Contents lists available at ScienceDirect

Catalysis Communications

Short communication

Rhodium-catalyzed borylative carbon monoxide reduction to *gem*-diborylmethane

Jian-Xing Xu [a], Fu-Peng Wu [b], Xiao-Feng Wu [a,b,*]

[a] *Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Science, 116023 Dalian, Liaoning, China*
[b] *Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany*

ARTICLE INFO

ABSTRACT

Herein, we developed a rhodium-catalyzed reduction of CO with bis(pinacolato)diboron (B_2pin_2) under atmospheric pressure of CO with silane as the hydride source, gem-diborylmethane [$H_2C(Bpin)_2$] as a versatile and fundamental C1 compound can be formed. Notably, this is the first example on transition metal-catalyzed borylation of CO.

The production of value-added chemicals from simple, economical, and renewable sources is one of the most important goals for chemists. Particularly, converting C_1 oxygenates (CO, CO_2) to high value compounds (e.g., synthetic fuels) present a far-reaching implication, as it can make use of greenhouse gases and reduce humanity's dependence on non-renewable fossil fuels. Many homogeneous and heterogeneous catalysts on reducing CO_2 have been established, CO usually plays as a crucial intermediate or terminal product. In contrast, as an inexpensive and readily available C_1 building block, carbon monoxide is widely utilized to construct new C—C or C-heteroatom bonds in laboratorial and industrial processes via carbonylation and related procedures [1]. Among these procedures, the σ-C-O bond of CO usually remains intact in most cases besides the Fischer-Tropsch process which is the only process that C≡O triple bond is completely broken and C—C coupling is proceeded on the heterogeneous catalyst surface under high temperature and pressure (Scheme 1, A).

The cleavage of the C≡O triple bond under mild conditions remains an attractive fundamental challenge. The C≡O triple bond is the strongest known chemical bond in neutral molecules with a high bond dissociation energy (1076 kJ/mol at 298 K). To date, several transition-metal complexes are reported been able to cleave the C≡O triple bond [2–6], with metal-carbide complexes [3] or hydrocarbons [4–6] as the majority products. On the other hand, complexes of the *p*-block elements are also capable of C≡O triple bond cleavage [7–17], including boron [10–13], silicon [14,15], and germanium [16], etc.

Remarkably, due to its unique property and readily transformable ability of C—B bonds, organoboron compounds are widely utilized in organic synthesis, including CO reduction. Brown and co-workers reported homologation of CO and alkylboranes to C_1-elongated alkylboranes with $LiHAl(OMe)_3$ (LTMA) and $LiAlH_4$ [17]. Yalpani et al. reported the carbonylation of Et_2BH to give butanol where C≡O is completely cleaved (Scheme 1, B) [18]. Combining Lewis acidic boranes and Lewis bases (Frustrated Lewis Pairs, FLPs), Stephan's and Erker's groups described the FLP promoted reduction of CO with H_2 or $HB(C_6F_5)_2$ (Scheme 1, C) [19,20] Siebert et al. presented the insertion of CO into the B—B bond of a cyclic diborane to form a dimeric spiro boron compound [21], whereas Braunschweig's group reported the coupling of CO with a B≡B triple bond to form a bicyclic, bis(boralactone) in which four CO molecules are incorporated (Scheme 1, D) [22].

Recently, Marder's group reported that a combination of B_2pin_2 with quantitative $Ru_3(CO)_{12}$ cleaves the C—O bond to give carbon-borylated ruthenium clusters and carbon-borylated products [23]. The products obtained included $CH_2(Bpin)_2$, $CH(Bpin)_3$, $C(Bpin)_4$, and also $C_2(Bpin)_6$. Notably, $C(Bpin)_4$ and $C_2(Bpin)_6$ were crystallographically characterized, and the latter one results from C—C coupling of two CO molecules. Here, we found that, with rhodium as the catalyst, the C≡O triple bond in CO can be completely broken by borylation with B_2pin_2 to give *gem*-diborylmethane [$CH_2(Bpin)_2$] under atmospheric pressure of CO gas with silane as the hydride source. Different from the other methylene building blocks, *gem*-diborylmethane is a versatile and fundamental intermediate that has attracted much attention for producing multi-functionalized molecules (Scheme 2) [24,25]. From a synthetic point

---

Scheme 1. CO reduction to methylene derivatives.

Scheme 2. Functionalization of *gem*-diborylmethane.

of view, several practical procedures have been developed for diborylmethane preparation [24,25]. Srebnik and co-workers reported the reaction of diazomethane with B_2pin_2 in 2001 [26]. As the first example on using CH_2N_2 for *gem*-diborylmethane synthesis, good yields were obtained with Pt as the catalyst. Marder and co-workers developed a Cu(II)-catalyzed borylation of alkyl bromides and chlorides (including DCM) with B_2pin_2 in 2016 [27]. The reaction proceed effectively at low temperature under air. $CH_2(Bpin)_2$ can even be produced from methane through C—H bond borylation [28,29].

Employing [Rh(*cod*)Cl]$_2$/PPh$_3$ as the catalyst, CO can react with B_2pin_2 to form *gem*-diborylmethane [H$_2$C(Bpin)$_2$] in toluene under 1 bar

of CO gas for 12 h at 100 °C, utilizing sodium *tert*-butoxide (NaO^{t}Bu) as the base and diethoxymethylsilane [(EtO)$_2$MeSiH] as the hydride source (Table 1, entry 1). In the absence of a hydride reagent, no *gem*-diborylmethane was observed. As [B]-H-containing boranes could react with CO, and even reduce CO in some cases, we tested some [B]-H compounds as the hydride reagent. Only BH$_3$ give a small amount of *gem*-diborylmethane, whereas HBpin, NaBH$_4$ were not efficient. Alcohols are used as effective hydride sources in some case, including *gem*-hydrodiborylation of carboxylic esters. Only a trace amount of *gem*-diborylmethane was obtained instead of (EtO)$_2$MeSiH by EtOH or ^{i}PrOH. Similarly, H$_2$ is incompetent for this transformation. Interestingly, when boronic acids, such as methylboronic acid or phenylboronic acid, were added, the transformation efficiency could be increased (Table 1, entry 9). Although it is far from clear how they work, gave the corresponding boronic pinacol ester could be observed, indicating that the -B(OH)$_2$ group may play a role in the transformation. Replacement of a boronic acid by B(OH)$_3$ or B$_2$(OH)$_4$, gave no *gem*-diborylmethane.

Various hydrosilanes were also investigated for the reductive borylation of CO. As shown in Table 2, alkyl-only substituted silanes such as Et$_3$SiH, PhMe$_2$SiH, Ph$_2$MeSiH were found to be inactive. When employing alkoxy-substituted silanes as the reductant, *gem*-diborylmethane can be obtained, but di-alkoxy substitution gave the best yield (Table 1, entry 9). Diphenyl silane Ph$_2$SiH$_2$ was also tested, but a low yield of *gem*-diborylmethane was observed. Polymethylhydrosilane (PMHS), as a non-toxic, inexpensive, air and moisture stable silane, only gave a low yield. Increasing the equivalent of (EtO)$_2$MeSiH was negative for *gem*-diborylmethane formation. Further reactions were carried out to study the effect of the bases. Control experiment showed the base plays an important role in this reaction, which might be needed for B_2pin_2 activation [30,31]. The reaction did not proceed in the absence of base. Furthermore, the cation of the base was found to be crucial, sodium salts are much better than potassium or lithium salts. Additionally, NaO^{t}Bu gives better results than other sodium bases, such as NaOMe, NaOEt, sodium isopropoxide (NaO^{i}Pr), and sodium trimethylsilanolate (NaOTMS). Increasing or decreasing the loading of NaO^{t}Bu, decreased the yield of *gem*-diborylmethane.

After extensive optimization of the hydride sources and bases, we then investigated the influence of catalytic system (Table 3). In the absence of rhodium catalysts, no *gem*-diborylmethane was detected. Without a phosphine ligand, the reaction proceeded but in lower yield. Ligands increase the yield of *gem*-diborylmethane and monophosphines are better than Xantphos, while relatively electron-poor ligands exhibit better results. Different rhodium catalysts were also tested. [Rh(*cod*)Cl]$_2$ and [Rh(CO)$_2$Cl]$_2$ showed the same performance, and gave better results than the other rhodium catalysts such as [Rh(*cod*)OH]$_2$, RhCl$_3$, and [Rh(OAc)$_2$]$_2$. Cu-NHC species are widely employed as the catalyst in borylation or hydroborylation of unsaturated compounds, including reduction of CO$_2$ to CO. [32–34] Replacement of [Rh(*cod*)Cl]$_2$ by 10 mol% (IPr)CuCl, gave no *gem*-diborylmethane. The reaction pathway is not clear yet. From our control experiments, we could confirm the formation of BpinOBpin and tBuOBpin. Based on our knowledge, we speculate that Bpin(*CO*)Bpin is produced initially and then reduced with silane acting as the reductant [35].

In conclusion, we developed a rhodium-catalyzed reduction of CO with bis(pinacolato)diboron, B_2pin_2. Under atmospheric pressure of CO, B_2pin_2 can react with CO to give *gem*-diborylmethane in the presence of [Rh(*cod*)Cl]$_2$/PPh$_3$ catalytic system, employing diethoxymethylsilane as the hydride source and sodium *tert*-butoxide as the base. This is the first catalytic transition metal-catalyzed borylation of CO to a highly borylated C$_1$ compound. Although the yield of the *gem*-diborylmethane and the TON of the reaction are still relatively low, we believe it provides a

Table 1

Investigation of hydride sources for the borylation of CO.[a]

entry	hydride source	TON[b]	product (mmol)[b]	yield[b]
1	$(EtO)_2MeSiH$	2.4	0.0115	3.8%
2	–	–	–	–
3	HBpin (0.4 mmol)	trace	trace	trace
4	$BH_3 \cdot THF$ (0.2 mmol)	1.8	0.0086	2.9%
5	$NaBH_4$ (0.2 mmol)	trace	trace	trace
6	EtOH (0.4 mmol)	trace	trace	trace
7	^iPrOH (0.4 mmol)	trace	trace	trace
8	H_2 (5 bar)	–	–	–
9[c]	$(EtO)_2MeSiH$	6.7	0.0322	10.7%
10[d]	$(EtO)_2MeSiH$	4.6	0.0221	7.4%
11[e]	$(EtO)_2MeSiH$	–	–	–
12[f]	$(EtO)_2MeSiH$	trace	trace	trace

[a] Reaction conditions: [Rh(*cod*)Cl]$_2$ (1.6 mol%; 0.0048 mmol), PPh$_3$ (6.4 mol%; 0.0192 mmol), B$_2$pin$_2$ (0.3 mmol), NaO^{t}Bu (0.26 mmol), (EtO)$_2$MeSiH (0.4 mmol), toluene (2 mL), CO (1 bar), 100 °C, 12 h. [b]Determined by GC using hexadecane as the internal standard, and yields were calculated based on B$_2$pin$_2$. [c]PhB(OH)$_2$ (0.2 mmol) as additive. [d]MeB(OH)$_2$ (0.2 mmol) as additive. [e]B(OH)$_3$ (0.2 mmol) as additive. [f]B$_2$(OH)$_4$ (0.2 mmol) as additive.

Table 2

Silanes and bases screening.[a]

entry	base	silane	TON[b]	product (mmol)[b]	yield[b]
1	NaO^{t}Bu	$(EtO)_3SiH$	2.6	0.0125	4.2%
2	NaO^{t}Bu	$(EtO)_2MeSiH$	5.0	0.024	8%
3	NaO^{t}Bu	Et_3SiH	trace	trace	trace
4	NaO^{t}Bu	Ph_2SiH_2	2.8	0.0134	4.5%
5	NaO^{t}Bu	$MePh_2SiH$	trace	trace	trace
6	NaO^{t}Bu	PMHS	3.0	0.0144	4.8%
7[c]	NaO^{t}Bu	$(EtO)_2MeSiH$	3.3	0.0158	5.3%
8[d]	NaO^{t}Bu	$(EtO)_2MeSiH$	3.5	0.0168	5.6%
9	–	$(EtO)_2MeSiH$	–	–	–
10	LiO^{t}Bu	$(EtO)_2MeSiH$	–	–	–
11	KO^{t}Bu	$(EtO)_2MeSiH$	trace	trace	trace
12	NaOMe	$(EtO)_2MeSiH$	2.8	0.0134	4.5%
13	NaOEt	$(EtO)_2MeSiH$	3.8	0.0182	6.1%
14	NaO^{i}Pr	$(EtO)_2MeSiH$	4.5	0.0216	7.2%
15	NaOTMS	$(EtO)_2MeSiH$	3.6	0.0173	5.8%

[a] Reaction conditions: [Rh(*cod*)Cl]$_2$ (1.6 mol%; 0.0048 mmol), PPh$_3$ (6.4 mol%; 0.0192 mmol), B$_2$pin$_2$ (0.3 mmol), NaO^{t}Bu (0.26 mmol), (EtO)$_2$MeSiH (0.4 mmol), PhB(OH)$_2$ (0.2 mmol), toluene (2 mL), CO (1 bar), 100 °C, 12 h. [b]Determined by GC using hexadecane as the internal standard, and yields were calculated based on B$_2$pin$_2$. [c](EtO)$_2$MeSiH (0.6 mmol), [d](EtO)$_2$MeSiH (0.8 mmol).

new possibility for the reduction of carbon monoxide and transforming toxic, difficult to handle gaseous CO into a stable and solid C$_1$ building block.

Credit author statement

X.W. directed the project and revised the manuscript. J.X.X. and F.P. W. performed all the experiments and prepared the manuscript.

Declaration of Competing Interest

There are no conflicts to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.catcom.2020.106205.

Table 3
The effect of catalysts system.[a]

	catalyst	ligand	TON[b]	product (mmol)[b]	yield[b]
1	–	–	–	–	–
2	[Rh(cod)Cl]$_2$	–	3.6	0.0173	5.8%
3	[Rh(cod)Cl]$_2$	PPh$_3$	6.7	0.0322	10.7%
4	[Rh(cod)Cl]$_2$	PCy$_3$	5.2	0.0250	8.3%
5	[Rh(cod)Cl]$_2$	PtBu$_3$HBF$_4$	3.8	0.0182	6.1%
6	[Rh(cod)Cl]$_2$	Ph$_2$PPy	5.7	0.0274	9.1%
7[c]	[Rh(cod)Cl]$_2$	XantPhos	4.1	0.0197	6.6%
8[c]	[Rh(cod)Cl]$_2$	IPr·HCl	4.2	0.0202	6.7%
9	[Rh(cod)OH]$_2$	PPh$_3$	4.4	0.0211	7.0%
10	RhCl$_3$	PPh$_3$	5.6	0.0269	9.0%
11	[Rh(OAc)$_2$]$_2$	PPh$_3$	6.0	0.0288	9.6%
12	[Rh(CO)$_2$Cl]$_2$	PPh$_3$	6.5	0.0312	10.4%
13[d]	[Rh(cod)Cl]$_2$	PPh$_3$	3.3	0.0079	2.6%
14	(IPr)CuCl	–	–	–	–

[a] Reaction conditions: [Rh(*cod*)Cl]$_2$ (1.6 mol%; 0.0048 mmol), PPh$_3$ (6.4 mol%; 0.0192 mmol), B$_2$pin$_2$ (0.3 mmol), NaO^{t}Bu (0.26 mmol), (EtO)$_2$MeSiH (0.4 mmol), PhB(OH)$_2$ (0.2 mmol), toluene (2 mL), CO (1 bar), 100 °C, 12 h. [b]Determined by GC using hexadecane as the internal standard, and yields were calculated based on B$_2$pin$_2$. [c]3.2 mol% of ligand. [d][Rh(*cod*)Cl]$_2$ (0.8 mol%; 0.0024 mmol), PPh$_3$ (3.2 mol%; 0.0096 mmol). Ph$_2$PPy = diphenyl-2-pyridylphosphine; XantPhos = 4,5-bis (diphenylphosphino)-9,9-dimethylxanthene; IPr·HCl = 1,3-bis-(2,6-diisopropylphenyl) imidazolinium chloride. Cod = 1,5-cyclooctadiene.

References

[1] Z. Yin, J.-X. Xu, X.-F. Wu, ACS Catal. 10 (2020) 6510–6531.
[2] N.M. West, A.J.M. Miller, J.A. Labinger, J.E. Bercaw, Coord. Chem. Rev. 255 (2011) 881–898.
[3] R.L. Miller, P.T. Wolczanski, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 10422–10423.
[4] T. Matsuo, H. Kawaguchi, J. Am. Chem. Soc. 127 (2005) 17198–17199.
[5] Z. Jian, G. Kehr, C.G. Daniliuc, B. Wibbeling, T. Wiegand, M. Siedow, H. Eckert, M. Bursch, S. Grimme, G. Erker, J. Am. Chem. Soc. 139 (2017) 6474–6483.
[6] J.A. Buss, G.A. Bailey, J. Oppenheim, D.G. VanderVelde, W.A. Goddard, T. Agapie, J. Am. Chem. Soc. 141 (2019) 15664–15674.
[7] S. Yadav, S. Saha, S.S. Sen, ChemCatChem 8 (2016) 486–501.
[8] M.D. Anker, C.E. Kefalidis, Y. Yang, J. Fang, M.S. Hill, M.F. Mahon, L. Maron, J. Am. Chem. Soc. 139 (2017) 10036–10054.
[9] A. Heilmann, J. Hicks, P. Vasko, J.M. Goicoechea, S. Aldridge, Angew. Chem. Int. Ed. 59 (2020) 4897–4901.
[10] M.-A. Légaré, C. Pranckevicius, H. Braunschweig, Chem. Rev. 119 (2019) 8231–8261.
[11] T. Wang, G. Kehr, C.G. Daniliuc, G. Erker, Organometallics 37 (2018) 1040–1049.
[12] Y. Katsuma, N. Tsukahara, L. Wu, Z. Lin, M. Yamashita, Angew. Chem. Int. Ed. 57 (2018) 6109–6114.
[13] A. Phanopoulos, S. Pal, T. Kawakami, K. Nozaki, J. Am. Chem. Soc. 142 (2020) 14064–14068.
[14] M. Majumdar, I. Omlor, C.B. Yildiz, A. Azizoglu, V. Huch, D. Scheschkewitz, Angew. Chem. Int. Ed. 54 (2015) 8746–8750.
[15] Y. Wang, A. Kostenko, T.J. Hadlington, M.-P. Luecke, S. Yao, M. Driess, J. Am. Chem. Soc. 141 (2019) 626–634.
[16] X. Wang, Z. Zhu, Y. Peng, H. Lei, J.C. Fettinger, P.P. Power, J. Am. Chem. Soc. 131 (2009) 6912–6913.
[17] H.C. Brown, T.M. Ford, J.L. Hubbard, J. Org. Chem. 45 (1980) 4067–4068.
[18] M. Yalpani, R. Köster, J. Organomet. Chem. 434 (1992) 133–141.
[19] R. Dobrovetsky, D.W. Stephan, J. Am. Chem. Soc. 135 (2013) 4974–4977.
[20] M. Sajid, L.-M. Elmer, C. Rosorius, C.G. Daniliuc, S. Grimme, G. Kehr, G. Erker, Angew. Chem. Int. Ed. 52 (2013) 2243–2246.
[21] J. Teichmann, H. Stock, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. (1998) 459–463.
[22] H. Braunschweig, T. Dellermann, R.D. Dewhurst, W.C. Ewing, K. Hammond, J.O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A.K. Phukan, A. Vargas, Nat. Chem. 5 (2013) 1025–1028.
[23] A.S. Batsanov, J.A. Cabeza, M.G. Crestani, M.R. Fructos, P. García-Álvarez, M. Gille, Z. Lin, T.B. Marder, Angew. Chem. Int. Ed. 55 (2016) 4707–4710.
[24] R. Nallagonda, K. Padala, A. Masarwa, Org. Biomol. Chem. 16 (2018) 1050–1064.
[25] N. Miralles, R.J. Maza, E. Fernández, Adv. Synth. Catal. 360 (2018) 1306–1327.
[26] H.A. Ali, I. Goldberg, M. Srebnik, Organometallics 20 (2001) 3962–3965.
[27] S.K. Bose, S. Brand, H.O. Omoregie, M. Haehnel, J. Maier, G. Bringmann, T. B. Marder, ACS Catal. 6 (12) (2016) 8332–8335.
[28] A.K. Cook, S.D. Schimler, A.J. Matzger, M.S. Sanford, Science 351 (2016) 1421–1424.
[29] K.T. Smith, S. Berritt, M. González-Moreiras, S. Ahn, M.R. Smith III, M.-H. Baik, D. J. Mindiola, Science 351 (2016) 1424–1427.
[30] S. Pietsch, E.C. Neeve, D.C. Apperley, R. Bertermann, F. Mo, D. Qiu, M.S. Cheung, L. Dang, J. Wang, U. Radius, Z. Lin, C. Kleeberg, T.B. Marder, Chem. Eur. J. 21 (2015) 7082–7099.
[31] R.D. Dewhurst, E.C. Neeve, H. Braunschweig, T.B. Marder, Chem. Commun. 51 (2015) 9594–9607.
[32] D.S. Laitar, P. Müller, J.P. Sadighi, J. Am. Chem. Soc. 127 (2005) 17196–17197.
[33] H. Zhao, Z. Lin, T.B. Marder, J. Am. Chem. Soc. 128 (2006) 15637–15643.
[34] C. Kleeberg, M.S. Cheung, Z. Lin, T.B. Marder, J. Am. Chem. Soc. 133 (2011) 19060–19063.
[35] F.-P. Wu, X. Luo, U. Radius, T.B. Marder, X.-F. Wu, J. Am. Chem. Soc. 142 (2020) 14074–14079.