Borylation

Deutsche Ausgabe: DOI: 10.1002/ange.201601121
Internationale Ausgabe: DOI: 10.1002/anie.201601121

Fully Borylated Methane and Ethane by Ruthenium-Mediated Cleavage and Coupling of CO

Andrei S. Batsanov, Javier A. Cabeza, Marco G. Crestani, Manuel R. Fructos, Pablo García-Álvarez, Marie Gille, Zhenyang Lin, and Todd B. Marder**

***Abstract:** Many transition-metal complexes and some metal-free compounds are able to bind carbon monoxide, a molecule which has the strongest chemical bond in nature. However, very few of them have been shown to induce the cleavage of its C−O bond and even fewer are those that are able to transform CO into organic reagents with potential in organic synthesis. This work shows that bis(pinacolato)diboron, B_2pin_2, reacts with ruthenium carbonyl to give metallic complexes containing borylmethylidyne (CBpin) and diborylethyne (pinBC≡CBpin) ligands and also metal-free perborylated C_1 and C_2 products, such as $C(Bpin)_4$ and $C_2(Bpin)_6$, respectively, which have great potential as building blocks for Suzuki–Miyaura cross-coupling and other reactions. The use of ^{13}CO-enriched ruthenium carbonyl has demonstrated that the boron-bound carbon atoms of all of these reaction products arise from CO ligands.*

The strongest chemical bond in nature is that of carbon monoxide, which has a dissociation energy of 1076 kJ mol^{-1} at 298 K. The robustness of this triple bond has a key influence on the chemistry of this simple molecule.

Although carbon monoxide is inexpensive and readily available, the synthetic chemical industry only uses it as a feedstock in very few processes, such as the water-gas shift reaction (synthesis of CO_2 and H_2 from CO and water), the hydroformylation of olefins, the preparation of phosgene, methanol, and acetic acid, and the Fischer–Tropsch synthesis of hydrocarbons (hydrogenation of CO).[1] Among these industrial processes, the latter is the only one in which the C−O bond of carbon monoxide is cleaved.

From the point of view of fundamental research, the cleavage of CO under mild reaction conditions has long been an attractive challenge because it could provide new ways of transforming CO into highly functionalized C_1, C_2, and C_n molecules. To date, apart from some ruthenium and osmium carbonyl clusters, which are able to transform two CO ligands into CO_2 and a carbide ligand,[2,3] only a handful of transition-metal complexes are known to cleave CO ligands with[4–6] or without[7–16] the help of other reagents. These reactions have, in some cases, afforded metal-free CO-derived organic products,[4–6,13,16] but all these products are hydrocarbons.

In contrast, it has recently been shown that some reagents of low-valent p-block elements are able to activate free or metal-coordinated CO. Regarding boron-containing reagents, Stephan and co-workers and Erker and co-workers have reported that some frustrated Lewis pairs promote the reduction of CO with either hydrogen[17] or $HB(C_6F_5)_2$,[18,19] Siebert and co-workers have reported the insertion of CO into a cyclic diborane,[20] and Braunschweig and co-workers have reported the coupling of CO at a boron–boron triple bond[21] and at a metal–boron double bond.[22] By using other p-block elements, we note that CO can be reduced by certain singlet carbenes[23] and transient triplet carbenes,[24] a germylene compound can couple two CO units head-to-head,[25,26] and CO and N_2 can react on a hafnium complex to give an oxamide precursor.[27]

We now report that, by studying the reactivity of the diborane(4) compound B_2pin_2 (pin = pinacolato) with ruthenium carbonyl, we have discovered that the C−O bond of coordinated CO can be cleaved by borylation with B_2pin_2 to give metallic complexes containing borylmethylidyne (CBpin) and diborylethyne (pinBC≡CBpin) ligands and also perborylated metal-free C_1 and C_2 products, that is, $C(Bpin)_4$ and $C_2(Bpin)_6$, respectively, which have a great potential in organic synthesis as highly functionalizable C_1 and C_2 building blocks for Suzuki–Miyaura C−C bond coupling and other reactions.[28–31]

Reactions of $[Ru_3(CO)_{12}]$ with excess B_2pin_2 in octane at 130 °C led to dark-red solutions which contained mixtures of products (experimental details and characterization data are given in the Supporting Information). Preparative column and/or thin-layer chromatography allowed the isolation of three novel tetraruthenium clusters, namely, $[Ru_4(\mu\text{-}\kappa^1O\text{-}OBpin)(\mu_4\text{-}\kappa^1C\text{-}CBpin)(CO)_{12}]$ (**1**), $[Ru_4(\mu\text{-}H)(\mu_4\text{-}\kappa^1C\text{-}CBpin)(CO)_{12}]$ (**2**), and $[Ru_4\{\mu_4\text{-}\kappa^2C,C\text{-}C_2(Bpin)_2\}(CO)_{12}]$ (**3**; Figure 1), in yields (5–35 %) which depended upon the concentration of the reagents and the (trace) water content

---

[*] Prof. Dr. J. A. Cabeza, Dr. P. García-Álvarez, Dr. M. Gille
Departamento de Química Orgánica e Inorgánica-IUQOEM
Centro de Innovación en Química Avanzada (ORFEO-CINQA)
Universidad de Oviedo-CSIC, 33071 Oviedo (Spain)
E-mail: jac@uniovi.es

Dr. A. S. Batsanov, Dr. M. G. Crestani, Dr. M. R. Fructos,
Prof. Dr. T. B. Marder
Department of Chemistry, Durham University
South Road, Durham DH1 3LE (UK)

Prof. Z. Lin
The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong (P.R. China)

Prof. Dr. T. B. Marder
Current address:
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: todd.marder@uni-wuerzburg.de

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201601121.

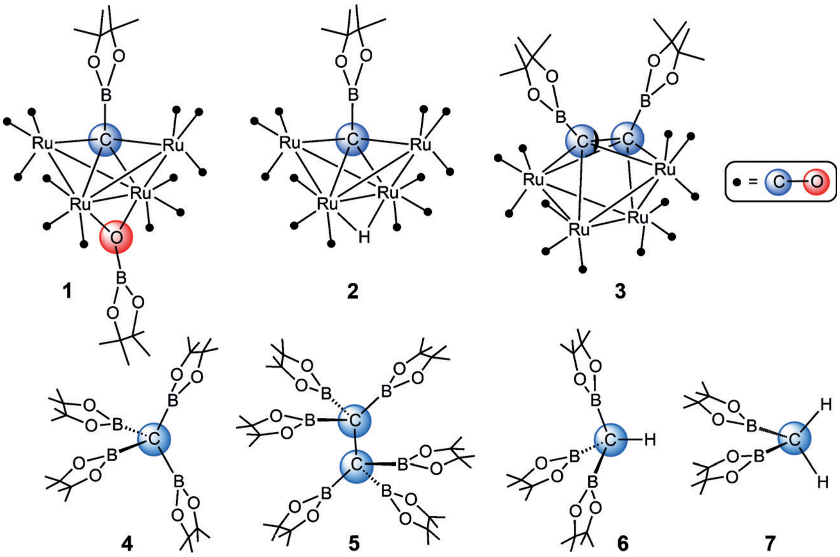

Figure 1. Carbon-borylated ruthenium clusters (**1**–**3**) and metal-free carbon-borylated products (**4**–**7**) isolated from the reaction of $[Ru_3(CO)_{12}]$ with B_2pin_2.

of the solvent. Two clusters of higher nuclearity, $[Ru_5(\mu_5\text{-}C)(CO)_{12}]$[32] and $[Ru_6(\mu_6\text{-}C)(CO)_{17}]$,[33] which are known to arise from the thermolysis of $[Ru_3(CO)_{12}]$, were also formed in these reactions in small amounts (< 6 %).

The structures of compounds **1**–**3**, shown in Figure 1, were determined by X-ray diffraction[42] (see the Supporting Information). They all are tetranuclear, have a common butterfly-type metallic skeleton, and are stabilized by twelve terminal CO ligands, but they differ in their bridging ligands. While **1** contains a quadruply-bridging borylated methylidyne ligand (CBpin) and an edge-bridging oxoboryl ligand (OBpin), **2** can be described as resulting from the formal substitution of a hydride for the edge-bridging OBpin ligand of **1**. Remarkably, **3** possesses a diborylated alkyne ligand, pinBC≡CBpin, thus forming part of a distorted C_2Ru_4 octahedron. Metallic clusters containing borylated alkylidyne ligands are rare, with the iron compounds $[Fe_4(\mu\text{-}H)(\mu_4\text{-}\kappa^1C\text{-}BXY)(CO)_{12}]$ (X = Y = H, Cl, Br; X = H, Y = Cl, Br, OH)[34,35] being the closest to **1** and **2**, but they are formed by borylation of carbon–halogen bonds. Although diborylated alkynes are known,[36] they have never been prepared from CO and their coordination to transition metals has been hitherto observed only in the dicobalt complex $[Co_2\{\mu\text{-}\kappa^2C,C\text{-}C_2(Bcat)_2\}(CO)_6]$ (cat = catecholato).[37] The ^{13}C NMR signals of the ruthenium-bound carbon atoms of the CBpin fragments of **1**–**3** ($\delta = 303.8$, 275.9, and 180.2 ppm, respectively) were only observed in samples prepared using 60 % ^{13}CO-enriched ruthenium carbonyl as a starting material. This fact unequivocally demonstrates that the ruthenium-bound carbon atoms of the CBpin fragments of **1**–**3** arise from CO groups. A reaction carried out in the presence of 75 % ^{18}O-enriched water helped determine that the ruthenium-bound oxygen atom of the OBpin ligand in **1** does not arise from water, because the mass spectra of samples of this compound prepared with and without ^{18}O-enriched water are identical. Therefore, the CBpin and OBpin fragments of **1**–**3** arise from CO ligands.

The formation of carbide ligands (and CO_2) from coordinated CO is well known in transition-metal carbonyl cluster chemistry and proceeds by thermal activation,[2] but we do not think that **1**–**3** arise from reactions of B_2pin_2 with carbide cluster intermediates because this proposal does not explain the formation of the OBpin fragment of **1** (which is the major reaction product), and because we have experimentally checked that the treatment of $[Ru_5(\mu_5\text{-}C)(CO)_{12}]$ with an excess of B_2pin_2 in octane at 130 °C does not lead to **1**–**3**. In fact, we believe that the mechanism of the carbonyl C−O activation process which leads to **1**–**3** may be similar to that proposed for the synthesis of the tetrairon cluster $[Fe_4(\mu\text{-}H)(\mu_4\text{-}\kappa^1C\text{-}CAuPh_3)(CO)_{12}]$, and involves intermediates having κ^2C,O-coordinated CO ligands which are prone to suffer C−O bond activation in the presence of Lewis acids[38] (B_2pin_2 in our case).

With the aim of shedding light on the origin of the hydride ligand of **2**, we treated **1** with a small amount of D_2O in octane at 130 °C, but no reaction occurred. However, an analogous reaction carried out in the presence of B_2pin_2 allowed the isolation of $[Ru_4(\mu\text{-}D)(\mu_4\text{-}\kappa^1C\text{-}CBpin)(CO)_{12}]$, while $(pinB)_2O$ was detected in the resulting solution by GC/MS analysis. Therefore, **2** arises from **1** and its formation requires the presence of both water and B_2pin_2. While moisture is the source of the hydride ligand of **2**, the role of the additional B_2pin_2 should be the abstraction of the OBpin ligand from **1**.

The generation of the diborylated acetylene ligand of **3**, which formally arises from the coupling of two CBpin units on an undetected intermediate, represents a remarkable example of reductive coupling and deoxygenation of CO ligands. Although some boron-[21] and metal-mediated (see citations in Ref. [20]) reductive couplings of two or more CO ligands have already been reported, oxygen-free coupled products are formed only when strong reducing conditions are used,[5,6,8,12,13] but this is not the case in our system. For example, the reductive coupling of the two pairs of carbonyl ligands of the cluster $[Fe_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}CO)_4]$, to form the bis(acetylene) derivative $[Fe_4(\eta^5\text{-}C_5H_5)_4(\mu_4\text{-}C_2H_2)_2]$, is only achieved when a large excess of $LiAlH_4$ is used.[12]

The results described above confirm the ability of B_2pin_2 to convert coordinated CO into three different types of ligands, namely, borylalkylidyne, boryloxo, and diborylalkyne, but these already significant findings were surpassed when the crude reaction solutions from the treatment of $[Ru_3(CO)_{12}]$ with B_2pin_2 were analyzed by GC/MS and NMR spectroscopy (see the Supporting Information). These analyses indicated that the cluster complexes described above were accompanied by $O(Bpin)_2$ and by small amounts of various metal-free C-borylated products, namely, $C(Bpin)_4$ (**4**), $C_2(Bpin)_6$ (**5**), $HC(Bpin)_3$ (**6**), and $H_2C(Bpin)_2$ (**7**; Figure 1; individual spectroscopic yields of < 5 % are based on initial B_2pin_2). To establish unequivocally their nature, they were isolated by preparative HPLC and characterized by standard analytical methods. We also determined the molecular structures of **4** and **5** by single-crystal X-ray diffraction (see the Supporting Information).[42] Compounds **4** and **6** have been previously prepared in several steps by borylation of CCl_4 or $CHCl_3$,[30,31] and compound **7** by treating B_2pin_2 with diazomethane in the presence of $[Pt(PPh_3)_4]$.[39] Compound **5** is a novel product, although a platinum-catalyzed double diboration of the alkyne $C_2(Bcat)_2$ with B_2cat_2 has been reported to afford the Bcat analogue of **5**, $C_2(Bcat)_6$.[40]

Isotopic-labelling experiments (see the Supporting Information) were used to determine the origin of the boron-bound carbon atoms of **4**–**7** and the carbon-bound hydrogen atoms of **6** and **7**. The use of ^{13}CO-enriched $[Ru_3(CO)_{12}]$ helped establish that the former arise from CO ligands of $[Ru_3(CO)_{12}]$ (^{13}C-enriched **4**–**7** were obtained), while the addition of D_2O to the initial reaction mixture led to the deuterium-labelled compounds $DC(Bpin)_3$ and $D_2C(Bpin)_2$, thus confirming that water is the source of the carbon-bound hydrogen atoms of **6** and **7**.

The use of small amounts of solvent in the reactions (concentrated solutions) increased the yields of **1**, **3**, **4**, and **5**, while diluted solutions favored the formation of **2**, **6**, and **7**. This observation not only supports that hydrolytic processes participate in the synthesis of **2**, **6**, and **7** (the more dilute the reaction solution the greater the water/reactants ratio), but also demonstrates that, when working on a small scale, residual water from "dry solvent" and/or from the glassware surface allows the formation of hydrolyzed products. In fact, the amount of water necessary to make 26 mg (0.030 mmol) of **2** is only 0.27 μL.

The participation of the borylated clusters **1**–**3** in the synthesis of the metal-free products **4**–**7** is not yet clear because only small amounts of **6** and **7** (but not **4** and **5**) were detected by GC/MS in the reaction solutions obtained by treating **1**–**3** with B_2pin_2 in octane at 130 °C. However, the low concentration of the starting clusters may favor the formation of the hydrolysis-derived products **6** and **7**.

In summary, this work has shown that a combination of a diborane(4) reagent, B_2pin_2, with a transition-metal carbonyl complex, $[Ru_3(CO)_{12}]$, can promote the cleavage and reductive coupling of coordinated CO, in the absence of strong reducing conditions, to give metal complexes containing borylmethylidyne (CBpin) and diborylethyne ($pinBC{\equiv}CBpin$) ligands, and also metal-free perborylated products, such as $C(Bpin)_4$ and $C_2(Bpin)_6$. Considering the relevant role that borylated compounds play in modern organic synthesis,[28,29,41] the discovery that CO ligands can be transformed into highly borylated C_1 and C_2 organic chemicals (such as **4**–**7**, which contain up to six C–B bonds) is of great importance, thereby suggesting that the possibility of using CO as a carbon feedstock to prepare borylated, and subsequently other highly functionalized organic products, may not be very far away.

Acknowledgments

This work was supported by MINECO-FEDER (grants CTQ2010-14933 and DELACIERVA-09-05) and the European Union (Marie Curie action FP7-2010-RG-268329 and Erasmus Programme). We thank NetChem Inc. and AllyChem Co. Ltd. for gifts of diboron reagents and Dr. D. S. Yufit for assistance with one of the X-ray structures.

Keywords: boron · borylation · carbon monoxide · cluster compounds · ruthenium

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4707–4710
Angew. Chem. **2016**, *128*, 4785–4788

---

[1] Wikipedia, the free encyclopedia: *Carbon Monoxide*, http://en.wikipedia.org/wiki/Carbon_monoxide.
[2] *The Chemistry of Metal Cluster Complexes* (Eds.: D. F. Shriver, H. D. Kaesz, R. D. Adams), VCH, Weinheim, **1990**.
[3] P. J. Bailey, B. F. G. Johnson, J. Lewis, *Inorg. Chim. Acta* **1994**, *227*, 197–200.
[4] P. A. Belmonte, F. G. N. Cloke, R. R. Schrock, *J. Am. Chem. Soc.* **1983**, *105*, 2643–2650.
[5] T. Matsuo, H. Kawaguchi, *J. Am. Chem. Soc.* **2005**, *127*, 17198–17199.
[6] A. Wong, J. D. Atwood, *J. Organomet. Chem.* **1980**, *199*, C9–C12.
[7] R. Toreki, R. E. Lapointe, P. T. Wolczanski, *J. Am. Chem. Soc.* **1987**, *109*, 7558–7560.
[8] D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. VanDuyne, P. T. Wolczanski, *J. Am. Chem. Soc.* **1989**, *111*, 9056–9072.
[9] M. H. Chisholm, C. E. Hammond, V. J. Johnston, W. E. Streib, J. C. Huffman, *J. Am. Chem. Soc.* **1992**, *114*, 7056–7065.
[10] R. L. Miller, R. Toreki, R. E. LaPointe, P. T. Wolczanski, G. D. Van Duyne, D. C. Roe, *J. Am. Chem. Soc.* **1993**, *115*, 5570–5588.
[11] R. L. Miller, P. T. Wolczanski, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 10422–10423.
[12] M. Okazaki, T. Ohtani, S. Inomata, N. Takagi, H. Ogino, *J. Am. Chem. Soc.* **1998**, *120*, 9135–9138.
[13] T. Shima, Z. Hou, *J. Am. Chem. Soc.* **2006**, *128*, 8124–8125.
[14] G. Christian, R. Stranger, S. Petrie, B. F. Yates, C. C. Cummins, *Chem. Eur. J.* **2007**, *13*, 4264–4272.
[15] D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 10553–10564.
[16] J. Ballmann, F. Pick, L. Castro, M. D. Fryzuk, L. Maron, *Organometallics* **2012**, *31*, 8516–8524.
[17] R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 4974–4977.
[18] M. Sajid, L. M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2013**, *52*, 2243–2246; *Angew. Chem.* **2013**, *125*, 2299–2302.
[19] M. Sajid, G. Kehr, C. G. Daniliuc, G. Erker, *Angew. Chem. Int. Ed.* **2014**, *53*, 1118–1121; *Angew. Chem.* **2014**, *126*, 1136–1139.
[20] J. Teichmann, H. Stock, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 459–463.
[21] H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jiménez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan, A. Vargas, *Nat. Chem.* **2013**, *5*, 1025–1028.
[22] H. Braunschweig, K. Radacki, R. Shang, C. W. Tate, *Angew. Chem. Int. Ed.* **2013**, *52*, 729–733; *Angew. Chem.* **2013**, *125*, 757–761.
[23] W. Sander, G. Bucher, S. Wierlacher, *Chem. Rev.* **1993**, *93*, 1583–1621.
[24] V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2006**, *45*, 3488–3491; *Angew. Chem.* **2006**, *118*, 3568–3571.
[25] X. Wang, Z. Zhu, Y. Peng, H. Lei, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 6912–6913.
[26] Z. D. Brown, P. P. Power, *Inorg. Chem.* **2013**, *52*, 6248–6259.

[27] D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *Nat. Chem.* **2010**, *2*, 30 – 35.

[28] H. Doucet, *Eur. J. Org. Chem.* **2008**, 2013 – 2030.

[29] *Boronic Acids: Preparation and Applications in Organic Synthesis Medicine and Materials*, 2nd ed. (Ed.: D. G. Hall), VCH, Weinheim, **2011**.

[30] D. S. Matteson, R. A. Davis, L. A. Hagelee, *J. Organomet. Chem.* **1974**, *69*, 45 – 51.

[31] D. S. Matteson, *Synthesis* **1975**, 147 – 158.

[32] D. H. Farrar, P. F. Jackson, B. F. G. Johnson, J. Lewis, J. N. Nicholls, M. McPartlin, *J. Chem. Soc. Chem. Commun.* **1981**, 415 – 416.

[33] R. Mason, W. R. Robinson, *Chem. Commun.* **1968**, 468 – 469.

[34] X. Meng, N. P. Rath, T. P. Fehlner, *J. Am. Chem. Soc.* **1989**, *111*, 3422 – 3423.

[35] X. Meng, N. P. Rath, T. P. Fehlner, A. L. Rheingold, *Organometallics* **1991**, *10*, 1986 – 1993.

[36] H. Schulz, G. Gabbert, H. Pritzkow, W. Siebert, *Chem. Ber.* **1993**, *126*, 1593 – 1995.

[37] C. Ester, A. Maderna, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2000**, 1177 – 1184.

[38] C. P. Horwitz, D. F. Shriver, *J. Am. Chem. Soc.* **1985**, *107*, 8147 – 8153.

[39] H. A. Ali, I. Goldberg, M. Srebnik, *Organometallics* **2001**, *20*, 3962 – 3965.

[40] M. Bluhm, A. Maderna, H. Pritzkow, S. Bethke, R. Gleiter, W. Siebert, *Eur. J. Inorg. Chem.* **1999**, 1693 – 1700.

[41] I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890 – 931.

[42] CCDC 883149 (**α-1**), 1005685 (**β-1**), 883150 (**2**), 1005745 (**2′**), 883151 (**3**), 883152 (**4**), 883153 (**5**), and 1005710 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: January 31, 2016