clogged for CO$_2$ gas flow. Therefore, we tried addition of 4 mL of THF in the vessel to increase the solubility. As expected, the CO$_2$ gas flowed smoothly in this solution. Then we scanned Grignard reagents (entries 2−4), such as *n*-propylmagnesium chloride (*n*-PrMgCl), isopropylmagnesium chloride (*i*-PrMgCl), and isobutylmagnesium chloride (*i*-BuMgCl). It was found that the reaction proceeded well using *n*-BuMgCl (entry 1). Screening solvents such as tetrahydrofuran (THF) and *n*-hexane (entries 5 and 6) revealed that *n*-hexane was a better solvent (entry 6). During the course of our study, we found that the reaction proceeded well to afford the desired benzoic acid **3a** in 52% yield without utilization of any solvents (entry 7). In order to further improve the yield, greater excesses of *n*-BuMgCl were added (entries 8−10). To our delight, 4-methoxybenzoic acid **3a** was obtained in 71% yield when 5 equiv of *n*-BuMgCl was added (entry 9). Notably, the reaction was also treated in the absence of *n*-BuMgCl or Cp$_2$TiCl$_2$ and the desired product **3a** was not observed and the starting material **1a** remained (entries 11 and 12). Different reaction times were examined (entries 9, 13, and 14), and 6 h was preferred (entry 9). Under the optimized reaction conditions, treatment of the reaction mixture with D$_2$O instead of CO$_2$ afforded anisole-4-D (**4a′**) in

Table 1. Screening the Reaction Conditions[a]
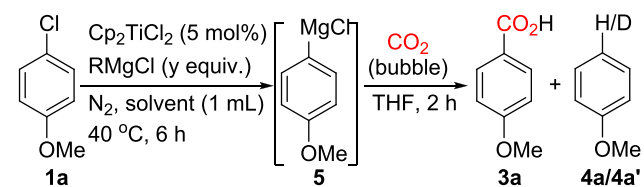
entry	RMgCl (y equiv)	solvent	yield of 3a/4a (%)[b]
1	n-BuMgCl (3)	Et$_2$O	39/39
2	n-PrMgCl (3)	Et$_2$O	25/32
3	i-PrMgCl (3)	Et$_2$O	trace/trace
4	i-BuMgCl (3)	Et$_2$O	trace/trace
5	n-BuMgCl (3)	THF	26/41
6	n-BuMgCl (3)	n-hexane	46/36
7	n-BuMgCl (3)		52/43
8	n-BuMgCl (4)		60/29
9	n-BuMgCl (5)		71(63)/28
10	n-BuMgCl (6)		66/35
11			
12[c]	n-BuMgCl (5)		
13[d]	n-BuMgCl (5)		55/32
14[e]	n-BuMgCl (5)		65/32
15[f]	n-BuMgCl (5)		0/80(75)

[a]Reaction conditions unless specified otherwise: 1a (0.5 mmol), Cp$_2$TiCl$_2$ (0.025 mmol), Grignard reagent, solvent, N$_2$, 40 °C, 6 h; CO$_2$ bubble, THF (4 mL), room temperature, 2 h. [b]NMR yield, dibromomethane as the internal standard, isolated yield in parentheses. [c]Without Cp$_2$TiCl$_2$. [d]The reaction time was 3 h. [e]The reaction time was 12 h. [f]The reaction mixture was treated with D$_2$O instead of CO$_2$ to afford 4a'.

75% isolated yield (entry 15). This result indicates that the Cp$_2$TiCl$_2$-catalyzed magnesium chloride exchange reaction occurred to give (4-methoxyphenyl)magnesium chloride (5); although ArMgCl can be prepared by the direct reaction of ArCl with magnesium, most of the methods require harsh conditions such as high temperature and tedious processing for the preparation of highly activated magnesium turnings and give a low yield for the utilization of aryl chlorides.[13]

With the optimized reaction conditions (Table 1, entry 9), the substrate scope was explored and the representative results are summarized in Table 2. The carboxylation of electron-rich aryl chlorides proceeded well (entries 1−5). Methyl groups are tolerated, and 3- and 4-chlorotoluenes are reactive to afford the corresponding methylbenzoic acids in good yields (entries 1 and 2). Alkoxy or alkylthiol groups are also tolerated, and 3- and/or 4-chloroanisoles are also reactive to give the corresponding methoxybenzoic acids or (methylthio)benzoic acid in satisfying yields (entries 3 and 4). Heterocyclic 2-chlorothiophene (1f) (entry 5) is carboxylated to afford thiophene-2-carboxylic acid (3f) in 88% yield. When 4-chloro-1,1′-biphenyl (1g) and 2-chloronaphthalene (1h) were employed, the corresponding products were obtained in 57% and 49% yields (entries 6 and 7), respectively. Hindered aryl chlorides, such as 1-chloro-2-methylbenzene (1i) (entry 8), 1-chloro-2-methoxybenzene (1j) (entry 9) and 1-chloronaphthalene (1k) (entry 10), are less reactive. Carboxylation of electron-poor aryl chlorides also proceeded: for example, 4- and 3-fluorochlorobenzenes (1m,n) could also be carboxylated to give fluorobenzoic acids 3m,n in 59% and 60% yields (entries 12 and 13), respectively. When 1,4-dichlorobenzene was used, 4-chlorobenzoic acid (3o) was obtained in 44% yield

Table 2. Scope of Aryl Chloride for Carboxylation[a]

entry	Ar-Cl	Ar-CO$_2$H	yield of 3(%)[b]
1	1b	3b	64
2	1c	3c	62
3	1d	3d	60
4	1e	3e	61
5	1f	3f	88
6	1g	3g	57
7	1h	3h	49
8[c]	1i	3i	36
9	1j	3j	13
10	1k	3k	25
11	1l	3l	66
12	1m	3m	59
13	1n	3n	60
14	1o	3o	44
15	1p	3p	11
16	1q	3l	61
17	1r	3l	72

[a]Reaction conditions unless specified otherwise: 1 (0.5 mmol), Cp$_2$TiCl$_2$ (0.025 mmol), n-BuMgCl (2.55 mmol, 2.0 M in THF solution), N$_2$, 40 °C, 6 h; CO$_2$ bubble, THF (4 mL), room temperature, 2 h. [b]Isolated yield. [c]The reaction time was 12 h.

along with 26% of benzoic acid (**3l**) (entry 14). However, 1-chloro-4-(trifluoromethyl)benzene (**1p**) was less carboxylated under these conditions and only an 11% yield of **3p** was observed (entry 15). The reduction of **1p** to **4p** was observed. It is noteworthy that, when the aryl chlorides were extended to reactive functional groups such as ketone, ester, aldehyde, amide, and cyano, a mixture of products was observed with few desired products, respectively. In addition, reactions of the corresponding aryl bromides and iodides also proceeded in a sequential magnesium halide exchange reaction and carboxylation with CO_2 to give the desired benzoic acid (**3l**) in 61% and 72% yields (entries 16 and 17), respectively.

In combination with known facts, a plausible pathway of this reaction is outlined in Scheme 1 (path a). Electron transfer

Scheme 1. Possible Reaction Mechanisms
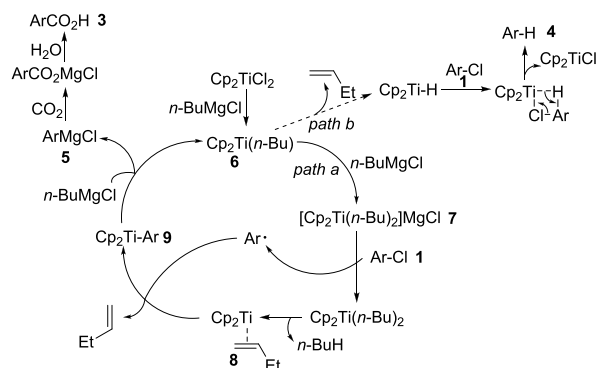
from the ate complex[14] $[Cp_2Ti(n\text{-Bu})_2]MgCl$ (**7**) to the aryl chloride **1** forms an aryl radical species and $Cp_2Ti(n\text{-Bu})_2$, which decomposes to afford Cp_2Ti along with butene and butane.[15] The aryl radical species reacts with the generated $Cp_2Ti(CH_2=CHEt)$ (**8**) to give **9**. Subsequent transmetalation of **9** with n-BuMgCl affords the arylmagnesium chloride **5** and $Cp_2Ti(n\text{-Bu})$ (**6**). The generated arylmagnesium chloride **5** reacts with CO_2 to afford the benzoic acid **3** after hydrolysis. Since the reaction is often accompanied by the dechlorination product **4** as a byproduct, we also give a path b for the formation of dechlorination product **4**.[12] Paths a and b are competitive reactions. The utilization of an excess amount of n-BuMgCl may result in path a being more advantageous than path b. To further understand the reaction, the compound **9l** generated by the reaction of Cp_2TiCl_2 with i-PrMgCl and PhMgBr[16] was treated using different amounts of n-BuMgCl, and CO_2 and benzoic acid **3l** was observed, respectively (for details of the procedures and results, see the Supporting Information). These results indicate that the intermediate **9** was formed in this reaction.

In conclusion, Cp_2TiCl_2-catalyzed carboxylation of aromatic chlorides with CO_2 in the presence of n-butylmagnesium reagent has been described. In contrast to the Cp_2TiCl_2-catalyzed dechlorination of aryl chlorides using alkylmagnesium reagents, the use of excess amounts of n-BuMgCl may result in the transformation toward a magnesium halide exchange reaction to give a wide range of arylmagnesium reagents, which reacted with CO_2 to form benzoic acids.

■ ASSOCIATED CONTENT

⊛ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00712.

Experimental procedures, full characterization including ^{1}H NMR and ^{13}C NMR data for all products, and NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Sakakura, T.; Choi, J.-C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365−2387. (b) Boogaerts, I. I. F.; Nolan, S. P. Direct C-H Carboxylation with Complexes of the Coinage Metals. *Chem. Commun.* **2011**, *47*, 3021−3024. (c) Nakamura, A.; Ito, S.; Nozaki, K. Coordination-Insertion Copolymerization of Fundamental Polar Monomers. *Chem. Rev.* **2009**, *109*, 5215−5244. (d) Ackermann, L. Transition-Metal-Catalyzed Carboxylation of C-H Bonds. *Angew. Chem., Int. Ed.* **2011**, *50*, 3842−3844. (e) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge? *Angew. Chem., Int. Ed.* **2011**, *50*, 8510−8537. (f) Tsuji, Y.; Fujihara, T. Carbon Dioxide as a Carbon Source in Organic Transformation: Carbon-Carbon Bond Forming Reactions by Transition-Metal Catalysts. *Chem. Commun.* **2012**, *48*, 9956−9964. (g) Martín, R.; Kleij, A. W. Myth or Reality? Fixation of Carbon Dioxide into Complex Organic Matter under Mild Conditions. *ChemSusChem* **2011**, *4*, 1259−1263. (h) Correa, A.; Leon, T.; Martín, R. Ni-Catalyzed Carboxylation of C(sp^2)- and C(sp^3)-O Bonds with CO_2. *J. Am. Chem. Soc.* **2014**, *136*, 1062−1069. (i) Zhang, S.; Chen, W.-Q.; Yu, A.; He, L.-N. Palladium-Catalyzed Carboxylation of Benzyl Chlorides with Atmospheric Carbon Dioxide in Combination with Manganese/Magnesium Chloride. *ChemCatChem* **2015**, *7*, 3972−3977. (j) Shimomaki, K.; Murata, K.; Martín, R.; Iwasawa, N. Visible-Light-Driven Carboxylation of Aryl Halides by the Combined Use of Palladium and Photoredox Catalysts. *J. Am. Chem. Soc.* **2017**, *139*, 9467−9470. (k) Yan, S.-S.; Fu, Q.; Liao, L.-L.; Sun, G.-Q.; Ye, J.-H.; Gong, L.; Bo-Xue, Y.-Z.; Yu, D.-G. Transition Metal-Catalyzed Carboxylation of Unsaturated Substrates with CO_2. *Coord. Chem. Rev.* **2018**, *374*, 439−463. (l) Tortajada, A.; Julia-Hernandez, F.; Borjesson, M.; Moragas, T.; Martín, R. Transition-Metal-Catalyzed Carboxylation Reactions with Carbon Dioxide. *Angew. Chem., Int. Ed.* **2018**, *57*, 15948−15982. (m) Hong, J.; Li, M.; Zhang, J.; Sun, B.; Mo, F. C-H Bond Carboxylation with Carbon Dioxide. *ChemSusChem* **2019**, *12*, 6−39.

(2) (a) Mutule, I.; Suna, E. Arylzinc Species by Microwave Assisted Grignard Formation-Transmetallation Sequence: Application in the Negishi Coupling. *Tetrahedron* **2005**, *61*, 11168−11176. (b) Mander, L. N.; Sethi, S. P. Regioselective Synthesis of β-Ketoesters from Lithium Enolates and Methyl Cyanoformate. *Tetrahedron Lett.* **1983**, *24*, 5425−5428. (c) Wanklyn, J. A. Ueber die Bildung der Propionsäure aus Kohlensäure und einer Aethylverbindung. *Liebigs Ann.* **1858**, *107*, 125−128. (d) Kekuié, A. Untersuchungen über Aromatische Verbindungen Ueber die Constitution der Aromatischen Verbindungen. I. Ueber die Constitution der Aromatischen Verbindungen. *Liebigs Ann.* **1866**, *137*, 129−196.

(3) (a) Ukai, K.; Aoki, M.; Takaya, J.; Iwasawa, N. Rhodium(I)-Catalyzed Carboxylation of Aryl- and Alkenylboronic Esters with CO₂. *J. Am. Chem. Soc.* **2006**, *128*, 8706–8707. (b) Ohishi, T.; Nishiura, M.; Hou, Z. Carboxylation of Organoboronic Esters Catalyzed by N-Heterocyclic Carbene Copper(I) Complexes. *Angew. Chem., Int. Ed.* **2008**, *47*, 5792–5795. (c) Takaya, J.; Tadami, S.; Ukai, K.; Iwasawa, N. Copper(I)-Catalyzed Carboxylation of Aryl- and Alkenylboronic Esters. *Org. Lett.* **2008**, *10*, 2697–2700. (d) Ochiai, H.; Jang, M.; Hirano, K.; Yorimitsu, H.; Oshima, K. Nickel-Catalyzed Carboxylation of Organozinc Reagents with CO₂. *Org. Lett.* **2008**, *10*, 2681–2683. (e) Yeung, C. S.; Dong, V. M. Beyond Aresta's Complex: Ni- and Pd-Catalyzed Organozinc Coupling with CO₂. *J. Am. Chem. Soc.* **2008**, *130*, 7826–7827. (f) Shi, M.; Nicholas, K. M. Palladium-Catalyzed Carboxylation of Allyl Stannanes. *J. Am. Chem. Soc.* **1997**, *119*, 5057–5058. (g) Johansson, R.; Wendt, O. F. Insertion of CO₂ into a Palladium Allyl Bond and a Pd(II) Catalysed Carboxylation of Allyl Stannanes. *Dalton Trans* **2007**, 488–492. (h) Wu, J.; Hazari, N. Palladium Catalyzed Carboxylation of Allylstannanes and Boranes Using CO₂. *Chem. Commun.* **2011**, *47*, 1069–1071. (i) Feng, X.; Sun, A.; Zhang, S.; Yu, X.; Bao, M. Palladium-Catalyzed Carboxylative Coupling of Benzyl Chlorides with Allyltributylstannane: Remarkable Effect of Palladium Nanoparticles. *Org. Lett.* **2013**, *15*, 108–111. (j) Ueno, A.; Takimoto, M.; O, W. W. N.; Nishiura, M.; Ikariya, T.; Hou, Z. Copper-Catalyzed Formal C-H Carboxylation of Aromatic Compounds with Carbon Dioxide through Arylaluminum Intermediates. *Chem. - Asian J.* **2015**, *10*, 1010–1016. (k) Takimoto, M.; Hou, Z. Cu-Catalyzed Formal Methylative and Hydrogenative Carboxylation of Alkynes with Carbon Dioxide: Efficient Synthesis of α,β-Unsaturated Carboxylic Acids. *Chem. - Eur. J.* **2013**, *19*, 11439–11445. (l) Wang, S.; Shao, P.; Chen, C.; Xi, C. Copper-Catalyzed Carboxylation of Alkenylzirconocenes with Carbon Dioxide Leading to α,β-Unsaturated Carboxylic Acids. *Org. Lett.* **2015**, *17*, 5112–5115.

(4) (a) Greenhalgh, M. D.; Thomas, S. P. Iron-Catalyzed, Highly Regioselective Synthesis of α-Aryl Carboxylic Acids from Styrene Derivatives and CO₂. *J. Am. Chem. Soc.* **2012**, *134*, 11900–11903. (b) Shirakawa, E.; Ikeda, D.; Masui, S.; Yoshida, M.; Hayashi, T. Iron−Copper Cooperative Catalysis in the Reactions of Alkyl Grignard Reagents: Exchange Reaction with Alkenes and Carbometalation of Alkynes. *J. Am. Chem. Soc.* **2012**, *134*, 272–279.

(5) (a) Shao, P.; Wang, S.; Chen, C.; Xi, C. Cp₂TiCl₂-Catalyzed Regioselective Hydrocarboxylation of Alkenes with CO₂. *Org. Lett.* **2016**, *18*, 2050–2053. (b) Hang, W.; Zou, S.; Xi, C. Titanocene-Catalyzed Sequential Carbocarboxylation of Dienes and Alkenes with Organic Halides and Carbon Dioxide in the Presence of *n*-BuMgCl. *ChemCatChem* **2019**, *11*, 3814–3817.

(6) (a) Goossen, L. J.; Rodríguez, N.; Goossen, K. Carboxylic Acids as Substrates in Homogeneous Catalysis. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100–3120. (b) Bew, S. P. In *Comprehensive Organic Functional Groups Transformation II*; Katritzky, A. R., Taylor, R. J. K., Eds.; Elsevier: Oxford, 2005; p 19.

(7) Correa, A.; Martín, R. Palladium-Catalyzed Direct Carboxylation of Aryl Bromides with Carbon Dioxide. *J. Am. Chem. Soc.* **2009**, *131*, 15974–15975.

(8) (a) Fujihara, T.; Nogi, K.; Xu, T.; Teao, J.; Tsuji, Y. Nickel-Catalyzed Carboxylation of Aryl and Vinyl Chlorides Employing Carbon Dioxide. *J. Am. Chem. Soc.* **2012**, *134*, 9106–9109. (b) Leon, T.; Correa, A.; Martín, R. Ni-Catalyzed Direct Carboxylation of Benzyl Halides with CO₂. *J. Am. Chem. Soc.* **2013**, *135*, 1221–1224. (c) Charboneau, D. J.; Brudvig, G. W.; Hazari, N.; Lant, M. C. H.; Saydjari, K. A. Development of An Improved System for the Carboxylation of Aryl Halides through Mechanistic Studies. *ACS Catal.* **2019**, *9*, 3228–3241.

(9) Tran-Vu, H.; Daugulis, O. Copper-Catalyzed Carboxylation of Aryl Iodides with Carbon Dioxide. *ACS Catal.* **2013**, *3*, 2417–2420.

(10) Hites, R. A. Environmental Behavior of Chlorinated Dioxins and Furans. *Acc. Chem. Res.* **1990**, *23*, 194–201.

(11) (a) Wang, S.; Xi, C. Recent Advances in Nucleophile-Triggered CO₂-Incorporated Cyclization Leading to Heterocycles. *Chem. Soc.*

Rev. **2019**, *48*, 382–404. (b) Wang, S.; Shao, P.; Chen, C.; Xi, C. Copper-Catalyzed Carboxylation of Alkenylzirconocenes with Carbon Dioxide Leading to α,β-Unsaturated Carboxylic Acids. *Org. Lett.* **2015**, *17*, 5112–5115. (c) Wang, S.; Xi, C. Nickel-Catalyzed Arylative Carboxylation of Alkynes with Arylmagnesium Reagents and Carbon Dioxide Leading to Trisubstituted Acrylic Acids. *Org. Lett.* **2018**, *20*, 4131–4134. (d) Guo, Z.; Zhang, B.; Wei, X.; Xi, C. 1,4-Dioxane-Tuned Catalyst-Free Methylation of Amines by CO₂ and NaBH₄. *ChemSusChem* **2018**, *11*, 2296–2299.

(12) (a) Colomer, E.; Corriu, R. Activations des Reactifs de Grignard par les Complexes du Titane. Application du Systeme "Cp₂TiCl₂-*i*-PrMgBr" Comme Agent Reducteur. *J. Organomet. Chem.* **1974**, *82*, 367–373. (b) Rilatt, J. A.; Kitching, W. Mechanistic Aspects of the Titanocene Dichloride-Isopropyl Grignard Reduction of Alkyl Bromides. *Organometallics* **1982**, *1*, 1089–1093. (c) Hara, R.; Sato, K.; Sun, W.-H.; Takahashi, T. Catalytic Dechlorination of Aromatic Chlorides Using Grignard reagents in the Presence of (C₅H₅)₂TiCl₂. *Chem. Commun.* **1999**, 845–846. (d) Hara, R.; Sun, W.-H.; Nishihara, Y.; Takahashi, T. Zirconocene Catalyzed Dehalogenation of Aromatic Halides by Alkylmagnesium Reagents. *Chem. Lett.* **1997**, *26*, 1251–1252.

(13) (a) Bogdanović, B.; Schwickardi, M. Transition Metal Catalyzed Preparation of Grignard Compounds. *Angew. Chem., Int. Ed.* **2000**, *39*, 4610–4612. (b) Piller, F. M.; Appukkuttan, P.; Gavryushin, A.; Helm, M.; Knochel, P. Convenient Preparation of Polyfunctional Aryl Magnesium Reagents by A Direct Magnesium Insertion in the Presence of LiCl. *Angew. Chem., Int. Ed.* **2008**, *47*, 6802–6806. (c) Sherry, B. D.; Fürstner, A. Iron-Catalyzed Addition of Grignard Reagents to Activated Vinyl Cyclopropanes. *Chem. Commun.* **2009**, 7116–7118.

(14) (a) Martin, H. A.; Jellinek, F. Synthesis of Allyldicyclopentadienyltitanium(III) Complexes from Dienes. *J. Organomet. Chem.* **1968**, *12*, 149–161. (b) Luinstra, G. A.; Ten Cate, L. C.; Heeres, H. J.; Pattiasina, J. W.; Meetsma, A.; Teuben, J. H. Synthesis and Reactivity of Tervalent Paramagnetic Titanium Compounds $(\eta^5\text{-}C_5Me_5)_2TiR$: Molecular Structure of $(\eta^5\text{-}C_5Me_5)_2TiCH_2CMe_3$. *Organometallics* **1991**, *10*, 3227–3237.

(15) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. Synthesis and Reactions of Bis(cyclopentadienyl)titanium(IV) Metallocycles. *J. Am. Chem. Soc.* **1976**, *98*, 6529–6536.

(16) Yamamoto, Y.; Matsumi, D.; Hattori, R.; Itoh, K. The Cp₂TiPh-Mediated Reductive Radical Cyclization of Cyanoketones and Related Reactions. Efficient Trapping of Ketyl Radicals by Cp₂TiPh-Coordinated Polar Multiple Bonds. *J. Org. Chem.* **1999**, *64*, 3224–3229. (b) De Boer, E. J. M.; Teuben, J. H. Dimerization of Organic Cyanides Ligated to Di-η5-cyclopentadienylaryltitanium(III). *J. Organomet. Chem.* **1978**, *153*, 53–57.