Inorganic Chemistry Communications 13 (2010) 1396–1398

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Catalytic hydroboration of vinylarenes using a zwitterionic arylspiroboronate ester iridium complex

Jennifer A. Melanson [a], Christopher M. Vogels [a], Andreas Decken [b], Stephen A. Westcott [a,*]

[a] *Department of Chemistry and Biochemistry, Mount Allison University, Sackville, New Brunswick, E4L 1G8, Canada*
[b] *Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada*

ARTICLE INFO

Article history:
Received 16 April 2010
Accepted 31 July 2010
Available online 7 August 2010

Keywords:
Arylspiroboronate ester
Catalysis
Hydroboration
Regioselectivity
Zwitterion

ABSTRACT

Addition of B_2cat_3 (cat = 1,2-$O_2C_6H_4$) to Ir(acac)(dppb) (**1**; where dppb = 1,4-bis(diphenylphosphino)butane) gave the novel arylspiroboronate ester iridium complex Ir(η^6-catBcat)(dppb) (**2**), the first example of an iridium compound containing a coordinating $[Bcat_2]^-$ anion. Complex **2** is a remarkably selective catalyst precursor for the hydroboration of unhindered vinylarenes using pinacolborane.

The addition of boranes to unsaturated organic molecules has become a remarkably important synthetic methodology in organic synthesis [1]. Although $H_3B{\cdot}X$ (X = THF, SMe_2) adds readily to alkenes at –80 °C [2], other hydroboration reagents, such as diorganyloxyboranes, are slow to react even at room temperature. For instance, catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) and pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$) add to alkenes and alkynes only at elevated temperatures [3] or in the presence of a transition metal catalyst [4].

A considerable amount of research has focused on investigating the mechanism and scope of the catalyzed hydroboration reaction [5]. Although a number of transition metals have been found to catalyze hydroborations with HBcat and HBpin, reactions using rhodium complexes are usually the most effective for reactions with alkenes. For instance, phosphinorhodium acetylacetonato complexes are remarkably active catalyst precursors for the hydroboration of a wide range of vinylarenes ($ArCH{=}CH_2$) using HBcat, giving selective formation of the unusual branched products, $ArCH(Bcat)CH_3$ [6]. The catalyst resting states in these systems are believed to be the zwitterionic complexes of the type Rh(η^6-catBcat)(P_2) (P_2 = diphosphine), arising from the redistribution of borane substituents [7]. The unusual arylspiroboronate ester $[Bcat_2]^-$ is bound to the rhodium fragment via all six carbons of one of the catecholato rings.

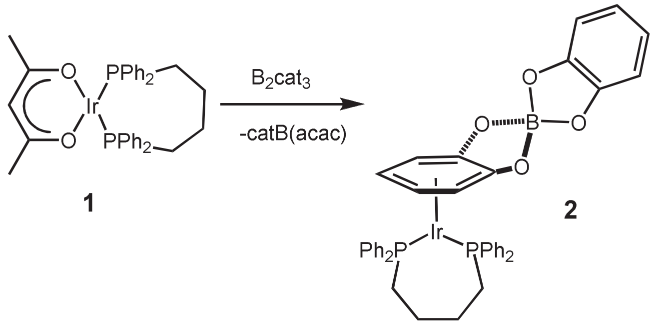
Recently, there has also been considerable interest in the use of iridium complexes in an effort to expand the scope of these catalyzed hydroborations [8–15]. With this is mind, we have found that addition of B_2cat_3 [16] to Ir(acac)(dppb) (**1**; where dppb = 1,4-bis(diphenylphosphino)butane) [17] gave the novel arylspiroboronate ester iridium complex Ir(η^6-catBcat)(dppb) (**2**) in 68% yield (Scheme 1) [18]. While rhodium compounds containing arylspiroboronate esters are well documented [19], and the ruthenium complex RuH(η^6-catBcat)$(PCy_3)_2$ has been prepared by the addition of HBcat to $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ [20], complex **2** represents, to the best of our knowledge, the first example of an iridium compound containing a coordinating $[Bcat_2]^-$ anion. Complex **2** has been characterized by a number of physical methods, including multinuclear NMR spectroscopy. The $^{11}B\{^1H\}$ NMR spectrum shows a sharp singlet at δ 13.6 ppm for the four coordinate boron anion [21] and the $^{31}P\{^1H\}$ NMR peak shifts from δ 10.8 ppm in **1** to 4.0 ppm for complex **2**. More diagnostic, however, are the ^1H NMR data, as the resonances for the hydrogens on the Bcat group bound directly to iridium are observed at δ 5.20 and 4.68 ppm, while the uncoordinated catecholato peaks remain downfield at δ 6.56–6.38 ppm. In comparison, the aryl peaks in $[NBu_4][Bcat_2]$ are observed at δ 6.57 ppm in the ^1H NMR data [22]. Significant upfield shifts are also observed in **2** by $^{13}C\{^1H\}$ NMR spectroscopy, where carbon atoms of the Bcat group coordinated to the iridium fragment are located at δ 140.3, 84.4, and 79.7 ppm. For comparison, the related carbon resonances in $[NBu_4][Bcat_2]$ are observed at δ 151.8, 117.9, and 108.5 ppm.

Complex **2** has also been characterized by a single crystal x-ray diffraction study (Fig. 1), confirming that the arylspiroboronate ester is bound to the iridium fragment in a η^6 fashion [23–26]. Within the bound Bcat group, four of the iridium carbon distances Ir(1)–C(33) 2.270(3), Ir(1)–C(34) 2.297(3), Ir(1)–C(32) 2.302(3), and Ir(1)–C(31) 2.312(3) Å, are noticeably shorter than the other two at Ir(1)–C(30) 2.446(3) and Ir(1)–C(29) 2.456(3) Å. This slippage away from a true η^6 bonding mode has been observed in the rhodium analogues where the potential surface for such distortions is reputably quite shallow, and is

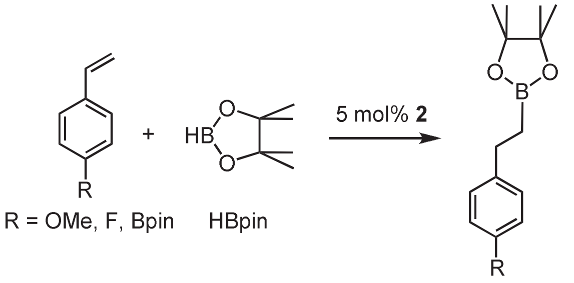
---

[*] Corresponding author. Tel.: +1 506 364 2372; fax: +1 506 364 2313.
E-mail address: swestcott@mta.ca (S.A. Westcott).

1387-7003/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2010.07.044



Scheme 1. Synthesis of arylspiroboronate ester iridium complex **2** by addition of B_2cat_3 to Ir(acac)(dppb) (**1**).



Scheme 2. Catalyzed hydroboration of vinylarenes using complex **2** and HBpin.

presumably a ground-state phenomenon. Bond distances and angles within the arylspiroboronate ester are similar to those reported previously [19,27].

We then decided to examine complex **2** for its potential to catalyze the addition of HBcat and HBpin to vinylarenes [28,29]. To our surprise, and contrary to the results using the highly active and selective rhodium analogues, no significant reaction was observed with HBcat and 4-vinylanisole using 5 mol% of **2** at room temperature after 16 h. Interestingly, however, reactions of HBpin and 4-vinylanisole proceeded smoothly at room temperature (T = 18 h) to give selective formation of the linear hydroboration product (Scheme 2) [30]. This observation is unusual as HBcat is normally the more active of the diorganyloxyboranes in catalyzed hydroborations. Similar regioselectivities in favour of the linear hydroboration product were observed in reactions with 4-fluorostyrene and 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane with HBpin. Unfortunately, attempts to add this borane to the more hindered substrates α- and β-methylstyrene proved unsuccessful. It is clear that hydroborations with this iridium complex are proceeding via a different mechanism, as compared to the rhodium analogues. In a recent report, Crudden et al. [31] suggested that cleavage of the B–H bond in HBpin is facilitated by an additional Lewis acid. While it is possible that a similar alternative pathway may be occurring in reactions with **2**, further work is needed to elucidate the mechanism in these hydroborations, the results of which will be reported in due course.

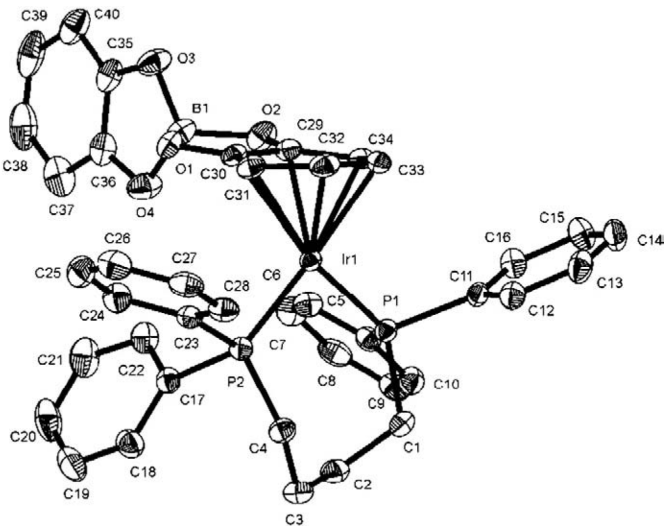


Fig. 1. Molecular structure of **2** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)–P(1) 2.2252(7), Ir(1)–P(2) 2.2348(7), Ir(1)–C(33) 2.270(3), Ir(1)–C(34) 2.297(3), Ir(1)–C(32) 2.302(3), Ir(1)–C(31) 2.312(3), Ir(1)–C(30) 2.446(3), Ir(1)–C(29) 2.456(3), B(1)–O(4) 1.463(4), B(1)–O(3) 1.469(4), B(1)–O(1) 1.503(4), B(1)–O(2) 1.506(4); P(1)–Ir(1)–P(2) 95.77(3), P(1)–Ir(1)–C(33) 103.53(8), O(4)–B(1)–O(3) 106.4(2), O(4)–B(1)–O(1) 112.0 (2), O(3)–B(1)–O(1) 110.8(2), O(4)–B(1)–O(2) 111.9(2), O(3)–B(1)–O(2) 112.2(2), and O(1)–B(1)–O(2) 103.7(2).

Acknowledgements

We thank NSERC, ACS-PRF (Grant Number 50093-UR3), the Canada Research Chair Programmes, and Mount Allison University for financial support. Shrubby Durant and Roger Smith are thanked for their valuable technical skills.

Appendix A. Supplementary material

CCDC 767792 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.07.044.

References

[1] A. Pelter, K. Smith, H.C. Brown, Borane Reagents, Academic Press, New York, 1988.
[2] C.F. Lane, G.W. Kabalka, Tetrahedron 32 (1976) 981.
[3] D. Männig, H. Nöth, J. Chem. Soc. Dalton Trans. (1985) 1689.
[4] D. Männig, H. Nöth, Angew. Chem. Int. Ed Engl. 24 (1985) 878.
[5] C.M. Crudden, D. Edwards, Eur. J. Org. Chem. (2003) 4695.
[6] C.M. Vogels, S.A. Westcott, Curr. Org. Chem. 9 (2005) 687.
[7] C. Dai, E.G. Robins, A.J. Scott, W. Clegg, D.S. Yufit, J.A.K. Howard, T.B. Marder, Chem. Commun. (1998) 1983.
[8] Y. Yamamoto, R. Fujikawa, T. Umemoto, N. Miyaura, Tetrahedron 60 (2004) 10695.
[9] A. Alexakis, D. Polet, C. Bournaud, M. Bonin, L. Micouin, Tetrahedron: Asymm. 16 (2005) 3672.
[10] J. Cipot, C.M. Vogels, R. McDonald, S.A. Westcott, M. Stradiotto, Organometallics 25 (2006) 5965.
[11] A. Pérez Luna, M. Bonin, L. Micouin, H.-P. Husson, J. Am. Chem. Soc. 124 (2002) 12098.
[12] J.A. Brinkman, T.T. Nguyen, J.R. Sowa Jr., Org. Lett. 2 (2000) 981.
[13] C.M. Crudden, Y.B. Hleba, A.C. Chen, J. Am. Chem. Soc. 126 (2004) 9200.
[14] D.A. Evans, G.C. Fu, A.H. Hoveyda, J. Am. Chem. Soc. 114 (1992) 6671.
[15] S.A. Westcott, T.B. Marder, R.T. Baker, J.C. Calabrese, Can. J. Chem. 71 (1993) 930.
[16] J.V.B. Kanth, M. Periasamy, H.C. Brown, Org. Process Res. Dev. 4 (2002) 550.
[17] M.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott, Organometallics 29 (2010) submitted.
[18] To a 3 mL toluene solution of Ir(acac)(dppb) (100 mg, 0.14 mmol) was added a 4 mL toluene solution of B_2cat_3 (50 mg, 0.14 mmol) [16]. The reaction mixture was heated at reflux for 2 h at which point solvent was removed under vacuum and the resulting solid washed with Et_2O (3 × 10 mL) to afford **2** as a pale orange solid. Yield: 80 mg (68%); m.p.: 210–215 °C (decomp.). Anal. Calc. for **2** ($C_{40}H_{36}BIrO_4P_2$, 845.79): C, 56.80; H, 4.30. Found: C, 56.45; H, 4.37. ^{1}H NMR (270 MHz, THF-d_8) (ppm): δ 7.63 (m, 8H, Ar), 7.44–7.34 (ov m, 12H, Ar), 6.56–6.38 (ov m, 4H, $C_6\mathit{H}_4O_2$), 5.20 (m, 2H, η^6-$C_6\mathit{H}_4O_2$), 4.68 (m, 2H, η^6-$C_6\mathit{H}_4O_2$), 2.61 (br m, 4H, $PC\mathit{H}_2$), 1.61 (br m, 4H, $PCH_2C\mathit{H}_2$); ^{11}B NMR (87 MHz, THF-d_8) (ppm): δ 13.6 (s); ^{13}C{^{1}H} NMR (67 MHz, THF-d_8) (ppm): δ 152.2, 151.9, 140.3, 139.2 (m, *C*P), 132.9 (t, J_{CP} = 5.6 Hz, C_6H_5), 129.6, 127.9 (t, J_{CP} = 5.1 Hz, C_6H_5), 117.5, 116.5, 108.0, 107.8, 84.4, 79.7, 31.3 (m, PCH_2), 23.3 (s, PCH_2CH_2); ^{31}P{^{1}H} NMR (109 MHz, THF-d_8) (ppm): δ 4.0.
[19] W. Clegg, M.R.J. Elsegood, A.J. Scott, T.B. Marder, C. Dai, N.C. Norman, N.L. Pickett, E.G. Robins, Acta Cryst. C55 (1999) 733.
[20] S. Lachaize, K. Essalah, V. Montiel-Palma, L. Vendier, B. Chaudret, J.C. Barthelat, S. Sabo-Etienne, Organometallics 24 (2005) 2935.
[21] H. Nöth, B. Wrackmeyer, *In* Nuclear magnetic resonance spectroscopy of boron compounds, Springer-Verlag, Berlin, 1978.
[22] J.M. Carr, P.J. Duggan, D.G. Humphrey, J.A. Platts, E.M. Tyndall, Aust. J. Chem. 58 (2005) 901.

[23] Orange plate-like crystals of **2** were grown from a saturated Et_2O solution at room temperature. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times at a temperature of 173(1) K. The detector distance was 5 cm. The data were reduced [SAINT, 24] and corrected for absorption [SADABS, 25]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 [SHELXTL, 26]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model. Crystallographic data for **2**: $C_{40}H_{36}BIrO_4P_2$, $M_r = 845.64$, monoclinic, space group $P2_1/n$ with $a = 12.4711(16)$ Å, $b = 21.718(3)$ Å, $c = 12.7368(16)$ Å, $\alpha = 90^o$, $\beta = 96.698(2)^o$, $\gamma = 90^o$, $V = 3426.2(7)$ Å^3, $Z = 4$, $D_c = 1.639$ Mg m^{-3}, $F(000) = 1680$, $GoF = 1.068$, $R_1 = 0.0205$, and $\omega R_2 = 0.0554$ for all data.

[24] SAINT 7.23A, Bruker AXS Inc, Madison, WI, USA, 2006.

[25] G.M. Sheldrick, SADABS 2004, Bruker AXS Inc., Madison, WI, USA, 2004.

[26] G.M. Sheldrick, SHELXTL, Acta Cryst. A64 (2008) 112.

[27] C.M. Vogels, A. Decken, S.A. Westcott, Can. J. Chem. 84 (2006) 146.

[28] A.M. Segarra, R. Guerrero, C. Claver, E. Fernández, Chem. Eur. J. 9 (2003) 191.

[29] A.M. Segarra, E. Daura-Oller, C. Claver, J.M. Poblet, C. Bo, E. Fernández, Chem. Eur. J. 10 (2004) 6456.

[30] The appropriate borane (1.2 equivalents) in 0.5 mL of C_6D_6 was added to a 0.5 mL C_6D_6 solution of **2** (5 mol%) and the vinylarene (1 equivalent). Reactions were monitored over time by multinuclear NMR spectroscopy and products were identified by comparison to previously reported compounds [D.A. Kanas, S.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott, Inorg. Chem. 47 (2008) 8727 as well as by GC-MS analysis.

[31] C.J. Lata, C.M. Crudden, J. Am. Chem. Soc. 132 (2010) 131.