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Bulky rhodium diimine complexes for the catalyzed borylation of vinylarenes

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Abstract

Rhodium(I) complexes containing the bulky diimine ligand (2,6-i-$Pr_2C_6H_3$)DAB (DAB = 1,4-diaza-1,3-butadiene) have been prepared and characterized fully. The zwitterionic complex Rh(η^6-catBcat){(2,6-i-$Pr_2C_6H_3$)DAB} (**3**) was prepared in high yield by addition of B_2cat_3 to Rh(acac){(2,6-i-$Pr_2C_6H_3$)DAB} (**2**). These rhodium complexes have been examined for their ability to catalyze the borylation of vinylarenes.

Keywords: Borylation; Catalysis; Diimine; Rhodium; Zwitterion

Introduction

There has been considerable recent interest in the use of transition metal complexes for their ability to catalyze the addition of B–H and B–B bonds to alkenes [1–5]. An interesting alternative to these reactions is the metal catalyzed dehydrogenative borylation of alkenes to give (*E*)-alkenyl boronate esters [6–12]. This latter reaction is believed to occur via initial oxidative addition of the B–E (E = H or B) bond to the metal centre, followed by coordination and insertion of the alkene into the M–B bond. A subsequent and selective β-hydride elimination step affords the corresponding alkenylboronate ester and either dihydrogen or R_2B–H (Scheme 1). Unfortunately, early work in this area was complicated by the formation of side products arising from the addition of dihydrogen or R_2B–H with the starting alkene or the newly formed alkenylboronate ester. Marder and co-workers, however, have recently shown that *trans*-[RhCl(CO)(PPh_3)$_2$] can be used with B_2pin_2 (pin = 1,2-$O_2C_2Me_4$) to give a wide variety of 1,1-disubstituted alkenylboronate esters in excellent yields [12]. As part of our investigation into designing new rhodium complexes for borylation reactions we report herein on the synthesis and reactivity of bulky rhodium(I) diimine complexes and their ability to catalyze the dehydrogenative borylation of vinyl arenes using boranes and diboron compounds.

Experimental

Reagents and solvents used were purchased from Aldrich Chemicals. NMR spectra were recorded on a JEOL JNM-GSX270 FT spectrometer. ^1H NMR chemical shifts are reported in ppm and referenced to residual solvent protons in deuterated solvent at 270 MHz. ^{11}B NMR chemical shifts are reported in ppm and are referenced to $BF_3 \cdot OEt_2$ as an external standard at 87 MHz. ^{13}C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz and are reported in ppm. Multiplicities are reported as singlet (s), doublet (d), septet (sept), multiplet (m), and overlapping (ov). Microanalyses for C, H, and N were carried out at

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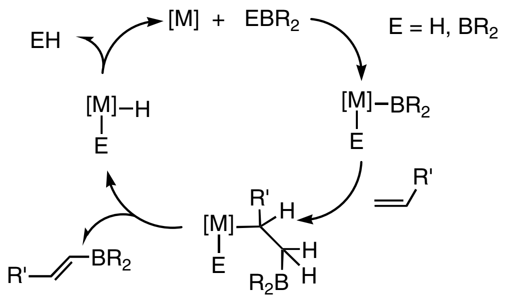

Scheme 1.

Guelph Chemical Laboratories (Guelph, ON). All reactions were carried out under an atmosphere of dinitrogen.

Preparation of [Rh(κ^2-2,6-^{i}Pr$_2$C$_6$H$_3$N=C(Me)C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)(μ-Cl)]$_2$ (1)

To a toluene solution (4 mL) of $[RhCl(coe)_2]_2$ (coe = *cis*-cyclooctene, 150 mg, 0.21 mmol) was added a toluene solution (1 mL) of (2*E*)-*N*-((*E*)-3-(2,6-diisopropylphenylimino)butan-2-ylidene)-2,6- diisopropylbenzenamine (169 mg, 0.42 mmol). The mixture was heated to reflux for 18 h at which point solvent was removed under vacuum. The resulting solid was washed with hexane (2 × 1 mL) to afford **1**. Yield: 175 mg (77%) of a red-brown solid. Spectroscopic NMR data (in C_6D_6): ^{1}H δ: 7.35 (t, $J = 8$ Hz, 4H, Ar), 7.22 (d, $J = 8$ Hz, 8H, Ar), 3.25 (sept, $J = 7$ Hz, 8H, CH), 1.55 (d, $J = 7$ Hz, 24H, CH$_3$), 0.99 (d, $J = 7$ Hz, 24H, CH$_3$), −0.53 (s, 12H, CH$_3$); ^{13}C{^{1}H} δ: 155.8, 149.1, 140.5, 126.4, 123.0, 28.4, 24.2, 23.5, 19.0. Anal. calcd. for $C_{56}H_{80}Cl_2N_4Rh_2$: C 61.92, H 7.44, N 5.16; found C 61.60, H 7.73, N 5.09.

Preparation of [Rh(acac)(κ^2-2,6-^{i} Pr$_2$C$_6$H$_3$N=C(Me)C-(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)] (2)

To a toluene solution (4 mL) of $Rh(acac)(coe)_2$ (200 mg, 0.47 mmol) was added a toluene solution (1 mL) of (2*E*)-*N*-((*E*)-3-(2,6-diisopropylphenylimino)butan-2-ylidene)-2,6-diisopropylbenzenamine (191 mg, 0.47 mmol). The mixture was heated to reflux for 18 h at which point solvent was removed under vacuum. The resulting solid was washed with cold hexane (1 mL) to afford **2**. Yield: 235 mg (82%) of a red-brown solid. Spectroscopic NMR data (in C_6D_6): ^{1}H δ: 7.49–7.44 (ov m, 2H, Ar), 7.36-7.33 (ov m, 4H, Ar), 4.58 (s, 1H, CH=C), 3.50 (sept, $J = 7$ Hz, 4H, CH), 1.58 (s, 6H, C(O)CH$_3$), 1.50 (d, $J = 7$ Hz, 12H, CH$_3$), 1.16 (d, $J = 7$ Hz, 12H, CH$_3$), −0.11 (s, 6H, CH$_3$); ^{13}C{^{1}H} δ: 182.9, 159.6, 149.2, 141.2, 126.4, 123.0, 98.1, 28.7, 26.5, 24.4, 23.4, 19.1. Anal. calcd. for $C_{33}H_{47}N_2O_2Rh$: C 65.32, H 7.82, N 4.62; found C 64.95, H 7.87, N 4.42.

Preparation of [Rh(catBcat)(κ^2-2,6-^{i}Pr$_2$C$_6$H$_3$N=C(Me)-C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$] (3)

To a toluene solution (3 mL) of **2** (100 mg, 0.16 mmol) was added a toluene solution (1 mL) of B_2cat_3 (57 mg, 0.16 mmol). The reaction was stirred for 3 days at which point a dark brown precipitate was collected by suction filtration. The solid was washed with toluene (1 mL) and hexane (3 × 3 mL) to afford **3**. Yield: 95 mg (81%) of a red-brown solid. Spectroscopic NMR data (in CDCl$_3$): ^{1}H δ: 7.35-7.27 (ov m, 6H, Ar), 6.70-6.61 (ov m, 4H, Ar), 5.17 (m, 2H, η^6-C$_6$H$_4$O$_2$), 4.99 (m, 2H, η^6-C$_6$H$_4$O$_2$), 3.11 (sept, $J = 7$ Hz, 4H, CH), 1.53 (s, 6H, CH$_3$), 1.38 (d, $J = 7$ Hz, 12H, CH$_3$), 1.06 (d, $J = 7$ Hz, 12H, CH$_3$); ^{11}B δ: 13.7; ^{13}C{^{1}H} δ: 154.0, 151.8, 150.9, 140.3, 138.8, 127.8, 124.1, 118.6, 118.2, 84.1 (d, $J_{Rh-C} = 6$ Hz), 79.8 (d, $J_{Rh-C} = 4$ Hz), 28.0, 24.6, 24.2, 18.8. Anal. calcd. for $C_{40}H_{48}BN_2O_4Rh$: C 65.40, H 6.60, N 3.81; found C 65.84, H 6.91, N 3.81.

General procedure for the catalyzed borylation of vinylarenes

The appropriate borylation reagent (1.2 equivalents), in 0.5 mL of C_6D_6, was added to a 0.5 mL C_6D_6 solution of **1**–**3** (2 mol%) and the vinylarene. Reactions were allowed to proceed for 18 h and then monitored by multinuclear NMR spectroscopy.

X-ray crystallography

Crystals of **1** were grown from a saturated hexane solution at −25 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold 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 time. The detector distance was 5 cm. The data were reduced [13] and corrected for absorption [14]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically. Crystals of **3** were grown from a saturated THF solution at −25 °C. Single crystals were coated with Paratone-N oil, mounted using a 20 μm cryo-loop 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 30 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT) and corrected for absorption (SADABS). The structure was solved by direct methods and refined by full-matrix least squares on F2 (SHELXTL). One of the THF molecules was disordered and the site occupancy fixed at 0.5 for C(60), C(62), C(64), C(70), C(71) and C(72). All non-hydrogen atoms were refined anisotropically. Distinction between oxygen and carbon atoms in the THF molecules was not successful and all positions were refined as C atoms. Hydrogen atoms were included in calculated positions and refined using a riding model. The THF hydrogen atoms were omitted.

Results and discussion

Catalyzed hydroborations of alkenes using $RhCl(PPh_3)_3$ and excess PPh_3 have been reported to give considerable amounts of the corresponding alkenylboronate esters, presumably arising from a competing dehydrogenative borylation reaction [16a]. Coordination of excess phosphine and hence, increased steric bulk around the metal center presumably facilitated a β-hydride elimination pathway. On this premise, we have prepared novel rhodium complexes containing the bulky α-diimine ligand (2,6-*i*-$Pr_2C_6H_3$)DAB (DAB = 1,4-diaza-1,3-butadiene). Late metal complexes containing this ligand are well known for their ability to catalyze the polymerization of alpha olefins [17]. Addition of (2,6-*i*-$Pr_2C_6H_3$)DAB to $[RhCl(coe)_2]_2$ (coe = *cis*-cyclooctene) afforded high yields of [RhCl(2,6-*i*-$Pr_2C_6H_3$)DAB$]_2$ (**1**). Complex **1** has been characterized by a number of physical methods including multinuclear NMR spectroscopy and X-ray diffraction. Data are consistent with the related complex RhI(CO)(2,6-*i*-$Pr_2C_6H_3$)DAB [18] and the molecular structure of **1** is shown in Fig. 1. The metal centre lies in a square planar geometry with relatively short rhodium nitrogen bond distances of 1.966(2) Å (avg), indicative of the strong σ-donor π-acceptor ability of the diazabutadiene ligand.

Addition of (2,6-*i*-Pr_2Ph)DAB to $Rh(acac)(coe)_2$ (acac = acetylacetonato) gave the corresponding complex Rh(acac){(2,6-*i*-$Pr_2C_6H_3$)DAB} (**2**). Although related phosphinorhodium acetylacetonato complexes are active and selective catalysts for the hydroboration of a wide range of alkenes, the catalyst resting state in these systems is believed to be the zwitterionic complexes Rh(η^6-catBcat)(P_2) (cat = 1,2-$O_2C_6H_4$), arising from the redistribution of substituents on catecholborane (HBcat) [16a]. Indeed, hydroborations with HBcat using these zwitterionic complexes gave similar selectivities to those observed for the acetylacetonato precursors. In an elegant study, Marder and co-workers found that addition of B_2cat_3 to Rh(acac)(P_2) led to the zwitterionic complexes Rh(η^6-catBcat)(P_2) in high yields, along with concomitant formation of acacBcat [12b]. The diboron species B_2cat_3 is generated as an unwanted decomposition product in nucleophilic reactions with HBcat or when HBcat is heated at elevated temperatures [16b]. In this study, we have found that addition of B_2cat_3 to **2** gave zwitterionic Rh(η^6-catBcat){(2,6-*i*-$Pr_2C_6H_3$)DAB} (**3**) in high yields. The ^{11}B NMR spectrum has a sharp peak at 14 ppm, consistent with the boron atom being four coordinate [12b]. The molecular structure of **3** has been confirmed by a single crystal X-ray diffraction study (Fig. 2) and shows that the N_2Rh fragment is bound to the catBcat anion via one of the catecholato groups in a η^6-fashion. As with related systems, there appears to be considerable slippage of the N_2Rh group with respect to the π-bound arene ring. Indeed, four bond distances are considerably shorter (ranging from 2.237(4) to 2.267(4) Å) than the two remaining Rh(1)–C(33) and Rh(1)–C(34) bonds at 2.375(5) and 2.392(5) Å, respectively. The potential surface for such distortions is most likely quite shallow.

In order to compare complexes **1**–**3** against other rhodium catalysts, we have examined their ability to catalyse the hydroboration and diboration of a series of vinylarenes (i.e., 4-vinylanisole, 2-vinylnaphthalene, perfluorostyrene,

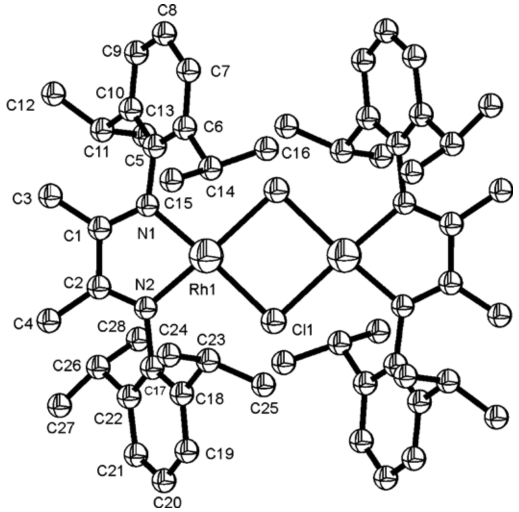

Fig. 1. Molecular structure of one of the independent molecules of **1** with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–N(1) 1.975(2), Rh(1)–N(2) 1.970(2), Rh(1)–Cl(1) 2.3816(7), N(1)–C(1) 1.325(3), N(2)–C(2) 1.316(3); N(2)–Rh(1)–N(1) 78.36(8), N(2)–Rh(1)–Cl(1) 98.54(6), N(1)–Rh(1)–Cl(1) 176.82(6), Cl(1)#1-Rh(1)–Cl(1) 83.74(2), C(1)–N(1)–Rh(1) 116.62(17), C(2)–N(2)–Rh(1) 117.38(17).

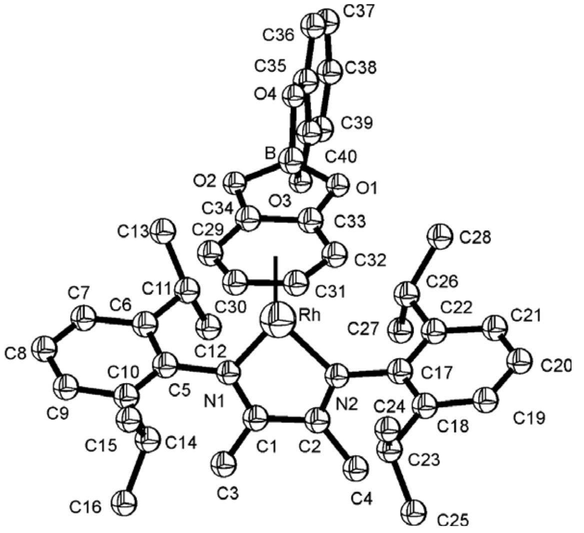

Fig. 2. Molecular structure of **3** with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Rh–N(2) 1.968(3), Rh–N(1) 1.977(3), Rh–C(30) 2.237(4), Rh–C(31) 2.250(5), Rh–C(29) 2.260(5), Rh–C(32) 2.267(4), Rh–C(33) 2.375(5), Rh–C(34) 2.392(5), B–O(3) 1.445(7), B–O(4) 1.456(6), B–O(2) 1.511(8), B–O(1) 1.521(8); N(2)–Rh–N(1) 78.04(14), O(3)–B–O(4) 108.2(5), O(3)–B–O(2) 112.4(4), O(4)–B–O(2) 111.7(4), O(3)–B–O(1) 112.0(4), O(4)–B–O(1) 110.7(4), O(2)–B–O(1) 101.8(4).

etc.). Although initial reactions using HBcat or pinacolborane (HBpin) with catalytic amounts of complexes **1**–**3** gave complex products distributions, reactions using B_2pin_2 gave predominately the corresponding alkenylboronate ester *trans*-ArCH=CHBpin, arising from a selective dehydrogentative borylation reaction. For example, addition of B_2pin_2 to 4-fluorostyrene using a catalytic amount of **3** in toluene at 80 °C gave 98% of *trans*-4-F-$C_6H_4CH{=}CHB$-pin (by ^1H NMR spectroscopy and GC/MS), along with minor amounts of hydrogenation product 4-F-$C_6H_4CH_2CH_3$. Similar selectivities were observed in reactions run in other solvents, such as THF-d_8. It appears that a competing hydroboration reaction with HBpin (arising from this dehydrogenative borylation) is too slow using this catalyst system. Unfortunately, reactions with B_2cat_2 also gave complex product distributions.

In summary, we have prepared three novel rhodium(I) complexes containing the bulky diimine ligand (2,6-*i*-$Pr_2C_6H_3$)DAB. Initial borylation studies demonstrate the potential for using these complexes as catalysts to generate alkenylboronate esters derived from vinylarenes. Further studies using these complexes are currently underway and the results of which will be published in due course.

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Appendix A. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications (CCDC 602790 and 602791). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.05.001.

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