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Coinage metal-catalyzed hydroboration of imines ☆

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Abstract

The preparation of several new coinage metal complexes containing bulky, chelating bis(phosphine) ligands is described. The molecular structures of $[AuCl(\mu\text{-DiPPE})]_n$ (**4**), $[Cu(\mu\text{-Cl})(DHP)]_2$ (**6a**), and $[Au(DHP)(PEt_3)]Cl$ (**8**) have been determined (DiPPE = 1,2-bis(diisopropylphosphino)ethane, DHP = deerhead phosphine, *o*-phenylenebis(diisopropylphosphine). These new complexes are selective catalysts for the hydroboration of imines and thiazolines using catecholborane. The molecular structure of $\overrightarrow{NHPhCH_2C_6H_4O(Bcat)}$ (**11**) is also reported.

Keywords: Boron; Hydroboration; Phosphines; Coinage metals; Imine; Catalysis

1. Introduction

Reduction of imines to form secondary amines can be accomplished using a number of reagents such as $Mg(OMe)_2$, $LiAlH_4$ and $NaBH_4$ [1]. While homogeneous catalytic hydrogenation [2,3] and hydrosilation [4] have also been employed extensively for this transformation, relatively few reports on imine hydroborations have appeared [5] and none has addressed the metal-catalyzed variant. Recent work has demonstrated the utility of metal-catalyzed hydroborations using catecholborane (HBcat, $1,2\text{-}O_2C_6H_4$) for altering and/or controlling selectivity of alkene reductions [6]. The effectiveness of a metal complex as a hydroboration catalyst is highly dependent upon the nature of the substrate. For a large variety of alkenes, zwitterionic $Rh(P\text{-}P)(\eta^6\text{-catBcat})$ catalysts rule [7] (P-P = chelating diphosphine ligand), whereas Pd phosphine complexes are optimal for thioalkynes [8] and dienes [9], and cationic Ir complexes have been used for directed hydroborations [10]. We recently prepared a series of coinage metal complexes with bulky, electron-rich phosphines and, given the affinity of coinage metal complexes for nitrogen ligands [11], we are investigating these new complexes as hydroboration catalysts for imines. Our initial results are described herein.

2. Experimental

General procedures are given elsewhere [12]. NMR spectra were obtained using a GE Charm narrow-bore spectrometer (301 MHz ^1H, 121 MHz ^{31}P, 75.4 MHz ^{13}C and 96.4 MHz ^{11}B). Chemical shifts are positive downfield from external $SiMe_4$ (^1H, ^{13}C), 85% H_3PO_4 (^{31}P) and $BF_3 \cdot Et_2O$ (^{11}B). Coinage metal halides, AuCl(L) (L = CO, PEt_3), and alkenes were obtained from commercial sources and used as received. Imine substrates [13] and chelating phosphines DiPPE [14] and DHP [15] were prepared according to published procedures. Elemental analysis was performed by Mikroanalytisches Labor Pascher, Remagen, Germany.

2.1. Synthesis

2.1.1. Reactions of MCl (M = Cu, Ag) with DiPPE: generation of $MCl(DiPPE)_n$ [n = 0.5, M = Cu (1); n = 1, M = Cu, Ag (2a,b); n = 2, M = Ag (3a)]

A solution of 135 mg (0.5 mmol) of DiPPE in 0.5 ml of THF-d_8 (or CD_2Cl_2) was added to a suspension of 100 mg (1.0 mmol) of CuCl in 0.5 ml of THF-d_8 (or

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CD_2Cl_2). After 30 min the resulting colorless solution was analyzed by ^1H and ^{31}P NMR spectroscopy. A second aliquot of DiPPE was then added and the resulting colorless solution reexamined by NMR. ^1H NMR: **1** (THF-d_8) δ 2.01 (mult, 4H, *CH*), 1.73 (br s, 4H, CH_2), 1.21 (mult, 24H, CH_3). **2a** (CD_2Cl_2) δ 2.06 (br mult, 4H, *CH*), 1.73 (br s, 4H, CH_2), 1.21 (br mult, 24H, CH_3).

Analogous experiments using 73 mg (0.5 mmol) of AgCl gave similar colorless solutions which were characterized by ^{31}P NMR (Table 2).

2.1.2. Preparation of [AuCl(μ-DiPPE)]$_n$ (4) and generation of [Au(DiPPE)$_2$]Cl (3b)

A solution of 135 mg (0.5 mmol) of DiPPE in 2 ml of THF was added to a solution of 130 mg (0.5 mmol) of AuCl(CO) in 2 ml of THF. After 4 h, the resulting colorless solid was collected by filtration, washed with 2 ml of THF and 5 ml of pentane and dried in vacuo to give 187 mg **4** (76%). Solutions of **3b** were generated by addition of two equivalents of DiPPE to either AuCl(CO) or AuCl(PEt_3) in CD_2Cl_2 and were characterized spectroscopically. ^1H NMR in CD_2Cl_2: **4** δ 2.45 (s, 4H, CH_2), 2.37 (mult, 4H, *CH*), 1.26 (mult, 24H, CH_3). **3b** δ 2.10 (br mult, 4H, *CH*), 1.83 (br s, 4H, CH_2), 1.11 (br mult, 24H, CH_3).

2.1.3. Reactions of MCl (M = Cu, Ag) with DHP: generation of (CuCl)$_2$(μ-DHP) (5), [Cu(μ-Cl)(DHP)]$_2$ (6a), [AgCl(DHP)]$_x$ (6b), and [Ag(DHP)$_2$]Cl (7a)

A solution of 155 mg (0.5 mmol) of DHP in 0.5 ml of THF-d_8 was added to a suspension of 100 mg (1.0 mmol) of CuCl in 0.5 ml of THF-d_8. After 30 min the resulting yellow solution was analyzed by ^1H and ^{31}P NMR spectroscopy. A second aliquot of DHP was then added and the resulting yellow solution reexamined. Slow evaporation of the solvent afforded pale yellow crystals of **6a**. ^1H NMR in CD_2Cl_2: **5** δ 7.6, 7.5 (br, 2H, Ph), 2.3 (br, 4H, *CH*), 1.30, 0.94 (mult, 12H, CH_3). **6a** δ 7.70, 7.54 (br, 2H, Ph), 2.34 (br, 4H, *CH*), 1.58, 1.28 (br, 12H, CH_3).

Analogous experiments using 73 mg (0.5 mmol) of AgCl gave colorless solutions which were characterized by ^{31}P NMR.

2.1.4. Generation of [Au(DHP)$_2$]Cl (7b) and preparation of [Au(DHP)(PEt$_3$)]Cl (8)

A solution of 155 mg (0.5 mmol) of DHP in 2 ml of THF was added to a solution of 175 mg (0.5 mmol) of AuCl(PEt_3) in 10 ml of THF. After 4 h, the solution was concentrated to 2 ml and the resulting colorless solid was collected by filtration, washed with 5 ml of pentane and dried in vacuo to give 238 mg **8** (72%). ^1H NMR in CD_2Cl_2: δ 7.37, 7.11 (mult, 2H, Ph), 2.17 (mult, 4H, *CH*), 1.81 (d q, $^2J_{HP} = {}^3J_{HH} = 7.5$, 6H, CH_2 of PEt_3), 1.12 (d tr, $^3J_{HP} = 18$, $^3J_{HH} = 7.5$, 9H, CH_3 of PEt_3), 1.32, 0.84 (mult, 12H, CH_3). Solutions of **7b** were generated by addition of one equiv. of DHP to **8** in CH_2Cl_2 and characterized by ^{31}P NMR.

2.1.5. Hydroboration of imines

To a solution of imine (0.5 mmol) **9a–d** in 0.5 ml of THF-d_8 was added a solution of HBcat (60 mg, 0.5 mmol) in 0.5 ml of THF-d_8. The resulting yellow solutions were stirred for 0.5 h and then analyzed by high-field NMR spectroscopy. In uncatalyzed hydroborations, solutions became colorless upon conversion of adducts **10a–c** to reduction products **11a,b** and **12**. Catalyzed reactions had 5 mol% of metal complex in the solution containing the imine.

Spectroscopic data for **10a** in THF-d_8: ^1H NMR δ 8.97 (s, *CH*), 7.6–7.0 (ov mult, 14H, Ph and cat), 5.10 (s, 2H, CH_2). ^{11}B NMR 19.2 ppm (d, $J_{BH} = 165$ Hz).

Spectroscopic data for **11a** in THF-d_8: ^1H NMR δ 7.3–7.2 (ov m, 10H, Ph), 7.04, 6.91 (mult, 2H, cat), 4.13 (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR 150.3 (2C, *ipso* of cat), 139.7 (2C, *ipso* of Ph), 129.4, 129.0 (4C, *o*- and *m*- of Ph), 128.0 (2C, *p*- of Ph), 122.7, 112.4 (2C, cat), 48.5 (2C, CH_2). $^{11}B\{^1H\}$ NMR 26.4 ppm.

Spectroscopic data for **11b** in THF-d_8: ^1H NMR δ 7.4–6.8 (ov m, 14H, Ph and cat), 4.87 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR 149.8 (2C, *ipso* of cat), 145.6 (*ipso* of N-Ph), 140.5 (*ipso* of Ph), 129.6, 129.3 (2C, *o*- and *m*- of Ph), 127.9 (*p*- of Ph), 122.7, 124.2 (2C, *o*- and *m*- of N-Ph), 123.5 (*p*- of N-Ph), 112.9, 112.5 (2C, CH of cat). $^{11}B\{^1H\}$ NMR 26.0 ppm

Spectroscopic data for **12** in THF-d_8: ^1H NMR δ 8.47 (br t, 4, NH), 7.39 (d, 8, 2H of Ph), 7.1–7.25 (ov mult, 4H of Ph), 7.05 (d, 6, ^1H of Ph), 6.8–6.9 (ov mult, 2H of Ph), 6.4–6.5 (ov mult, 4H of cat), 4.61 (br, 2H, CH_2). $^{13}C\{^1H\}$ NMR 155.8 (*ipso* of N-Ph), 152.8 (2C, *ipso* of cat), 141.2, (*ipso* of Ph), 129.9 (*ipso* of O-Ph), 129.7, 123.7 (2C, *o*- and *m*- of N-Ph), 130.1, 128.3, 127.6, 119.4 (CH of Ph), 120.2 (*p*- of N-Ph), 119.4, 109.7 (2C, CH of cat), 52.3 (CH_2). $^{11}B\{^1H\}$ NMR 8.2 ppm. Anal. Calc. for **12** · THF, $C_{23}H_{24}BNO_4$: C, 70.97; H, 6.21; N, 3.60; B, 2.78. Found: C, 70.89; H, 6.01; N, 3.86; B, 2.53.

2.1.6. Determination of relative hydroboration rates

To a solution of 0.5 mmol imine and 0.005 mmol catalyst in 0.5 ml of THF-d_8 cooled at 10 °C were added 500 μl of a 1 M solution of HBcat in THF-d_8. The hydroboration was monitored by ^1H NMR at 10 °C over several half lives and the results were normalized to give an estimate of the relative hydroboration rates. The estimated relative rate for [AuCl(μ-DPPF)]$_n$ is a lower limit due to limited catalyst solubility. Although detailed comparisons were not made for all catalysts, the hydroboration rate using [AuCl(μ-DiPPE)]$_n$ in CD_2Cl_2 was approx. 5-times faster than that in THF-d_8.

2.1.7. Hydroboration of 2-Me-2-thiazoline (13) and 2-Et-2-oxazoline (17)

To a solution of **13** or **17** (0.5 mmol) in 0.5 ml of THF-d_8 was added a solution of HBcat (60 mg, 0.5 mmol) in 0.5 ml of THF-d_8. The resulting yellow solutions were stirred for 0.5 h and then analyzed by high-field NMR spectroscopy; the spectra were recorded again after 20 h. Catalyzed reactions had 5 mol% of metal complex in the solution containing the imine. Reactions of **13** and **17** with 2 equiv. of HBcat were also investigated by NMR spectroscopy.

Spectroscopic data for **14** in THF-d_8: ^{1}H NMR δ 6.70, 6.62 (mult, 2H of cat), 4.15 (tr, 8.5, SCH_2), 3.38 (tr, 8.5, NCH_2), 2.47 (s, CH_3). ^{13}C{^{1}H} NMR 153.0 (2 *ipso* C of cat), 118.2, 106.7 (2C of cat), 60.4 (SCH_2), 33.9 (NCH_2), 18.8 (CH_3). ^{11}B NMR −11.1 ppm (br s, $\Delta\nu_{1/2}$ = 405 Hz; 366 Hz upon decoupling).

Spectroscopic data for **15** in THF-d_8: ^{1}H NMR δ 7.05, 6.93 (mult, 2 CH of cat), 5.17 (q, 6.5, SCH), 3.97 (ddd, 9, 6, 3, SCH_2), 3.45 (ddd, 9, 11, 6, SCH_2), 3.05 (ddd, 10, 6, 3, NCH_2), 2.88 (ddd, 10, 11, 6, NCH_2), 1.50 (d, 6.5, CH_3). ^{13}C{^{1}H} NMR 150.9 (2 *ipso* C of cat), 120.7, 110.9 (2C of cat), 63.1 (SCH_2), 49.0 (SCH), 30.0 (NCH_2), 26.1 (CH_3). ^{11}B NMR 24.4 ppm (br s, $\Delta\nu_{1/2}$ = 195 Hz).

Spectroscopic data for **16** in THF-d_8: ^{1}H NMR δ 7.2–6.7 (ov mult, 8H of cat), 3.33 (tr, 7.5, SCH_2), 3.21 (q, 7, SCH_2), 2.69 (tr, 7.5, NCH_2), 1.16 (tr, 7, CH_3). ^{13}C{^{1}H} NMR 149.9, 149.1 (2C, *ipso* of cat), 122.7, 122.2, 112.4, 111.9 (2C of cat), 46.7 (SCH_2), 41.5 (SCH_2), 32.2 (NCH_2), 15.7 (CH_3). ^{11}B NMR 23.3 ppm (br s, $\Delta\nu_{1/2}$ = 675 Hz).

Spectroscopic data for **18** in THF-d_8: ^{1}H NMR δ 6.6–6.4 (ov mult, 4H of cat), 4.49 (tr, 10, OCH_2), 3.78 (tr, 10, NCH_2), 2.60 (q, 7.5, CH_2 of Et), 1.14 (tr, 7.5, CH_3 of Et). ^{11}B NMR −11.7 ppm (br s, $\Delta\nu_{1/2}$ = 500 Hz; 435 Hz upon decoupling).

Spectroscopic data for **19** in THF-d_8: ^{1}H NMR δ 7.2–7.0 (ov m, 4 CH of cat), 4.68 (tr, 10, 2H, OCH_2), 3.93 (tr, 10, 2H, NCH_2), 3.81 (tr, 6, OCHN), 2.70, 2.61 (mult, 1H, CH_2 of Et), 1.13 (tr, 7.5, CH_3 of Et). ^{11}B NMR 26 ppm (br, $\Delta\nu_{1/2}$ = 310 Hz).

Spectroscopic data for **20** in THF-d_8: ^{1}H NMR δ 7.20, 7.07 (mult, 2H of cat), 7.14 (ov mult, 4H of cat), 4.41 (tr, 6, NCH_2), 3.61 (tr, 6, ring OCH_2), 3.35 (tr, 7.5, OCH_2), 1.78 (sextet, 7.5, CH_2), 1.09 (tr, 7.5,

Table 1
Summary of X-ray diffraction data

Complex	[Cu(μ-Cl)(DHP)]$_2$ (**6a**)	[AuCl(μ-DiPPE)]$_n$ (**4**)	[Au(PEt$_3$)(DHP)]Cl (**8**)	PhNHCH$_2$C$_6$H$_4$OBcat (**12**) · THF
Formula	$C_{36}H_{64}Cl_2Cu_2P_4$	$C_{14}H_{32}AuClP_2$	$C_{24}H_{47}AuClP_3$	$C_{23}H_{24}BNO_4$
fw	818.79	494.78	660.98	389.26
a (Å)	12.615(4)	11.229(1)	17.059(3)	12.105(2)
b (Å)	13.361(2)	15.151(2)	17.611(3)	12.239(3)
c (Å)	12.803(4)	12.068(2)	18.633(5)	13.980(2)
α (deg)	–	–	–	–
β (deg)	108.33(2)	112.07(1)	–	104.17(1)
γ (deg)	–	–	–	–
V (Å^3)	2048.4	1902.7	5597.8	2008.2
Z	2	2	8	4
ρ_{calcd} (g cm^{-3})	1.327	1.727	1.568	1.287
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
Crystal dimensions (mm)	0.16 × 0.11 × 0.05	0.28 × 0.18 × 0.40	0.18 × 0.43 × 0.49	0.39 × 0.30 × 0.45
Temp. (°C)	−150	−100	−70	−100
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	13.5	80.13	55.21	0.81
Data collection method	oscillation	ω-2θ	ω-2θ	ω-2θ
Max 2θ (deg)	*h*, *k*, *l* = 16, 17, 16	55.0	55.0	56.0
Scan speed (deg min^{-1})	–	3.90–14.60	1.50–5.00	4.90–11.70
Scan width (deg)	–	0.32 ω	0.16 ω	1.40 ω
Total no. of observations	4908	4743	7038	5272
No. of unique data $I > 3\sigma(I)$	3300	3421	3596	2089
Final no. of variables	327	74	263	262
Final max. shift/error	0.05	0.01	0.06	0.11
Max. residual density (e$^-$ Å^{-3})	0.49	3.36	0.92	0.36
R [a]	0.043	0.037	0.033	0.055
R_w [b]	0.028	0.039	0.028	0.049

[a] $\Sigma \| F_o - |F_c| \| / \Sigma |F_o|$.
[b] $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

CH_3). $^{13}C\{^1H\}$ NMR 150.0, 149.3 (2C, *ipso* of cat), 122.9, 122.4 (2CH of cat), 112.5, 112.1 (2CH of cat), 69.7 (ring OCH_2), 49.7 (OCH_2), 48.0 (NCH_2), 23.5 (CH_2), 11.6 (CH_3). $^{11}B\{^1H\}$ NMR 24.6 ppm (br s, $\Delta\nu_{1/2} = 580$ Hz).

2.2. X-ray structure analysis

Crystals suitable for X-ray diffraction were obtained as described above. A summary of the crystallographic results is presented in Table 1. All data sets were collected at low temperatures on Enraf-Nonius CAD4, Syntex R3, or Rigaku R-axis (area detector) diffractometers using graphite-filtered Mo radiation. Data were reduced in the usual fashion for Lorentz-polarization, and absorption corrections were applied for **4** (DIFABS [16] range of transmission factors = 0.09–0.26) and **8** (numerical integration, 0.18–0.48). Structure solution and refinement were performed on a VAX/IBM cluster system using a local program set. Heavy atom positions were obtained via automated Patterson analysis and used to phase reflections for the remaining light atoms via the usual combination of structure factor, Fourier synthesis, and full-matrix least-squares refinement. The structure of **12** was solved by direct methods (MULTAN [17]). All refinements were performed using full-matrix least squares on F, with anisotropic thermal parameters for all non-hydrogen atoms (except for **4**), and included anomalous dispersion terms [18] for Au, Cu, P and Cl, as well as idealized hydrogen coordinates as fixed atom contributors. For **4** the asymmetric unit consists of one gold chloride and two half-DiPPE ligands lying on different inversion centers. For **6a** the asymmetric unit consists of half the molecule related by an inversion center. For **8** the asymmetric unit consists of one molecule in a general position; methyl hydrogens were idealized in orientations taken from a difference map. For **12** the asymmmetric unit consists of one molecule in a general position with one THF of solvation. For acentric structures the enantiomorph was chosen on the basis of an R-value test. Tables of bond distances and angles, final positional and thermal parameters for non-hydrogen atoms, general temperature factors, calculated hydrogen atom positions and structure factor listings are available from the authors (J.C.C.).

3. Results and discussion

3.1. New coinage metal bis(phosphine) complexes

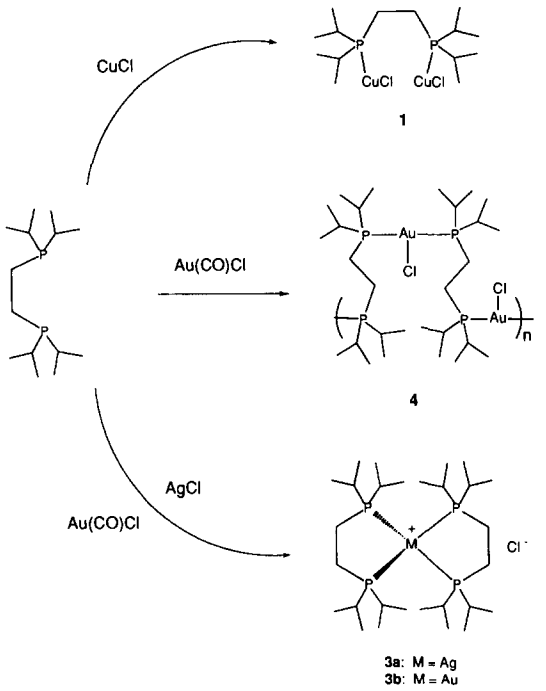
Electron-rich, chelating bis(phosphines) were used to stabilize the resulting coinage metal complexes against decomposition. While alkylated phosphines are known sometimes to act as reducing agents in these reactions [19], bulky ligands such as 1,2-bis(diisopropylphosphino)ethane (DiPPE) and *o*-phenylenebis(diisopropylphosphine) (DHP or deerhead [20] phosphine) should bind strongly to the d^{10} metal center [14] without formation of unreactive $[M(P\text{-}P)_2]^+$ cations such as those obtained with DMPE or analogous DIARS ligands (DMPE = 1,2-bis(dimethylphosphino)ethane and DIARS = *o*-phenylenebis(dimethylarsine)) [21].

The reactions were monitored by ^{31}P NMR spectroscopy (Table 2). Addition of 0.5 equiv. of DiPPE to CuCl in CD_2Cl_2 gave rise to a broad ^{31}P NMR resonance ($\Delta\nu_{1/2} = 180$ Hz) at 7.1 ppm due to $(CuCl)_2(\mu$-DiPPE) (**1**); broadening is caused presumably by quadrupolar coupling to ^{63}Cu ($I = 9/2$) as the ^1H NMR resonances are fairly narrow under these conditions. Upon addition of one or more equiv. of DiPPE to CuCl, however, both the ^1H and ^{31}P NMR spectra are broad, indicative of rapidly exchanging phosphine ligands presumably resulting from a mixture of oligomers,

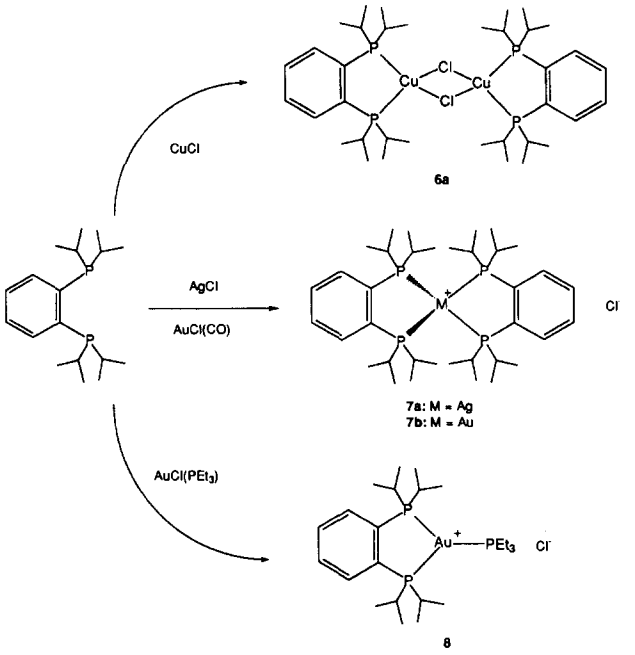
Table 2
$^{31}P\{^1H\}$ NMR spectra [a] of $MCl(P\text{-}P)_n$

M	n	P–P	No.	δ	$\Delta\nu_{1/2}$ (Hz)
Cu	0.5	DiPPE	**1**	7.1	180
Cu	1	DiPPE	**2a**	13.4	240
Cu [b]	0.5	DiPPE	**1**	4.9	240
Cu [b]	1	DiPPE	**2a**	11.2	120
Ag	1	DiPPE	**2b**	28.6	485
Ag	2	DiPPE	**3a**	17.5	90 (d, $J_{PAg} = 240$)
Au	1	DiPPE	**4**	75.5	55
Au	2	DiPPE	**3b**	40.0	25
Cu	0.5	DHP	**5**	7.2	85
Cu	1	DHP	**6a**	15.5	1940
Ag	1	DHP	**6b**	15.3	144
Ag	2	DHP	**7a**	17.1	5 (d, $J_{PAg} = 218$)
Au	2	DHP	**7b**	33.2	5
$[Au(DHP)(PEt_3)]Cl$			**8**	78.9	5 (d, $^2J_{PP} = 131$,2P)
				39.9	5 (tr)

[a] Recorded in CD_2Cl_2; [b] recorded in THF-d_8.



Scheme 1.



Scheme 2.

$[CuCl(DiPPE)]_x$ (**2a**). While similar results were obtained with a 1:1 ratio of DiPPE and AgCl to give **2b**, addition of two equiv. of DiPPE gave a doublet (J_{PAg} = 240 Hz) assigned to four coordinate $[Ag(DiPPE)_2]Cl$ (**3a**, Scheme 1).

Analogous reactions with Au(CO)Cl afforded the novel Au(I) polymer, $[AuCl(\mu\text{-DiPPE})]_n$ (**4**), which was characterized by single crystal X-ray diffraction. The metal center lies in a distorted T-shaped environment (P1–Au–P2 = 165.68 Å) with bridging adjacent DiPPE ligands forming an infinite chain (Fig. 1). The two independent Au–P distances are equivalent (2.301(1), 2.304(1) Å), although the P–Au–Cl angles are slightly different (98.76(5), 95.52(5)°). Comparison of the structure of **4** with the recently characterized $[AuCl(\mu\text{-DPPF})]_n$ polymer (DPPF = 1,1′-bis(diphenylphosphino)-ferrocene) shows the latter to be less distorted [22] (P–Au–P = 136.5(1), 143.0(2) and 155.2(1)° in the three polymorphs) with shorter Au–Cl distances (2.550(3), 2.624(9), and 2.709(2) Å vs. 2.822(2) Å in **4**). This correlation was noted previously [23] for the *trans*-spanning phosphine complexes, MCl(DPPBP) (M = Cu, Ag, Au; DPPBP = 2,11-bis(diphenylphosphinomethyl)-benzo[c]phenanthrene); the latter (P–Au–P = 175.7(1)°, Au–Cl = 2.818(3) Å) gives conducting solutions in polar solvents, indicative of linear $[AuL_2]^+$ cations.

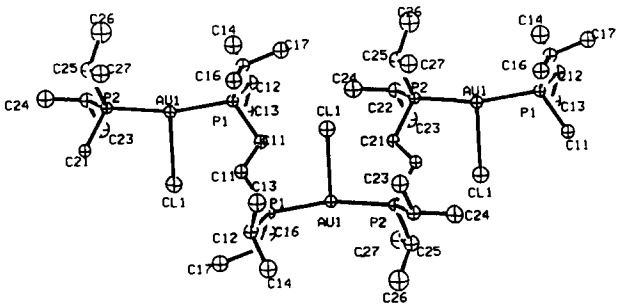


Fig. 1. The molecular structure of $[AuCl(\mu\text{-DiPPE})]_n$ (**4**) with hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–Cl(1) = 2.822(2), Au(1)–P(1) = 2.301(1), Au(1)–P(2) = 2.304(1), Cl(1)–Au(1)–P(1) = 98.76(5), Cl(1)–Au(1)–P(2) = 95.52(5), P(1)–Au(1)–P(2) = 165.68(6).

As for silver, treatment of **4** with additional phosphine gave four-coordinate $[Au(DiPPE)_2]Cl$ (**3b**). Tetrahedral Ag(I) and Au(I) complexes containing bis(phosphine) ligands are well established [24].

Reaction of CuCl with deerhead phosphine (DHP) gave both $(CuCl)_2(\mu\text{-DHP})$ (**5**) and dimeric $[Cu(\mu\text{-Cl})(DHP)]_2$ (**6a**), depending on the stoichiometry employed (Scheme 2). Although the ^{31}P NMR resonance of **6a** is very broad ($\Delta\nu_{1/2}$ = 1940 Hz), the broadening is due to quadrupolar effects, as the linewidth in the ^1H NMR spectrum depends on the distance from the Cu nucleus and no exchange is observed (on the NMR time scale) between **6a** and excess DHP. The molecular structure of **6a** was determined by X-ray diffraction (Fig. 2). The Cu–X distances ($Cu–P_{avg}$ = 2.2462(8) Å; $Cu–Cl_{avg}$ = 2.3647(7) Å) are comparable with other structurally characterized copper(I) phosphine complexes [25]. The bite angle (P1–Cu–P2 = 92.44(3)°) of the DHP ligand in **6a** is similar to that observed for the *cis*-1,2-bis(diphenylphosphino)ethylene (DPPEY) ligands in $[Cu(DPPEY)_2]PF_6$ (avg. 89.80(7)°) [24b] and for the DMPE ligands in $[Cu(DMPE)_2][Cu\{Co(CO)_4\}_2]$ (avg. 90.9(1)°) [21].

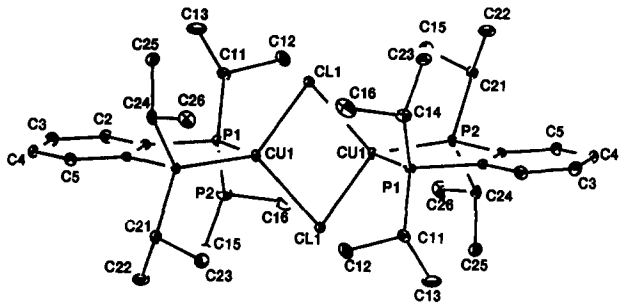


Fig. 2. The molecular structure of $[Cu(\mu\text{-}Cl)(DHP)]_2$ (**6a**) with hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–Cl1 = 2.3601(8), Cu1–Cl1a = 2.3692(7), Cu1–P1 = 2.2437(8), Cu1–P2 = 2.2486(8), Cu1–Cu1a = 3.0325(7), P1–Cu1–P2 = 92.44(3), P1–Cu1–Cl1 = 113.30(3), P1–Cu1–Cl1a = 114.79(3), P2–Cu1–Cl1 = 120.27(3), P2–Cu1–Cl1a = 116.76(3), Cl1–Cu1–Cl1a = 100.24(3).

Reactions of AgCl with DHP gave a broad ^{31}P NMR resonance due to $[Ag(Cl)(DHP)]_x$ (**6b**) and, with 2 equiv. of DHP, a sharp doublet ($J_{PAg} = 218$ Hz) assigned to tetrahedral $[Ag(DHP)_2]Cl$ (**7a**).

Addition of DHP to a solution of $Au(PEt_3)Cl$ in C_6D_6 gave monomeric species $[Au(DHP)(PEt_3)]Cl$ (**8**) as the major phosphine-containing species (95% by ^{31}P NMR). The molecular structure of **8** is shown in Fig. 3. The gold atom lies in a distorted trigonal environment coordinated to the bulky bis(phosphine) DHP as well as PEt_3 with P–Au–P angles that reflect the *ortho*-benzo constraint [17]. There is a slight perturbation of the gold towards the chloride ion, such that the Au atom is displaced 0.24 Å out of the P_3 plane. The Au–Cl distance is 3.073(2)Å, whereas the Au–Cl distance in polymer **4** is 2.822(2) Å. The DHP Au–P distances are slightly longer (approx. 0.10 Å) than that to the monodentate phosphine.

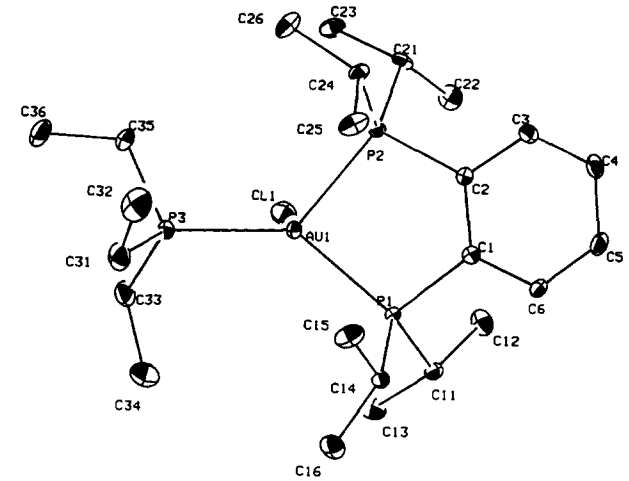


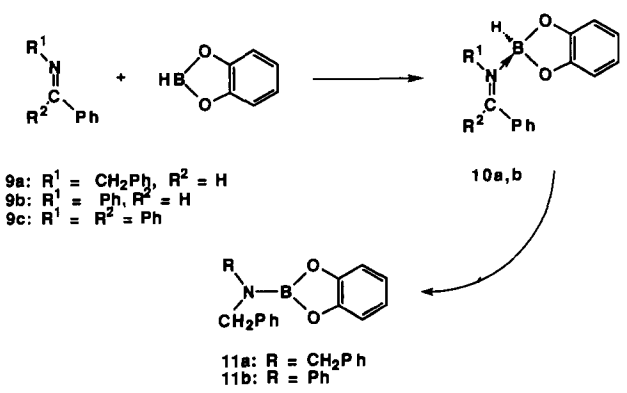
Fig. 3. The molecular structure of $[Au(DHP)(PEt_3)]Cl$ (**8**) with hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–P(1) = 2.366(2), Au(1)–P(2) = 2.394(1), Au(1)–P(3) = 2.296(2), Au(1)–Cl = 3.073(2), P(1)–Au(1)–P(2) = 87.82(5), P(1)–Au(1)–P(3) = 139.37(6), P(2)–Au(1)–P(3) = 129.16(6).

3.2. Hydroboration catalysis

Conventional late metal-catalyzed hydroborations [26] are believed to proceed via oxidative addition of HBcat followed by coordination of alkene to the metal center. Subsequent insertion into the M–H or M–B bond [27] and reductive elimination affords the hydroborated product. For $AuCl(PEt_3)$ and complexes **2a,b**, **4** and **8**, however, no reaction was observed with excess HBcat and simple alkenes are likely to bind reversibly to these d^{10} metal complexes [11]. Indeed, hydroborations of 4-vinylanisole with HBcat using **2a,b**, **4** and **8** did not give alkylboronate esters, but rather alkylborane products due to addition of BH_3 (from metal-promoted HBcat degradation) [7,12] to the alkenes.

In contrast, hydroborations of imines (substrates that can bind to Au through N) [11] using HBcat proceeded rapidly in the presence of a catalytic amount of coinage metal complexes **2a,b**, **4** and **8** to give the corresponding *N*-borylamines. No products arising from the degradation of HBcat were observed. In the absence of catalyst, addition of HBcat to imines **9a,b** initially gave yellow solutions due to small equilibrium amounts of the iminoborane adducts **10a,b**, which slowly reduced to the colorless *N*-borylamines **11a,b**. While the N-CH_2Ph iminoborane adduct **10a** was characterized by NMR spectrosocopy, the equilibrium amount of the bulkier N-Ph analogue **10b** was much smaller and its existence was inferred from the pale yellow color which faded upon formation of **11b**. No adduct formation or reduction was observed for the hindered trisubstituted imine $Ph_2C{=}NPh$ (**9c**).

In order to estimate the rate enhancement of the various catalysts, the hydroboration of **9a** was monitored at 10 °C using ^1H NMR spectroscopy (Table 3). While monochelate Cu complex **6a** showed significant rate enhancement, the analogous Au complexes were superior even to Wilkinson's catalyst, $RhCl(PPh_3)_3$, particularly with the less bulky 1,1'-bis(diphenylphosphino)ferrocene ligand. Qualitatively, we also noted that



Scheme 3.

Table 3
Relative rates of hydroboration of $PhCH_2N{=}CHPh$

Catalyst (1 mol%)	Relative rate [a]
None	1.0
$AuCl(PEt_3)$	2.0
$[Au(PEt_3)(DHP)]Cl$	3.7
$[Cu(\mu\text{-}Cl)(DHP)]_2$	4.8
$RhCl(PPh_3)_3$	10.3
$[AuCl(\mu\text{-DiPPE})]_n$	14.8
$[AuCl(\mu\text{-DPPF})]_n$	> 40

[a] Determined by ^1H NMR in THF-d_8 at 10°C.

excess chelate retarded the reaction while use of CH_2Cl_2 solvent gave significant rate enhancement.

Addition of HBcat to $[o\text{-}(HO)\text{-}C_6H_4]CH{=}NPh$ (**9d**) led rapidly to the novel heterocyclic compound $NHPhCH_2C_6H_4O(Bcat)$ (**12**), which has been characterized by multinuclear NMR spectroscopy as well as a single crystal X-ray diffraction study. The molecular structure of **12** (Fig. 4) features pseudotetrahedral nitrogen and boron centers. Initial hydroboration of the C=N functionality of **9d** followed by B–O bond formation and hydrogen transfer would afford complex **12** [5d].

We also examined the hydroboration of several cyclic imines. With 2-Me-2-thiazoline, addition of 1 equiv. of HBcat gives a mixture of the Lewis base adduct *N*-(BHcat)-2-Me-2-thiazoline (**14**) and the reduction product *N*-Bcat-2-Me-2-thiazolidine (**15**). The adduct **14** is quite stable and does not readily convert to **15** at 25 °C for 1 week. Two equiv. of HBcat gives the ring-opened product, $EtSCH_2CH_2N(Bcat)_2$ (**16**, Scheme 5).

The ^{11}B NMR spectrum of **14** contains a broad resonance to high field (−11 ppm) indicative of four-coordinate boron; the resonance sharpens somewhat upon ^1H decoupling. The ^1H NMR spectrum of **15** is

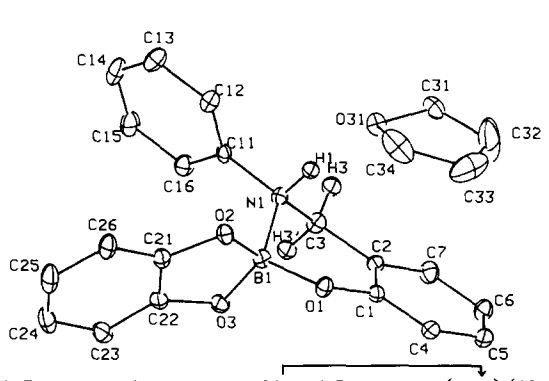
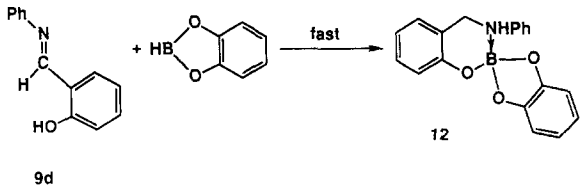
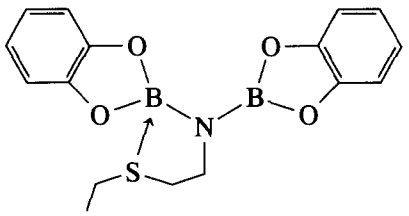


Fig. 4. The molecular structure of $NHPhCH_2C_6H_4O(Bcat)$ (**12**, THF solvate) with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): B(1)–N(1) = 1.636(4), B(1)–O(1) = 1.440(4), B(1)–O(2) = 1.452(4), B(1)–O(3) = 1.467(4), N(1)–C(3) = 1.492(4), N(1)–C(11) = 1.466(4), O(1)–B(1)–O(2) = 111.4(3), O(1)–B(1)–O(3) = 114.9(3), O(2)–B(1)–O(3) = 107.7(3), O(1)–B(1)–N(1) = 106.0(2), O(2)–B(1)–N(1) = 109.1(3), O(3)–B(1)–N(1) = 107.6(2), B(1)–N(1)–C(3) = 108.7(2), B(1)–N(1)–C(11) = 113.8(2), C(3)–N(1)–C(11) = 114.8(2).



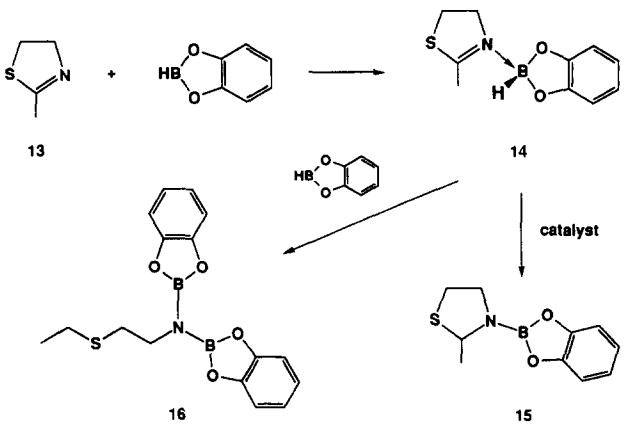
Scheme 4.

complex due to the heavily coupled diastereotopic ring protons. While the ^{11}B NMR spectrum of **16** contains a single broad resonance at 24 ppm, the ^1H and ^{13}C NMR clearly indicate two different catecholate environments which suggests the ring structure shown below.



Addition of 5 mol% of a metal phosphine complex catalyst enhanced the formation of the reduction product **15**. Although $RhCl(PPh_3)_3$ was an extremely active catalyst, selectivity for the hydroboration of **13** was poor, giving a complex mixture of **14**, **15** and **16** along with $[B(cat)_2]^-$ and some unidentified boron-containing products derived from the degradation of HBcat [12] (via ^{11}B NMR). While reactions employing gold catalysts were only moderately active, hydroborations using complex **8** gave predominant formation of *N*-borylamine product **15**, unobtainable in useful yields using conventional hydroboration techniques or a rhodium catalyst (see Table 4). Further addition of HBcat rapidly affords ring-opened product **16**.

Similar reactions with 2-Et-2-oxazoline (**17**) gave the the Lewis base adduct *N*(BHcat)2-Et-2-oxazoline (**18**) along with minor amounts of O-bound adducts and only a trace of the reduction product, *N*-Bcat-2-Et-2-oxazolidine (**19**); 2 equiv. of HBcat afforded the analo-



Scheme 5.

Table 4
Hydroboration of 2-Me-2-thiazoline

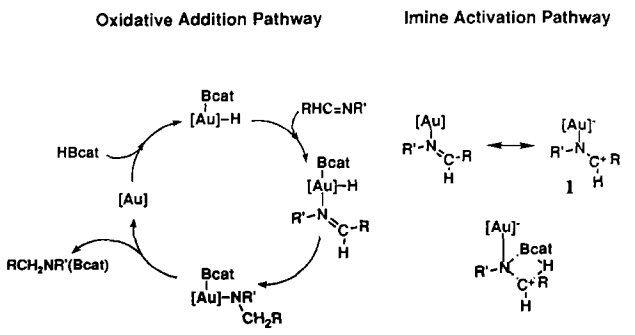
Catalyst	14/15
None	1.875
$[AgCl(DHP)]_x$	1.067
$[AuCl(\mu\text{-DiPPE})]_n$	0.833
$AuCl(PEt_3)$	0.467
$[Cu(\mu\text{-Cl})(DHP)]_2$	0.424
$RhCl(PPh_3)_3$	0.111
$[Au(PEt_3)(DHP)]Cl$	0.026

gous ring-opened product $CH_3(CH_2)_2O(CH_2)_2N(Bcat)_2$ (**20**). While catalyzed additions of HBcat to **17** gave significant amounts of **19**, useful selectivities were not obtained with the catalysts in Table 4.

3.3. Mechanistic considerations

Two possible mechanisms for the coinage metal-catalyzed hydroboration of imines are shown in Scheme 6. Mechanism A is analogous to that proposed for Rh catalysts involving oxidative addition of HBcat. While oxidative addition of Cl_2 to Au(I) phosphine complexes to give Au(III) complexes is known [28], as noted above no reaction was observed between HBcat and any of the coinage metal phosphine complexes **1–8**. Mechanism B, on the other hand, relies on the coinage metal phosphine complexes to activate the imine substrate via coordination through nitrogen. Development of positive charge on the imine carbon via resonance forms such as **I** increase its reactivity toward the $B^{\delta+}-H^{\delta-}$ bond of HBcat. This mechanism could also account for the greater reactivity of $[AuCl(\mu\text{-DPPF})]_n$ vs. the more electron-rich DiPPE analogue, as increased Lewis acidity of the gold center should enhance the activation of the coordinated imine. Unfortunately, attempts to utilize Au(III) precursors were unsuccessful due to reduction by catecholborane.

Further work will focus on examining the detailed mechanism of these coinage metal-catalyzed hydroborations as well as utilizing chiral gold phosphine complexes [29] for the asymmetric hydroboration of imines [30].



Scheme 6.

4. Conclusions

A number of new coinage metal complexes containing bulky, chelating bis(phosphine) ligands have been prepared. Several of these species are active catalyst precursors for the hydroboration of imines using catecholborane. Selectivities in hydroborations of thiazolines are complementary to those of the uncatalyzed variant. For both classes of substrates, gold phosphine complexes are superior to the commonly used alkene hydroboration catalyst, $RhCl(PPh_3)_3$.

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