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Small bite-angle 2-phosphinophosphinine ligands enable rhodium-catalysed hydroboration of carbonyls†

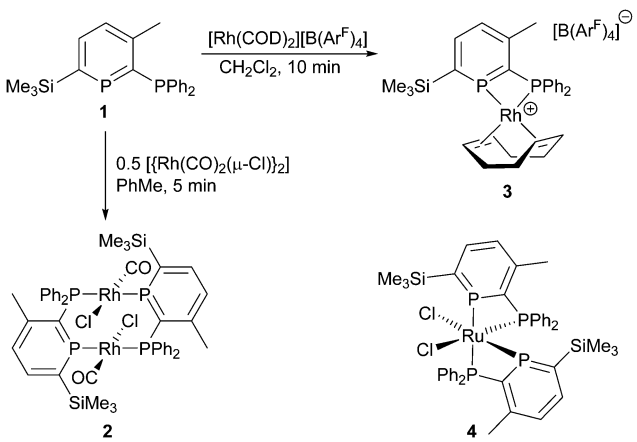
Robert J. Newland, [a] Jason M. Lynam [b] and Stephen M. Mansell *[a]

Two Rh complexes of the 2-phosphinophosphinine ligand 2-PPh_2-3-Me-6-$SiMe_3$-C_5H_2P (1) were prepared: dinuclear *trans*-[{Rh(CO)(Cl)(μ-1)}$_2$] (2) and chelating [Rh(1)(COD)][$B(Ar^F)_4$] (3). Despite the widespread use of Rh catalysts for the hydroboration of alkenes, 3 is reported to be the first Rh catalyst for ketone and ketimine hydroboration, with high activity observed at 0.1 mol% loading.

The catalytic hydroboration of carbonyl substrates[1] is of current interest due to the importance of the controlled reduction of carbonyls to alcohols under mild conditions and the considerable safety advantages over the use of stoichiometric metal hydrides and catalytic hydrogenation.[2] Transfer hydrogenation is an alternative reaction for the reduction of ketones, however, many catalysts require forcing conditions to achieve acceptable conversion.[3] There has been a great deal of interest in developing catalysts for the hydroboration of carbonyl compounds, with catalysts based on s-block (*e.g.* Li,[4] Na,[5] Mg[6]) and p-block (*e.g.* B,[7] Al,[8] Ge, Sn[9]) elements, as well as first-row (*e.g.* Ti,[10] Mn,[11] Fe,[12] Ni[13]), group 6 (Mo[14]) and late (Re,[15] Ru[16]) transition metals recently reported. Despite the prevalence of Rh catalysts for the hydroboration of alkenes,[17] to the best of our knowledge, there has been only one stoichiometric example of the use of a Rh complex in the hydroboration of a carbonyl compound (benzaldehyde) reported in the literature to date.[18] ‡ Based on the wide variety of hydroboration catalysts, and the wide-spread use of Rh catalysts in alkene hydroboration, its absence in carbonyl hydroboration was unexpected.

The use of phosphinine (the P-analogue of pyridine) ligands in catalysis is a growing field[19] with many recent contributions by Müller and co-workers in particular.[20] With regards to Rh catalysis, Breit developed the use of mono- and multidentate phosphinine ligands for hydroformylation catalysis that highlighted several advantages of these unusual ligand systems in an industrially valuable reaction over classical ligands such as PPh_3.[21] Small bite-angle ligands have become an increasingly popular choice in catalysis,[22] and our interests lie in the development of catalysts using small bite-angle 2-phosphinophosphinine ligands (Scheme 1, **1**) due to their unique properties.[19] In particular, the increased s-character (*ca.* 61%)[23] of the formally sp^2 phosphorus atom can lead to less-strained four-membered chelates. Evidence for this was observed in the chelating Ru complex *cis*-[Ru(**1**)$_2$(Cl)$_2$] (**4**),[24] as well as in a series of κ^2 group 6 tetracarbonyl complexes.[25] With the increasing popularity of small bite-angle ligands in homogeneous catalysis,[22] developing ligands that are less likely to form bridging architectures is highly desirable.

Initially, we probed the coordination properties of **1** using [{Rh(CO)$_2$(μ-Cl)}$_2$] (Scheme 1). A rapid reaction was observed affording a deep purple solution and the expected evolution of carbon monoxide. Crystalline **2** precipitated in 63% yield and was characterised as a bridged dinuclear complex by multinuclear



Scheme 1 Synthesis of Rh complexes of **1**, and the structure of **4**.

[a] *Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK. E-mail: s.mansell@hw.ac.uk; Web: www.mansellresearch.org.uk*

[b] *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*

† Electronic supplementary information (ESI) available: Additional synthetic details, analytical data and crystallographic data in CIF format. Additional research data supporting this publication are available from Heriot-Watt University's research data repository at DOI: 10.17861/14c23fe6-bc65-4806-ba5e-63642a6ad3e9. CCDC 1822415 and 1822416. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc01880d

NMR spectroscopy, high-resolution mass spectrometry, IR spectroscopy, X-ray diffraction and elemental analysis. $^{31}P\{^{1}H\}$-NMR spectroscopy revealed the formation of a single product with two apparent doublet-of-triplets resonances (Fig. S2 and S3, ESI†) observed at δ = 250.6 ppm (phosphinine P) and 25.5 ppm (PPh_2) that were successfully simulated (ESI†). Although a chelating complex was not achieved, **2** did facilitate comparisons to dppm and other diphosphines using the resulting carbonyl stretching frequency.[26] FTIR spectroscopy revealed a single carbonyl stretch at ν = 1977 cm^{-1} which correlates with **1** being a more π-accepting ligand than dppm (ν = 1968 cm^{-1} for the analogous complex).[26] The molecular structure of **2** (Fig. 1) displayed two bridging ligands with the CO and Cl ligands disordered across two positions. The $Rh_2(PCP)_2$ unit is non-planar, and has a dihedral angle for P(1)–Rh(1)–Rh(2)–P(2) of 16.88(4)°. Whilst stable in the solid state, **2** appears to be unstable in solution after prolonged periods or when heated (Fig. S11, ESI†).

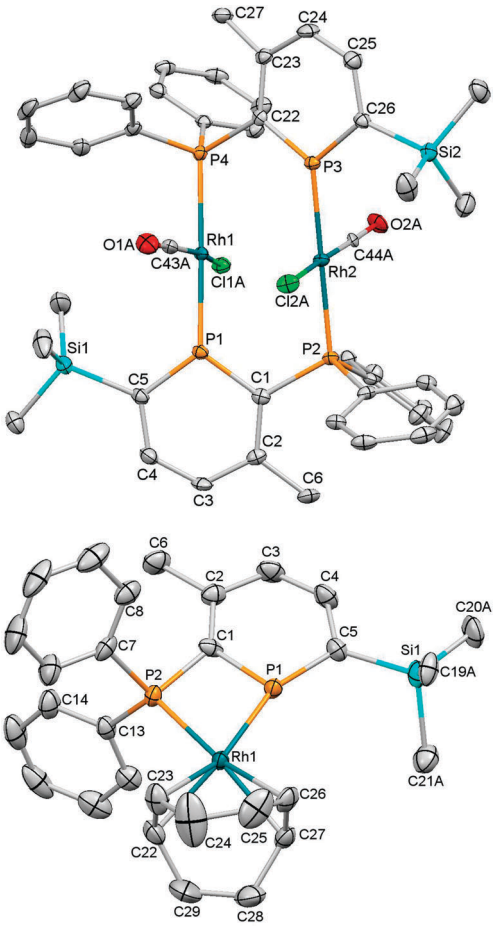


Fig. 1 Thermal ellipsoid plots (50%) of the molecular structures of **2** (top) and **3** (bottom, $B(Ar^F)_4$ anion excluded for clarity). Selected bond distances (Å) and angles (°) for **2**: P(1)–Rh(1) 2.2845(9), P(2)–Rh(2) 2.3228(10), P(1)–C(1) 1.734(4), C(1)–C(2) 1.411(5), C(2)–C(3) 1.402(5), C(3)–C(4) 1.386(5), C(4)–C(5) 1.394(5), C(5)–P(1) 1.725(3), C(1)–P(2) 1.844(3), C(1)–P(1)–C(5) 107.6(2), P(1)–C(1)–P(2) 114.9(2); For **3**: P(1)–Rh(1) 2.2932(8), P(2)–Rh(1) 2.2941(7), P(1)–C(1) 1.732(3), C(1)–C(2) 1.397(4), C(2)–C(3) 1.397(5), C(3)–C(4) 1.385(5), C(4)–C(5) 1.409(4), C(5)–P(1) 1.723(3), C(1)–P(2) 1.801(3), C(1)–P(1)–C(5) 106.9(2), P(1)–C(1)–P(2) 97.3(1), P(1)–Rh(1)–P(2) 70.64(3).

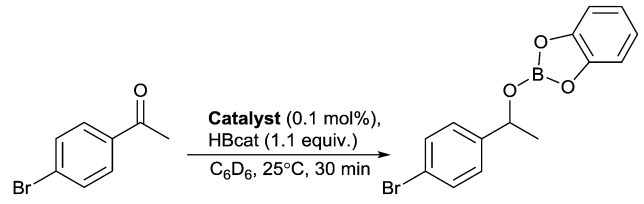
Monodentate phosphinine ligands have been structurally characterised binding to Rh in *trans*-$[Rh(CO)(L)_2Cl]$,[21d] $[Rh(L)_2(COD)]^+$,[27] and homoleptic $[Rh(L)_4]^+$ complexes (see ESI†).[21c] Rh complexes with tri-[28] and tetraphosphinine[29] ligands have also been structurally characterised (see ESI†).

In order to develop a mononuclear complex with a bidentate phosphinophosphinine ligand, a chelating co-ligand was utilised. Typically, sterically bulky ligands, such as dcpm (bis(dicyclohexylphosphino)methane),[30] are required to stabilise small bite-angle cationic $[Rh(diphosphine)(COD)]^+$ complexes[31] due to the Thorpe–Ingold effect,[22] and no chelating $[Rh(dppm)(COD)]^+$ complexes have been structurally characterised. Our initial efforts focused on reaction of **1** with $[\{Rh(COD)(\mu\text{-}Cl)\}_2]$ in the presence of a silver salt ($AgBF_4$, $AgSbF_6$) in CH_2Cl_2.[32] However, we observed multiple products, even with slow addition of **1** using dilute conditions. We were inspired by the use of a bis(cyclooctadiene) complex of Rh using the weakly coordinating anion $B(Ar^F)_4$ (tetrakis[3,5-bis(trifluoromethyl)phenyl]borate),[33] and observed a rapid reaction of this precursor with **1**, forming a single air-stable product in an 80% yield (Scheme 1). Complex **3** was characterised by X-ray diffraction, multinuclear NMR spectroscopy, high-resolution mass spectrometry and elemental analysis. $^{31}P\{^{1}H\}$-NMR spectroscopy revealed two sets of apparent doublets-of-doublets at δ = 189.4 ppm and −6.8 ppm. The clean formation of **3** and its stability is noteworthy with such an acute P–Rh–P bite angle of 70.64(3)° despite the minimal steric bulk on both donors.§ With two complexes in hand, and as there were no previous reports of Rh-catalysts for carbonyl hydroboration in the literature, a catalyst screen of Rh complexes and common phosphine ligands was conducted using 4′-bromoacetophenone and catecholborane (Table 1).

An initial test using 0.1 mol% **3** (run D) gave rapid conversion to the boronate ester, with a 94% yield observed within ten minutes and the reaction essentially complete after 30 minutes. A dramatic decrease in yield was observed when either the free ligand **1** (run B)¶ or complexes **2** and **4** were used (runs C and E), although **2** still proved to be more active than other Rh precursor/ligand combinations that were tested, including Wilkinson's catalyst (run F), which is a standard catalyst for alkene hydroboration.[17b,f] Only mixtures of $[Rh(COD)_2]$ $[B(Ar^F)_4]$ or $[\{Rh(COD)Cl\}_2]$ and PCy_3 (tricyclohexylphosphine, runs G and H respectively) gave higher than a 10% yield. Tests using $[Rh(COD)_2][B(Ar^F)_4]$ with less σ-donating PPh_3 and dppm ligands in a 1 : 2 or 1 : 1 ratio respectively (runs I and J) gave similar, low yields. Finally, to test if the π-accepting properties of **1** were the source of the increased activity of **3**, $P(OPh)_3$ (run K) was tested, however, a similar low yield was obtained.

Having established the catalytic activity of **3**, a screen of readily available acetophenone derivatives was carried out (Table 2). With the substrates tested, clean formation of the desired boronate ester was observed, with the exception of 4′-methoxyacetophenone, which produced multiple unidentified products (see Fig. S51, ESI†). Complex **3** also acted as a catalyst for the hydroboration of benzaldehyde, although the uncatalysed reaction also proceeds readily. Ketimines were then tested as more challenging substrates, and although room temperature reactions proceeded

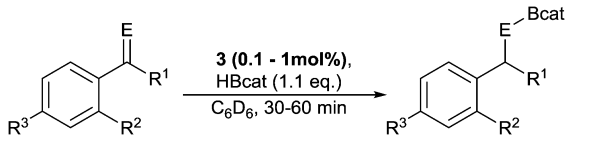
Table 1 Catalyst screen for Rh-catalysed hydroboration of a ketone



Run	Catalyst	Yield[c,d] (%)
A	—	1
B	**1**	20
C	**2**	35
D	**3**	96
E	**4**	12
F	$[Rh(PPh_3)_3Cl]$	3
G	$[Rh(COD)_2][B(Ar^F)_4]$ + 2 PCy_3[a]	22
H	0.5 $[\{Rh(COD)Cl\}_2]$ + 2 PCy_3[b]	18
I	$[Rh(COD)_2][B(Ar^F)_4]$ + 2 PPh_3[a]	7
J	$[Rh(COD)_2][B(Ar^F)_4]$ + dppm[a]	7
K	$[Rh(COD)_2][B(Ar^F)_4]$ + 2 $P(OPh)_3$[a]	6

[a] Premixed in THF (~0.1 ml) for 10 min before reaction. [b] Premixed in C_6D_6 (~0.1 ml) for 10 min before reaction. [c] Yield measured against 1,3,5-trimethoxybenzene internal standard. [d] Complete ^{1}H-NMR data for all catalytic runs available (ESI). Cat = catecholate: 1,2-$(O)_2C_6H_4$.

Table 2 Hydroboration of acetophenone derivatives, benzaldehyde and imines



				Yield[d] (%)		
E	R^1	R^2	R^3	10 min	30 min	60 min
O[a]	CH_3	H	H	91	97	—
O[a]	CH_3	H	Br	94	96	—
O[a]	CH_3	H	F	97	>99	—
O[a]	CH_3	H	NO_2	95	98	—
O[a]	CH_3	H	CH_3	66	90	92
O[a]	CH_3	OCH_3	H	97	99	—
O[b]	H	H	H	52	75	86
O[a]	H	H	H	95	>99	—
N-Ph[c]	CH_3	H	H	—	—	86
N-Ph[c]	CH_3	H	F	—	—	86
N-Ph[c]	CH_3	H	CH_3	—	—	85
N-(*p*-NO_2-C_6H_4)[c]	CH_3	H	H	—	—	16

Conditions: **3**, substrate (0.43 mmol), catecholborane (0.47 mmol, 1.1 eq.), C_6D_6 (0.6 cm^3). [a] 0.1 mol% **3**, 25 °C. [b] No catalyst, 25 °C. [c] 1 mol% **3**, 50 °C. [d] Yields measured against 1,3,5-trimethoxybenzene internal standard. Cat = 1,2-$(O)_2C_6H_4$.

slowly, heating to 50 °C achieved acceptable yields within 1 hour. However, heating the reaction further gave no observable increase in yield. In contrast to the carbonyl substrates, installation of an electron-donating or withdrawing substituent on the C–Ar ring made little difference to the obtained yield, whereas the presence of a nitro-group on the N–Ar substituent severely hindered the reaction.

Complex **3** was also a competent catalyst for the hydroboration of the N-heterocycles acridine and quinoline, and was shown to be active in the catalytic hydrogenation of styrene and cyclohexene (see ESI† for details).

In conclusion, we have synthesised and characterised the first two Rh complexes of a 2-phosphinophosphinine. Both were tested in the catalytic hydroboration of 4′-bromoacetophenone as well as a previously reported ruthenium phosphinophosphinine complex, Wilkinson's catalyst and a series of commonly used phosphine ligands. The results clearly demonstrated that significant activity is only observed for the chelating complex **3**, with high catalytic activity observed for several acetophenone derivatives at 0.1 mol% catalytic loading. Hydroboration of the more challenging *N*-phenyl ketimine substrates was also achieved, with good conversion in 1 hour at 1 mol% loading. Control reactions showed that simple electronic or bite-angle effects, as shown by the poor activity of different conventional monophosphine ligands and dppm, do not explain this catalytic activity. Future work will look to identify whether metal–ligand cooperativity or the hybrid nature of the ligand is playing a key role in generating highly active Rh catalysts.

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Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

‡ No catalysts for the hydroboration of ketones were mentioned in several key reviews[1,17g,34] or in additional thorough searches of the literature. Results by Männig & Nöth indicate that hydroboration of aliphatic ketones proceeds selectively over alkene hydroboration without a catalyst,[17a] however, this is not the case for aryl ketones at 25 °C (run A, Table 1). Evans & Hoveyda demonstrated that hydroboration of β-hydroxyketones in the presence of catalytic amounts (5 mol%) of Wilkinson's catalyst provides some measure of increased diastereocontrol, however, no improvements in reaction rate or conversion were observed.[35] Westcott *et al.* demonstrated the Rh catalysed hydroboration of aldimines with HBCat,[36] but it was previously reported that bulkier *N*-phenyl aldimines can react rapidly with HBCat without the need for a catalyst.[37]

§ For a histogram of Rh(κ_2-PEP) bite angles of entries found in the CSD (E = C, N, O), see Fig. S24 (ESI†).

¶ Thus confirming that the high yield observed for **3** was not a result of the ligand dissociating during the catalytic run. With 0.1 mol% **1**, the reaction gave a 95% yield after 14 hours. Upon mixing **1** and HBCat in C_6D_6, no Lewis adduct was observed.

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