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Wide bite angle diphosphine rhodium complexes: Synthesis, structure, and catalytic 1,4-addition of arylboronic acids to enones

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Abstract

A rhodium complex [ClRh(CO)(**L1**)] featuring a wide bite angle diphosphine ligand (**L1** = 1,3-bis(2-diphenylphosphinomethylphenyl)benzene) has been synthesized and structurally characterized. **L1** supports a bite angle (P–M–P angle, β) of 171.4° in the *trans*-square planar complex. **L1** was tested in Rh-catalyzed 1,4-addition reactions of arylboronic acids (six examples) to α,β-unsaturated ketones (five examples). In mixed aqueous/cyclohexane solution at 60 °C, addition reactions proceed in up to quantitative yield with a 1:1 arylboronic acid/enone ratio. Yields as high as 77% can be acquired even when one of the coupling partners is sterically encumbered 2,4,6-trimethylphenylboronic acid.

Keywords: Wide bite angle diphosphine; Rhodium; Conjugate addition; Arylboronic acid

1. Introduction

Catalytic processes mediated by transition metals are dramatically impacted by supporting ligands. Phosphines have been subject to particular scrutiny in this regard due to their utility in numerous functional group tolerant C–C bond-forming reactions. Consequently, a number of parameters are used to assist in the classification of phosphine properties most pertinent to their role in catalysis. Tolman cone angles [1] and molecular mechanics are used to quantify phosphine sterics [2,3] and various scales have been forwarded to describe phosphine electronics [4–11]. More recently, widespread application of bidentate P-donor ligands resulted in the introduction of a bite angle (P–M–P angle, β) [12] parameter that is applied to predict coordination modes. A definite correlation between bite angle and catalytic activity has been observed for numerous industrially important reactions [13–15]. This relationship has been particularly well studied for rhodium-catalyzed hydroformylation, where wide bite angles (greater than ~110°) can enhance activity and regioselectivity [16–18]. A number of scaffolds have been subsequently pursued to support wide bite angle diphosphines for use in catalysis [13,15,16,19–26]. Among the most well known wide bite angle diphosphines are those of the xantphos family (Fig. 1a). These ligands support high activity rhodium catalysts for hydroformylation, even with challenging substrates such as internal olefins. Xantphos has a natural bite angle of 111.7° [18], very close to the average P–M–P angle for all Xantphos complexes crystallographically characterized (104.6°), although a *trans*-spanning mode (P–M–P angle = 150.7°) is also attainable [27].

We are interested in flexible scaffolds for wide bite angle phosphines. Flexibility may be beneficial when a catalytic process requires a ligand to accommodate different geometries as its metal complex rearranges to form intermediates in the course of the mechanistic cycle. The *trans*-spanning "terphspan" diphosphine **L1** (Fig. 1b), for example, is built on a *m*-terphenyl scaffold capable of accommodating a range of bite angles. Crystallographically characterized pseudo-square planar palladium and nickel complexes

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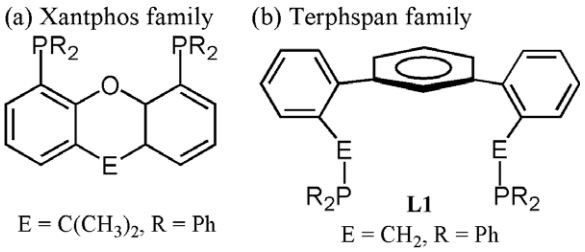


Fig. 1. Examples of wide bite angle diphosphines.

feature **L1** in a *trans*-spanning binding mode [28]. These complexes show high activity and regioselectivity in Suzuki and Heck coupling reactions, and cyclometallated palladacycle variations with C_2 symmetry are potential candidates for use in asymmetric catalysis [29,30].

Herein we describe the first rhodium complex employing this new class of wide bite angle phosphine and subsequent use of **L1** to support Rh-catalyzed 1,4-conjugate addition of aryl boronic acids to α,β-unsaturated ketones (Table 3).

2. Results and discussion

2.1. Synthesis and characterization

The first terphspan rhodium complex targeted for synthesis was [ClRh(CO)(**L1**)] (**1**). A convenient one-pot method, previously described for the preparation of *trans*-[ClRh(CO)(P(*t*-Bu)$_2$H)$_2$] [31], was selected for the preparation of **1**. The complex **1** was readily prepared in 43% yield by reacting $RhCl_3 \cdot 3H_2O$ with *N*,*N*-dimethylformamide (DMF) in the presence of **L1**, requiring generation of CO by thermal decomposition of the DMF. Compound **1** exhibits a C–O stretch in the IR spectrum at $\nu_{CO} = 1966\ cm^{-1}$, which compares well with the values observed in *trans*-[ClRh(CO)(PR$_3$)$_2$] complexes such as *trans*-[ClRh(CO)(PPh$_3$)$_2$] (1960 cm^{-1}) [31] and *trans*-[ClRh(CO)(P(*t*-Bu)$_2$H)$_2$] (1965 cm^{-1}) [32].

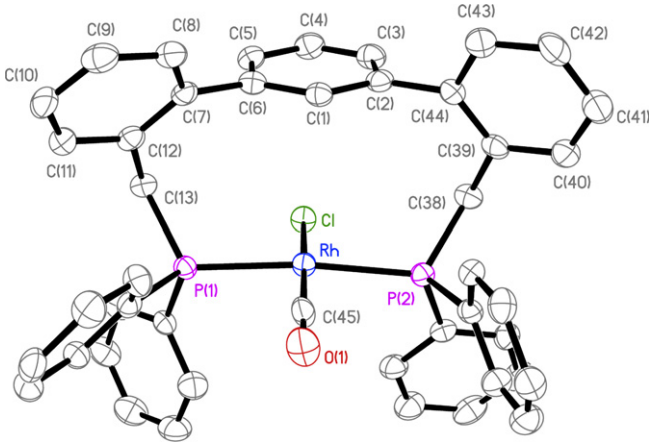


Fig. 2. ORTEP drawing (30% probability ellipsoids) of the molecular structure of **1**. Hydrogen atoms and the cocrystallized DMF solvent molecule are omitted for clarity.

Table 1
Crystal data and structure refinement details for **1** · DMF

Empirical formula	$C_{45}H_{36}ClOP_2Rh \cdot C_3H_7NO$
Formula weight (g/mol)	866.13
Temperature (K)	153 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{1/c}$
Unit cell dimensions	
a (Å)	18.623(4)
b (Å)	11.779(2)
c (Å)	18.629(4)
α (°)	90.00
β (°)	98.05(3)
γ (°)	90.00
Volume (Å^3)	4046.1(14)
Z	4
Calculated density (Mg/m^3)	1.422
Absorption coefficient (mm^{-1})	0.608
$F(000)$	1784
Crystal size (mm)	0.36 × 0.29 × 0.14
Crystal color and shape	Yellow plate
θ range for data collection (°)	2.05–25.10
Limiting indices	$-22 < h < 20$, $-14 < k < 14$, $-22 < l < 22$
Reflections collected	7182
Independent reflections	6016
Completeness to θ	25.10 (99.6%)
Maximum transmission	0.9197
Minimum transmission	0.8108
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7182/1/666
Goodness of fit on F^2	1.144
Final R indices ($I > 2\sigma(I)$)	
R_1	0.0489
wR_2	0.1182
R indices (all data)	
R_1	0.0604
wR_2	0.1273

The ^{1}H NMR spectrum of [ClRh(CO)(**L1**)] · DMF in $CDCl_3$ at room temperature is well-resolved, in contrast to the ^{1}H NMR spectra of [PdCl$_2$(**L1**)], which exhibited broad peaks due to a fluxional process [28]. This observation indicates that **L1** is more rigid (on the NMR timescale) in the Rh complex than in the Pd complex, despite very similar geometries about the metal centers in the two cases. Another noteworthy feature of the ^{1}H NMR spectrum of **1** is the distribution of aromatic resonances corresponding to protons on the central terphenyl ring (δ 6.18–8.04 ppm) as a result of interaction between the ring's π-electron cloud and the metal center. A similar effect was noted in the Pd and Ni complexes of **L1** [28]. The metal center for **1** sites 3.37 Å from H(1), even closer than in Pd (3.48 Å) and Ni (3.51 Å) complexes, but is not within the sum of van der Waals radii for C (1.20 Å) and Rh (2.00 Å).

The difference in ^{31}P NMR chemical shift ($\Delta\delta$) between free and complexed states can also be used to assess whether the proposed complex has formed in the desired coordination environment [33]. The $\Delta\delta$ between **L1** (−8.8 ppm) and **1** (27.3 ppm) is 36.1 ppm, in close agreement with $\Delta\delta$ (37.3 ppm) observed for PPh_3 (−4.8 ppm

Table 2
Select bond lengths (Å) and angles (°) for **1** · DMF

Rh–Cl	2.3839 (5)
Rh–P(1)	2.3146 (4)
Rh–P(2)	2.3228 (4)
Rh–C(45)	1.7978 (4)
C(45)–O(1)	1.1515 (3)
P(1)–Rh–P(2)	171.372 (10)
P(1)–Rh–Cl	87.887 (10)
P(1)–Rh–C(45)	91.104 (11)
P(2)–Rh–Cl	89.332 (9)
P(2)–Rh–C(45)	90.819 (11)
Cl–Rh–C(45)	174.048 (16)

free) vs. *trans*-[ClRh(CO)(PPh_3)$_2$] (32.5 ppm) [32]. The P–Rh coupling constant for **1** (137 Hz) is fairly low and diagnostic for the expected *trans*-diphosphine complex. The J_{Rh-P} for *trans*-diphosphine Rh(I) complexes (~140–145 Hz) are typically smaller than in corresponding *cis*-isomers (~190–195 Hz), an effect that has been attributed to the *trans* influence, though the electronegativity of the Cl and CO also contribute to a lower coupling constant [34–39].

2.2. Structure

X-ray quality crystals of [ClRh(CO)(**L1**)] (Fig. 2) were obtained by slowly cooling a saturated DMF solution from 60 °C to room temperature overnight. Somewhat lower quality, DMF-free crystals were obtained by diffusion of tetramethylsilane into a saturated CH_2Cl_2 solution of **1**. Crystal data and structure refinement details for **1** · DMF are provided in Table 1, and select bond lengths and angles are provided in Table 2. The salient feature of interest, the P–M–P angle of 171.4°, is quite similar to those observed in [$PdCl_2$(**L1**)] and [$NiCl_2$(**L1**)] (173.0° and 174.8°, respectively) [28]. Another feature of note is the selective formation of the regioisomer in which the carbonyl ligand is directed into the more sterically crowded cleft under the C(1) site of the terphenyl scaffold, while the more voluminous chloride substituent resides in the open space under the central terphenyl ring.

2.3. Catalysis

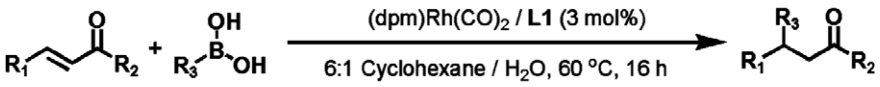
Having characterized a thermally stable rhodium complex supported by **L1** and reaffirmed a trans-spanning binding mode, we sought to investigate the use of **L1** to support Rh-catalyzed C–C bond formation. The first catalytic reaction investigated was the 1,4-conjugate addition of aryl boronic acids to α,β-unsaturated ketones (Scheme 1) [41–66]. The use of Rh complexes to catalyze this reaction has been aggressively pursued since the report by Miyaura and coworkers in 1997 [40]. Among the phosphines screened in Miyaura's study, the greatest activity was observed with dppb (1,4-bis(diphenylphosphino)butane), a flexible diphosphine capable of supporting large bite angle complexes. This observation suggests that a similarly disposed phosphine such as **L1** could exhibit similarly high activity. We thus selected a set of six arylboronic acids and five enones (Table 3) that would provide a breadth of steric and electronic diversity upon which future studies could be based.

Reaction conditions were initially selected to mimic those in the aforementioned study by Miyaura [40] to facilitate 1:1 correlation of results. The results of these trials, carried out at 60 °C in 6:1 cyclohexane/water with a 2:1 arylboronic acid/enone ratio, are summarized in Table 3. Under these conditions, reaction yields (determined by GC) are as good as or better than those observed with dppb [40]. An isolated yield of 58% was also determined for coupling of 2-cyclohexene-1-one and phenylboronic acid. Although stereogenic centers are present in all coupling products, the yields provided in Table 3 refer to mixtures of isomers; no stereoselectivity is expected employing achiral **L1** complexes.

One of the drawbacks of the 1,4-addition reaction has been that excess arylboronic acid is often necessary to reach acceptable yields. Having accomplished high yields in some of the initial trials, we attempted the same set of reactions with a 1:1 arylboronic acid/enone ratio and expanded our reactions to include the sterically encumbered 2,4,6-trimethyphenylboronic acid as a coupling partner (Table 3). Similar yields (within 11%) were observed in 10 out of the 25 trials as for those employing the 2:1 ratio, with depressed yields generally limited to the more sterically encumbered enones 4-phenyl-3-butene-2-one and phenyl styryl ketone. Coupling of encumbered 2,4,6-trimethyphenylboronic acid was moderately successful only with 3-octene-2-one (47%) and 2-octene-4-one (77%), while yields were low (6–31%) for the other enones. These data indicate that, for less sterically encumbered enones, the terphspan scaffold holds promise for elaboration to more commercially important asymmetric coupling reactions by modification of the terphspan scaffold with chiral phosphine moieties.

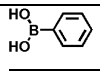
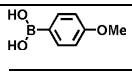
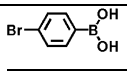
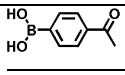
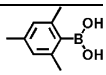
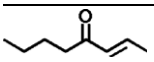
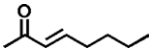
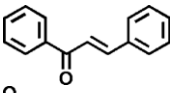
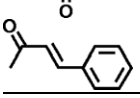
2.4. Concluding remarks

We have prepared and characterized the first terphspan rhodium complex (**1**) in which a *trans*-spanning mode similar to that observed in Ni and Pd complexes was observed by X-ray diffraction. The utility of terphspan ligand **L1** in rhodium-catalyzed 1,4-addition of aryl boronic acids to α,β-unsaturated ketones was examined, and moderate to



Scheme 1.

Table 3
Catalytic 1,4-addition of boronic acids to α,β-unsaturated enones

											
Boronic acid:Enone	2:1	1:1	2:1	1:1	2:1	1:1	2:1	1:1	2:1	1:1	1:1
	89	88	68	32	95	41	63	25	23	20	77
	91	98	58	46	98	~100	~100	32	~100	13	47
	84	90	90	83	98	9	~100	46	97	38	24
	98	77	34	23	83	36	62	30	36	27	6
	93	70	41	36	98	40	41	24	36	26	31

Conditions are described in the Section 2.

excellent yields were observed with many substrate pairs even when a 1:1 arylboronic acid/enone ratio was employed. Efforts are currently underway to modify **L1** for asymmetric catalysis and to extend the use of terphspan phosphines to other catalytic C–C bond-forming reactions.

3. Experimental

3.1. General

All synthesis was carried out in an inert atmosphere of nitrogen using an MBraun dry box or with standard Schlenck techniques. Ligand **L1** [28] and $Rh(CO)_2$(dipivaloylmethanoate) [67] were prepared as reported previously. Solvents were purified by passage through alumina columns under a N_2 atmosphere employing an Mbraun solvent purification system. All other reagents were used as received from TCI and Alfa Aesar. ^{31}P NMR spectra were collected using a Bruker Avance 300 instrument operating at 121.4 MHz, while proton and ^{13}C spectra were collected using a Bruker Avance 500 instrument operating at 500 MHz for proton and 125.7 MHz for carbon. Infrared spectra were collected using a Thermo Nicolet IR-100 FT-IR utilizing the EZ OMNIC analysis program. Gas Chromatographs and Mass Spectra were collected using a Shimadzu GCMS-QP2010 and analyzed using the GCMS solution software.

3.2. Preparation of [ClRh(CO)(L1)] (1)

A solution of $RhCl_3 \cdot 3H_2O$ (0.150 g, 0.570 mmol) and **L1** (0.393 g, 0.627 mmol) in 15 mL of *N*,*N*-dimethylformamide (DMF) was heated to 120 °C under nitrogen for 2.5 h. The resultant yellow solution was reduced to half its volume by vacuum distilling away some of the solvent. The solution was then cooled to 0 °C and 20 mL of cold methanol was added to produce a yellow precipitate. The precipitate was collected by filtration, washed with cold methanol three times and dried *in vacuo* to yield the target compound (0.196 g, 43.1%). An analytically pure sample of **1** · DMF was obtained by crystallization via slowly cooling a saturated DMF solution from 60 °C to room temperature overnight. IR: (CH_2Cl_2) $\nu_{CO} = 1966\ cm^{-1}$. ^1H NMR (500 MHz, $CDCl_3$): δ 2.88 (s, 3H, from cocrystallized DMF), 2.94 (s, 3H, from cocrystallized DMF), 3.36–3.39 (m, 2H), 4.82 (d, 2H, $J = 12$ Hz), 6.16 (d, 2H, $J = 8$ Hz), 6.79–6.83 (m, 6H), 7.05 (t, 4H, $J = 8$ Hz), 7.20–7.45 (m, 15H), 7.78–7.79 (m, 4H), 8.02 (s, 1H), 8.04 (s, 1H from cocrystallized DMF). ^{31}P NMR (121.4 MHz, $CDCl_3$): 27.4 (d, $J_{Rh-P} = 137$ Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$): 31.4 (m, CH_2 partially overlapping cocrystallized DMF), 36.4 (from cocrystallized DMF), 126.2, 126.6, 127.1 (t, $J = 5$ Hz), 127.7 (t, $J = 5$ Hz) 128.5, 128.9, 129.5, 129.7, 130.1, 131.6, 132.3, 133.5 (t, $J = 6$ Hz), 134.1 (t, $J = 6$ Hz), 142.0, 143.8, 162.5 (from cocrystallized DMF), (carbonyl not observed). Anal. Calc. for $C_{45}H_{36}ClOP_2Rh$: C, 68.15; H, 4.58; N, 0.00. Found: C, 67.84; H, 4.36; N < 0.5%.

3.3. General conditions for catalysis

To a preloaded conical vial containing the arylboronic acid (0.50 or 1.0 mmol) were sequentially added a solution of $Rh(dpm)(CO)_2$ (0.015 mmol) in 1 mL cyclohexane and **L1** (0.015 mmol in 1 mL 9:1 cyclohexane/CH_2Cl_2). This mixture was allowed to stir at room temperature for 15 min prior to addition of the enone (0.50 mmol) solution in 1 mL cyclohexane followed by 0.5 mL of water. The mixture was heated to 60 °C with stirring for 16 h. The mixture was collected and diluted with 10 mL THF for immediate GC/MS analysis.

3.4. X-ray crystallography

Intensity data were collected using a Rigaku Mercury CCD detector and an AFC8S diffractometer. Data reduction and absorbance corrections were achieved using CrystalClear [68]. The structure was solved by direct methods and subsequent Fourier difference techniques, and refined

anisotropically, by full-matrix least squares, on F^2 using SHELXTL 6.10 [69]. Hydrogen atom positions were calculated from the Fourier difference and then refined. C(13)–H(13B) was constrained to 1.083 Å.

Acknowledgement

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Appendix A. Supplementary material

CCDC 653769 contains the supplementary crystallographic data for the compound **1** · DMF. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via 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.jorganchem.2007.09.034.

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