Rhodium catalysed diboration of unstrained internal alkenes and a new and general route to zwitterionic [$L_2Rh(\eta^6$-catBcat)] (cat = 1,2-$O_2C_6H_4$) complexes†

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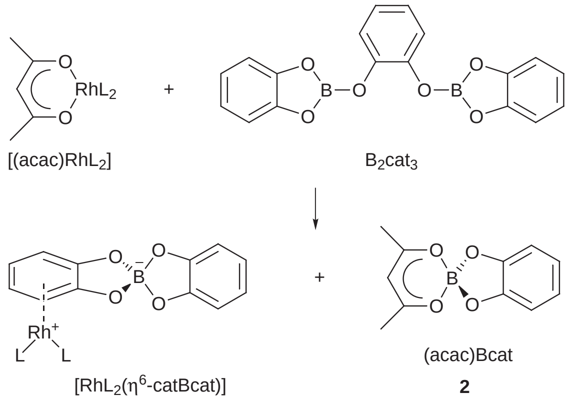
Reactions of [L_2Rh(acac)] (L = alkene or phosphine) with B_2cat_3 yield the zwitterionic complexes [$L_2Rh(\eta^6$-catBcat)] and [(acac)Bcat] cleanly; [(dppm)Rh(η^6-catBcat)], the X-ray structure of which is reported, is an excellent catalyst for the diboration of vinylarenes and unstrained internal alkenes *cis*- and *trans*-stilbene and *trans*-β-methylstyrene.

Catalysed 1,2-diborations of alkynes, 1,4-diboration of 1,3-dienes and α,β-unsaturated ketones, as well as additions of B–Si and B–Sn bonds to alkynes, α,ω-diynes and enynes have been the subject of a recent review.[1] These reactions are catalysed by platinum or palladium complexes and usually a single catalytic pathway leads to a single product. In contrast, the catalysed diboration of alkenes can lead to up to nine products owing to the competition between B–C reductive elimination and β-hydride elimination from the L_nM(Bcat)[CHRCHR′(Bcat)] intermediate formed by alkene insertion into the M–B bond. Initially, we examined[2] [(dppb)Rh(η^6-catBcat)], [dppb = $Ph_2P(CH_2)_4PPh_2$] an outstanding hydroboration catalyst,[3] for the addition of B_2cat_2 to 4-vinylanisole and obtained the desired 1,2-diboration product 4-$MeOC_6H_4CH(Bcat)CH_2(Bcat)$ in 44% yield. The remaining products included 23% of 4-$MeOC_6H_4CH(Bcat)CH_3$ and 22% of the unusual 2,2,2-tris(boronate) ester 4-$MeOC_6H_4CH_2C(Bcat)_3$, both arising from intermediates generated by the β-hydride elimination process. A catalyst system composed of [AuCl(PEt_3)] + $Cy_2P(CH_2)_2PCy_2$ gave exclusive formation of the 1,2-bis(boronate) ester; however, catalyst activity and stability were lower than desired. Miyaura and coworkers[4] reported the addition of B_2pin_2 (pin = $OCMe_2CMe_2O$) to terminal alkenes and cyclic alkenes having internal ring strain using a catalytic amount of Pt(dba)$_2$ at 50 °C, but attempts to diborate internal alkenes such as stilbene were unsuccessful. Iverson and Smith[5] reported similar results using Pt(cod)$_2$ or Pt(norbornene)$_3$ as catalyst precursors at ambient temperatures. Clean diboration was observed for norbornene and norbornadiene, but not for other internal alkenes, apparently as a result of complications arising from β-hydride elimination. In addition, neither of the base-free Pt systems is appropriate for modification with chiral ligands. We report herein the first catalyst system capable of diborating internal alkenes including *cis*- and *trans*-stilbene, and *trans*-β-methylstyrene without significant by-products.

Several zwitterionic [$L_2Rh(\eta^6$-catBcat)] complexes had been prepared previously[3] by addition of HBcat to either [$L_2Rh(\eta^3$-2-Me-allyl)] or [L_2Rh(acac)] precursors; however, with L = arylphosphine the reaction had to be carried out under hydroboration conditions (*i.e.* in the presence of excess alkene and HBcat) in order to isolate the [(dppb)Rh(η^6-catBcat)] cleanly. In addition, this approach is obviously inappropriate for L_2 = (alkene)$_2$ or diene. We have now found that reactions (Scheme 1) of [L_2Rh(acac)] with B_2cat_3 yield quantitatively the zwitterionic complexes [$L_2Rh(\eta^6$-catBcat)] [L_2 = $(C_2H_4)_2$ **1a**, $(C_8H_{14})_2$ **1b**, cod **1c**, $(PPh_2Me)_2$ **1d**, dppm **1e**, dppe **1f**, dppp = $Ph_2P(CH_2)_3PPh_2$ **1g**, dppb **1h**, dppf = 1,1-bis(diphenylphosphino)ferrocene **1i**] and (acac)Bcat **2** as evidenced by ^{1}H, ^{11}B, and ^{31}P NMR spectroscopy, full details of which will be reported elsewhere.



1a $L_2 = (C_2H_4)_2$
b $L_2 = (C_8H_{14})_2$
c L_2 = cod
d $L_2 = (PPh_2Me)_2$
e L_2 = dppm
f L_2 = dppe
g L_2 = dppp
h L_2 = dppb
i L_2 = dppf

Scheme 1 Synthesis of zwitterionic rhodium complexes

Of particular interest is the fact that 4 mol% of [(dppm)Rh(η^6-catBcat)] **1e**,‡ prepared *in situ* from [(dppm)Rh(acac)] and B_2cat_3 in THF, and whose molecular structure§ is shown in Fig. 1, catalyses the diboration of (addition of B_2cat_2 to) vinylarenes, norbornene and the

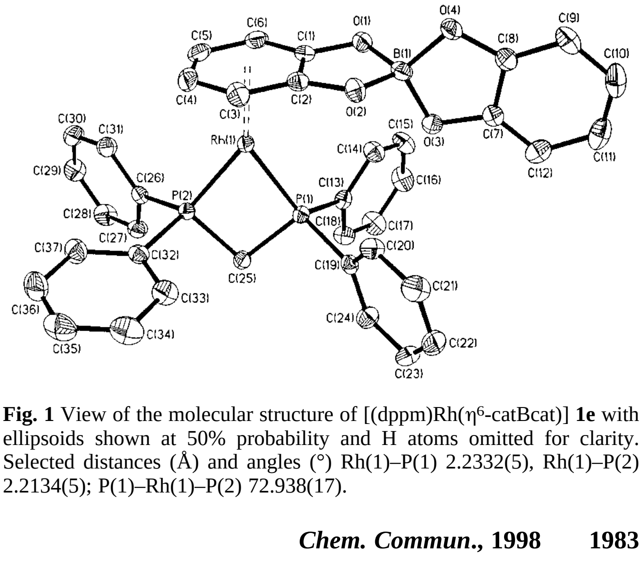
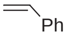
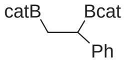
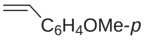
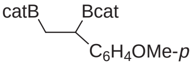
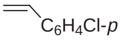
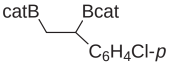
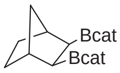
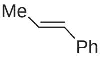
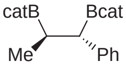
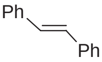
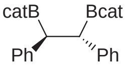
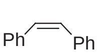
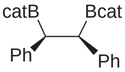


Fig. 1 View of the molecular structure of [(dppm)Rh(η^6-catBcat)] **1e** with ellipsoids shown at 50% probability and H atoms omitted for clarity. Selected distances (Å) and angles (°) Rh(1)–P(1) 2.2332(5), Rh(1)–P(2) 2.2134(5); P(1)–Rh(1)–P(2) 72.938(17).

Table 1 [(acac)Rh(dppm)]/B_2cat_3-catalyzed diboration of alkenes[a]

Entry	Alkene	Product	Time/h	Yield(%)
a			2	87
b			2.5	77
c			1	79
d			6	>99
e			30	>99
f			<72	92
g			<72	>99

[a] All reactions were carried out in THF or [$^2H_8$]THF at room temp. in the presence of 4 mol% catalyst [(acac)Rh(dppm)]/B_2cat_3, and alkene : B_2cat_2 = 1:1; product yields determined by ^1H and ^{13}C NMR spectroscopy.

unstrained internal alkenes *cis* and *trans*-stilbene and *trans*-β-methylstyrene at room temp. (Table 1).¶ *Syn*-addition of the B_2 unit to the alkene was evident in the NMR spectra of the norbornene diboration product (entry d). A crystal structure§ of the *trans*-stilbene diboration product (entry f) is also consistent with *syn*-addition. The disorder observed in the crystal structure results from the apparent superposition in space of the two enantiomers of the racemic compound; attempts to solve the structure based on the *meso*-model gave an unreasonable central C–C bond length. Likewise, in CD_2Cl_2, the signal for the unique benzylic C–H proton at δ 3.71 is distinct from that for the *cis*-stilbene diboration product (entry g) which occurs at δ 3.78 the latter thus being assigned to the *meso* compound. Diboration of *trans*-β-methylstyrene (entry e) proceeds in > 99% yield,¶ generating two adjacent and distinct chiral carbon centres.

Significantly reduced hapticity of the π-coordinated catecholate must be required in order to generate vacant sites for alkene and B–B activation. Although reaction times were found to be somewhat longer than in THF, the diborations can also be carried out in less polar C_6D_6 suggesting that complete dissociation into L_2Rh^+ and $[Bcat_2]^-$ is unlikely. The success of the dppm based catalyst system compared with the dppb system indicates that the relative rates of B–C reductive elimination *vs.* β-hydride elimination are a sensitive function of the bite angle of the chelating phosphine ligand.

This is the first report of the catalysed diboration of unstrained internal alkenes and of an efficient phosphine-containing catalyst system for alkene diboration. Further work will examine the mechanism of the reaction, the diboration of other unsaturated substrates and the use of chiral bis(phosphine)-containing zwitterionic Rh complexes for asymmetric diboration reactions.

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Notes and References

† Dedicated to Professor Warren Roper on the occasion of his 60th birthday. Preliminary results were presented at the Fifth Chemical Congress of North America, Cancun, Mexico, November 1997, Abstract No. 1493.

‡ *NMR spectroscopic data* for **1e** in C_6D_6: $^{31}P\{^1H\}$, δ −22.97 (d, $^1J_{RhP}$ 184.6 Hz); $^{11}B\{^1H\}$, δ 15.76; ^1H, δ 3.62 (td, $^3J_{RhH}$ 2.0, $^2J_{PH}$ 10.8 Hz, 2 H, CH_2), 4.74 (m, 2 H, η^6-$C_6H_4O_2$), 6.28 (m, 2 H, η^6-$C_6H_4O_2$), 6.60 (m, 1 H, $C_6H_4O_2$), 6.76 (overlapping m, 2 H, $C_6H_4O_2$), 6.87–7.13 (overlapping m, 13 H, $C_6H_4O_2$ and C_6H_5), 7.65 (m, 8 H, C_6H_5).

§ *Crystal data*: for **1e** from C_6D_6: $C_{37}H_{30}BO_4P_2Rh{\cdot}C_6D_6$, M = 798.42, orthorhombic, space group $P2_12_12_1$, a = 13.2932(7), b = 15.2327(8), c = 17.8046(10)Å, U = 3605.3(3)Å^3, Z = 4, D_c = 1.471 g cm^{-3}, μ(Mo-Kα) = 0.606 mm^{-1}, T = 160 K. Full-matrix least-squares refinement on F^2 (G. M. Sheldrick, SHELXTL manual, Bruker AXS Inc., Madison, WI, USA, 1994, version 5) anisotropic for all non-H atoms and isotropic for H (461 parameters) using 8415 unique data (including 3634 Friedel pairs; 26 554 total collected; R_{int} = 0.0251) from a Bruker AXS SMART CCD diffractometer (θ < 28.46°) gave $R1$ [$I > 2\sigma(I)$] = 0.0212, $wR2$ (all data) = 0.0473. Residual electron density within ± 0.28 e Å^{-3}.

For *rac*-PhCH(Bcat)CH(Ph)(Bcat) from [$^2H_8$]THF: $C_{26}H_{20}B_2O_4{\cdot}C_4D_8O$, M = 498.16, monoclinic, space group $P2_1/m$, a = 6.1548(5), b = 19.853(2), c = 10.4004(9)Å, β = 95.933(3)°, U = 1264.1(2) Å^3, Z = 2, D_c = 1.309 g cm^{-3}, μ(Mo-Kα) = 0.085 mm^{-1}, T = 100 K. Full-matrix least-squares refinement on F^2 as above, anisotropic for all non-disordered non-H atoms, isotropic for H and disordered atoms with disordered H atoms not included in the refinement (198 parameters) using 2970 unique data (14 317 total collected; R_{int} = 0.060) (θ < 27.50°) gave $R1$ [$I > 2\sigma$(I)] = 0.0827, $wR2$ (all data) = 0.1931. Residual electron density within ± 0.572 e Å^{-3}. CCDC 182/949.

¶ *A representative procedure for* the diboration of *trans*-β-methylstyrene: in a N_2-filled glove-box, [(acac)Rh(dppm)] (0.010 mmol) and B_2cat_3 (0.010 mmol) were charged into a 20 ml vial and dissolved in THF (0.5 ml). The solution was stirred rapidly for *ca.* 5 min and then a solution of *trans*-β-methylstyrene (0.250 mmol) in THF (0.5 ml) was added. Finally, B_2cat_2 (0.250 mmol) was added portionwise and the resulting reaction mixture allowed to stir rapidly at room temperature. Aliquots (1 µl) were removed regularly to monitor the disappearance of alkene *via* GC–MS. Crude product was isolated by reduction of the THF volume by *ca.* 50% followed by addition of *n*-hexane (2–3 ml). *Spectroscopic data* for PhCH(Bcat)CH(Me)(Bcat) in C_6D_6: ^1H NMR, δ 1.12 (d, 3 H, J 7.5 Hz), 2.39 (dq, 1 H, J 11.4, 7.5 Hz), 3.05 (d, 1 H, J 11.4 Hz), 6.69 (m, 4 H), 6.88 (m, 4 H), 7.02 (m, 1 H), 7.14 (m, 2 H), 7.29 (m, 2 H). $^{11}B\{^1H\}$ NMR, δ 35.6 (br s, 2B). HRMS. Calc. for $C_{21}H_{18}B_2O_4$: m/z 356.1391. Found m/z 356.1391.

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