



A new diphosphine-carbonyl complex of ruthenium: An efficient precursor for C-C and C-N bond coupling catalysis

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-ART-03-2018-001085.R5
Article Type:	Paper
Date Submitted by the Author:	09-Jul-2018
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A new diphosphine-carbonyl complex of ruthenium: An efficient precursor for C-C and C-N bond coupling catalysis†

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Reaction of 1,2-bis(diphenylphosphino)benzene (dppbz) with $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ affords $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$, where the two carbonyls are mutually *cis* and the two chlorides are *trans*. The molecular structure of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$, has been determined by X-ray crystallography, and the stability of the different available stereoisomers has been computationally evaluated. $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ has been found to serve as an excellent pre-catalyst for catalytic Suzuki-type C-C coupling and Buchwald-type C-N coupling reactions.

Introduction

The present work derives from our continued interest in ruthenium complexes having specifically designed coordination environments, with particular reference to their possible utilization in catalysis.¹ Ruthenium complexes are known to catalyze a variety of organic transformations, such as water splitting,² oxidation and oxo-transfer reactions,³ olefin metathesis,⁴ transfer hydrogenation,⁵ C-H bond activation,⁶ and C-C and C-hetero atom bond formation,⁷ etc. However, depending on the type of reaction, the catalyst precursors need to fulfill certain compositional requirements. For reactions involving C-C and C-N bond formation, which are addressed in this report, ruthenium(0) species are found to be highly effective.^{8,9} And it has been empirically demonstrated by researchers around the globe that compared to readily available ruthenium(0) species, such as $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Ru}(\text{cod})(\text{cot})]$ or $[\text{Ru}(\text{PPh}_3)_3(\text{CO})_2]$, which are capable of catalyzing such reactions, ruthenium(0) species that are generated *in situ* from suitable ruthenium(II) precursors display higher catalytic efficiency.^{8b,c} Selection of ruthenium(II) precursors for *in situ* generation of catalytically active ruthenium(0) species is therefore of significant importance. An exhaustive search of the literature reveals that a combination of carbonyl and phosphine as soft ligands around ruthenium has been very effective for this purpose, and this has prompted us to investigate the synthesis of new ruthenium(II)

carbonyl complexes possessing an ancillary diphosphine ligand (P-P) as catalyst precursors for the generation of ruthenium(0) species having the formula $[\text{Ru}(\text{CO})_2(\text{P-P})]$. During our recent effort in this direction, we carried out a set of reactions between selected diphosphine ligands of type $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 2$ (dppe), 3 (dppp), 4 (dppb)) with $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ in equimolar amounts expecting ruthenium(II) complexes of type $[\text{Ru}(\text{P-P})(\text{CO})_2\text{Cl}_2]$, but instead diruthenium complexes of type $[(\kappa^2\text{-P-P})(\text{CO})\text{Cl}_2\text{Ru}](\mu\text{-P-P})[\text{RuCl}_2(\text{CO})(\kappa^2\text{-P-P})]$ were obtained.^{1a} In these diruthenium complexes the diphosphine ligands are coordinatively flexible and function as chelating as well as bridging ligands. An in-depth analysis of the reaction mechanism has confirmed that the non-rigid nature of the chosen diphosphine ligands serves as a key factor in the formation of such complexes. In their native states, these ligands exhibit an unfolded chain form,¹⁰ and their flexible nature has enabled them to coordinate ruthenium centers as an intermolecular bridging ligand retaining their unfolded geometry, in addition to serving as a chelating ligand through intramolecular ring closure. The use of a diphosphine ligand that possesses a rigid platform with *cis*-oriented phosphines prohibits the more flexible intermolecular bridging ligation of ruthenium centers as exemplified by the reaction of $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 2, 3, 4$) with $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$. Guided by this concept, we have chosen another diphosphine ligand, *viz.* 1,2-(diphenylphosphino)benzene (dppbz) for the present study, where the initial goal was to synthesize a mononuclear ruthenium complex incorporating the rigid dppbz ligand along with labile carbonyls for the generation of high activity catalysts for use in C-C and C-N bond-coupling reactions.

The phosphorus donors in the dppbz ligand are bound to adjacent carbons in the aryl platform, and this orientation results in a rigid P-C-C-P auxiliary that lends itself to the chelation of a single metal versus the intermolecular bridging of two metal centers. While the dppbz ligand is known to coordinate a variety of different metals in a bidentate fashion through the formation of a five-membered chelate ring,¹¹ to our knowledge, no reports exist where dppbz functions as an intermolecular bridging ligand. The reaction

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† Electronic supplementary information (ESI) available: CCDC 1489486 contains the supplementary crystallographic data for $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ with selected bond distances and angles found in Table S1. Thermodynamics behind formation of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ (Fig. S1); optimization for catalytic C-C coupling reaction (Table S2); optimization for catalytic C-N coupling reaction (Table S3); X-ray diffraction and processing parameters (Table S4); cartesian coordinates for the optimized geometries of all the molecules in Figures 3 and 4 along with the computed electronic and zero-point energies (Table S5); See DOI: 10.1039/x0xx00000x

of dppbz with $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ has indeed afforded the targeted mono-ruthenium complex, and herein we describe our observations on the formation of the resulting complex, and its use as a catalyst precursor in C-C and C-N coupling reactions is reported.

Results and discussion

Syntheses and structures

The reaction of 1,2-(diphenylphosphino)benzene (dppbz) with $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ in equimolar ratio afforded a yellow complex,¹² whose preliminary characterization (elemental analysis, IR and NMR) was consistent with the formulated structure of the targeted mono-ruthenium complex, *viz.* $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$.¹³ In order to unambiguously establish the identity of the complex, with particular reference to coordination mode adopted by the dppbz ligand, the molecular structure was determined by X-ray crystallography. The structure is shown in Fig. 1, and selected bond parameters are listed in Table S1 (ESI[†]). The structure confirms the chelation of the ruthenium by the dppbz ligand. Two carbonyls and two chlorides are also coordinated to the metal center with the former ligands oriented mutually *cis* and coincident with the equatorial plane defined by the phosphorus atoms of the dppbz ligand. The two chloride groups are situated *trans* to each other and the aforementioned equatorial plane. The observed bond lengths for the Ru-P, Ru-Cl, and Ru-C vectors and the bond angles at the ruthenium center are unremarkable relative to octahedral ruthenium(II) complexes and require no comment.

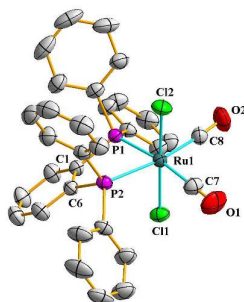


Figure 1 Crystal structure of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$.

As delineated in the introduction, the rigid nature of the P-C-C-P fragment of the diphosphine ligand is indeed a key factor in yielding this mono-ruthenium complex *vis-à-vis* the diruthenium complexes obtained earlier from similar reactions employing dppe, dppp, and dppb that possess more flexible carbon backbones.^{1a} Formation of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ may be viewed as arising from the addition of the dppbz ligand to the reactive $\text{Ru}(\text{CO})_2\text{Cl}_2$ fragment, whose origin is conceptually traced to the starting ruthenium complex. The thermodynamics for the formation of this complex was investigated computationally by electronic structure calculations.¹⁴ Here the monomeric $\text{Ru}(\text{CO})_2\text{Cl}_2$ fragment (**A**), the dppbz ligand (**B**), and the $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ product (**C**) were optimized by DFT. Three stereoisomers, each of which contains a chelating dppbz ligand,

were successfully optimized. The optimized structures and ground-state energy ordering for all the three species are depicted in Fig. S1 (ESI[†]). The union of **A** and **B** affords the mono-ruthenium complex $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ (**C**), whose formation is favorable by 64 kcal/mol. The computed thermodynamics for the $\text{A} + \text{B} \rightarrow \text{C}$ reaction are thus in good agreement with the facile formation of the $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ complex.

Three stereoisomers (*ct*, *tc*, and *cc* forms shown below) exist for $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ due to the different orientations possible for the ancillary chlorides and CO groups, and we have examined the three geometrical isomers and determined their relative energies by DFT.¹⁵ The determined solid-state structure of this complex corresponds to the *ct*-geometry. As octahedral ruthenium(II) compounds are known to prefer a *cis*-geometry for the carbonyls to maximize back-bonding to the superior π -acid ligands,¹⁶ we have computationally modeled the *ct* geometry using the solid-state structure as a starting point. The optimized structure for species *ct* is depicted in Fig. 2, and it was found to be intermediate in stability of the three isomers, lying 2.43 kcal/mol below *tc* and 4.95 kcal/mol higher in energy than *cc*. Interestingly, the *ct*-isomer of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ does not represent the most stable of the three computed stereoisomers, which in turn suggests that its experimental formation is under kinetic control. Attempts to promote the isomerization of *ct* to the thermodynamically favored *cc* product by control experiments at elevated temperatures were unsuccessful.¹⁷

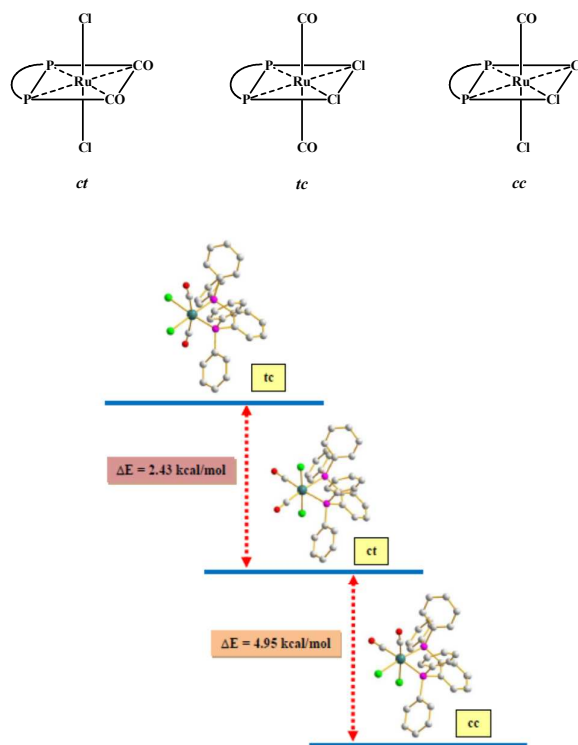


Figure 2 DFT-optimized structures of the possible stereoisomers of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$, and the energy differences (ΔE) between them.

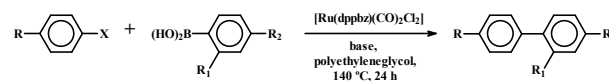
Catalytic activity

As indicated in the introduction, our principal objective with this study concerns the exploration of catalytic efficiency of the parent ruthenium complex in fundamental bond coupling (C-C and C-N) reactions. The dppbz-containing ruthenium(II) complex $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ is expected to serve as an excellent precursor for the *in situ* generation of the Ru(0) species, viz. $[\text{Ru}(\text{dppbz})(\text{CO})_2]$, which, in turn, should serve as the active catalyst in the planned C-C and C-N bond formation reactions.

We initiated our study on the Suzuki-type C-C coupling of phenylboronic acid with *p*-iodoacetophenone, using $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ as the pre-catalyst, to yield the biphenyl product 4-acetylbiphenyl. After extensive optimization (Table S2; ESI[†]), it was found that 1.0 mol% catalyst, 1.5 equiv. of K_3PO_4 as the base, polyethylene glycol as the solvent, and 24 h at 140 °C furnished the desired C-C coupled product in excellent yield (Table 1, entry 1). Similar C-C coupling reactions were performed with four aryl iodides and five arylboronic acids under the optimized conditions, and in each case, the expected biaryl product was obtained in good (77-97%) yield (Table 1, entries 1-20). Encouraged by the facile C-C coupling of aryl iodides with phenylboronic acids, similar coupling reactions of the C-Br bond of bromobenzene was also examined, but here we needed to employ hydrazine as a base to achieve optimal yields of the biaryl C-C bond coupled product. The reaction of bromobenzene was carried out with five different phenylboronic acids, and the desired C-C coupled product was obtained in good (61-88%) yield (Table 1, entries 21-25). Though aryl-I and aryl-Br bonds could be successfully activated using $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ as the pre-catalyst, attempts to activate an aryl-Cl bond, which is known to be much more difficult,¹⁸ remained unsuccessful.

$[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ is confirmed as an efficient catalyst-precursor for the Suzuki-type C-C coupling reactions. A plausible mechanism for the observed catalytic C-C cross-coupling reactions is presented in Scheme 1, where the initial step reaction involves the reduction of the ruthenium(II) pre-catalyst by the glycol solvent to the active ruthenium(0) species [1].¹⁹ This premise was tested by a control experiment and GC-MS analysis of the potential oxidation products for the *in situ* reduction of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ using ethylene glycol as the reducing agent. Here the oxidation products glycolaldehyde, glyoxal, and 1,4-dioxane-2,5-dione were observed. The four-coordinate intermediate that contains a chelating dppbz ligand and two carbonyl groups is unsaturated based on a formal electron count of 16-valence electrons. It is noteworthy that the observed Suzuki-type C-C coupling reactions require no additional ligand(s) to help stabilize the ruthenium species in the coupling reaction, which suggests that the soft dppbz and carbonyl ligands remain tethered to the ruthenium during autogeneous catalysis. The formation of [1] provides entry into the working catalytic cycle, leading to the intermediates [2], [3], and [4]. The last step in the reaction, [4]→[1] + biaryl product, involves the reductive elimination of the coupled product and regeneration of the active

catalyst [1]. The critical role played by the precatalyst $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ to afford the Ru(0) species [1] as the active catalyst that efficiently catalyzes C-C coupling under external ligand-free conditions is remarkable.

Table 1 Suzuki cross-coupling of aryl halides with phenylboronic acid^a

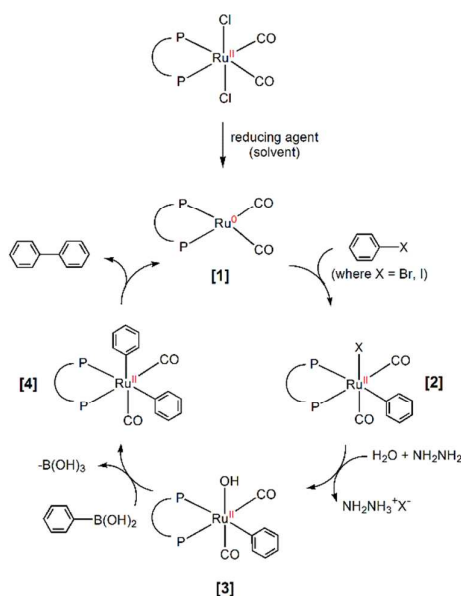
Entry	X	R	R ₁	R ₂	Yield ^b , %
1	I	COCH ₃	H	H	96 (84) ^c
2	I	COCH ₃	CH ₃	H	92
3	I	COCH ₃	H	CH ₃	97
4	I	COCH ₃	H	OCH ₃	86
5	I	COCH ₃	H	Cl	82
6	I	CHO	H	H	88 (72) ^c
7	I	CHO	CH ₃	H	85
8	I	CHO	H	CH ₃	87
9	I	CHO	H	OCH ₃	82
10	I	CHO	H	Cl	79
11	I	CN	H	H	86 (71) ^c
12	I	CN	CH ₃	H	84
13	I	CN	H	CH ₃	87
14	I	CN	H	OCH ₃	80
15	I	CN	H	Cl	77
16	I	H	H	H	90
17	I	H	CH ₃	H	92
18	I	H	H	CH ₃	96
19	I	H	H	OCH ₃	89
20	I	H	H	Cl	85
21 ^d	Br	H	H	H	79 (63) ^c
22 ^d	Br	H	CH ₃	H	81
23 ^d	Br	H	H	CH ₃	88
24 ^d	Br	H	H	OCH ₃	83
25 ^d	Br	H	H	Cl	61

^a Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_3PO_4 (1.5 mmol), Ru catalyst (1 mol%), polyethylene glycol (5 mL). ^b Determined by GCMS. ^c Isolated yield. ^d Hydrazine hydrate (1.0 mmol) was used instead of K_3PO_4 .



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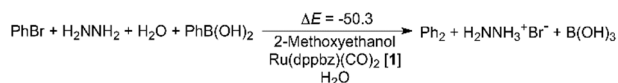
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Scheme 1. Probable mechanism for the observed C-C cross-coupling reactions. P-P represents the coordinated dppbz ligand.

The thermodynamics for the formation of biphenyl from bromobenzene and phenylboronic acid in the presence of hydrazine hydrate was computed to be favorable by 50.3 kcal/mol. Scheme 2 shows the stoichiometrically balanced equation for this process. The salient features of the mechanism depicted in Scheme 1 were successfully modeled by electronic structure calculations, starting from the four-coordinate ruthenium(0) species $\text{Ru}(\text{CO})_2(\text{dppbz})$ [1]. Figure 3 shows the energy surface and geometry-optimized ground- and transition-state structures involved in the C-C bond formation reaction. To our knowledge, this is the first computational study on the Suzuki-type C-C bond coupling reaction using a ruthenium catalyst.²⁰ The first step in the reaction involves the formation of a weakly bound $\text{PhBr} \rightarrow \text{Ru}$ dative complex [1'] between 1 and PhBr that serves as the precursor for the subsequent oxidative addition of the aryl bromide to the ruthenium to afford species [2]; the six-coordinate product lies 52.0 kcal/mol lower in energy than the starting materials, and the transition state for this step, $\text{TS}_{1' \rightarrow 2}$, is low at 15.2 kcal/mol. The conversion of [2] \rightarrow [3'] is best viewed as a hydrolysis step that furnishes the hydroxyl-substituted ruthenium(II) species [3'] that contains a molecule of HBr that is hydrogen bonded to the Ru-OH moiety. The HBr is scavenged by hydrazine to give [3]. The formation of [3'] lies 50.8 kcal/mol lower in energy and proceeds by $\text{TS}_{2 \rightarrow 3'}$. The critical nature of water in

this step of the reaction was independently tested by using KOH in place of K_3PO_4 . The near quantitative formation found for the biaryl product from the reaction between *p*-iodoacetophenone and phenylboronic acid (entry 1 in Table 1) plummeted to 15% in the presence of KOH.²¹ Clearly, the formation of the hydroxide species [3'] does not arise by a hydroxide-mediated substitution process. The penultimate step involves the transmetalation reaction between [3] and phenylboronic acid to furnish $\text{B}(\text{OH})_3$ and the crucial *cis*-substituted diaryl species [4].²² The rate-limiting step involves the C-C bond coupling of the two aryl groups and the barrier for this reductive elimination is 36.2 kcal/mol. Numerous computational studies on the palladium-catalyzed Suzuki-type C-C bond formation confirm the oxidative addition step as the rate-limiting step, and this is reasonable given the lower coordination number computed for the computed species in the catalytic cycle, which should facilitate the reductive elimination. In the case of our reactions with the six-coordinate ruthenium species, the release of the biphenyl product would be subject to greater steric interactions in the ruthenium(II) species leading up to the release of the product, which in turn raises the activation energy for C-C bond formation step vis-à-vis the palladium-catalyzed reactions.



Scheme 2. B3LYP-D3/6-31+G(2d,p)/SDD[Ru]//B3LYP/6-31+G(d')/SDD[Ru] computed thermodynamics for the Suzuki-type C-C bond coupling reaction (ΔE in kcal/mol).

The observed ease of the Suzuki-type C-C coupling reactions, with particular reference to the mild reaction conditions, low catalyst loading, and high yields, prompted us to investigate the catalytic activity of $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ in Buchwald-type C-N bond coupling reactions of halobenzenes with primary and secondary amines. After optimizing the conditions for the reaction between iodobenzene and aniline using $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ as the pre-catalyst (Table S3; ESI†), it was found that the reactions proceed smoothly at 130 °C and 2.0 mol% load of catalyst, 1.0 equiv of hydrazine hydrate as base, and polyethylene glycol as solvent over 24 h, to afford the expected product in good yield. Using these optimized conditions, the C-N bond coupling of iodobenzene with five primary aryl amines (*viz.* *para*-substituted anilines) and two secondary amines (*viz.* piperidine and morpholine) was attempted. All the reactions were found to afford the C-N coupled products in good (56-73%) yield (Table 2, entries 1-7). Replacement of iodobenzene by bromobenzene resulted in lowered products yields (35-49%; entries 8-14).

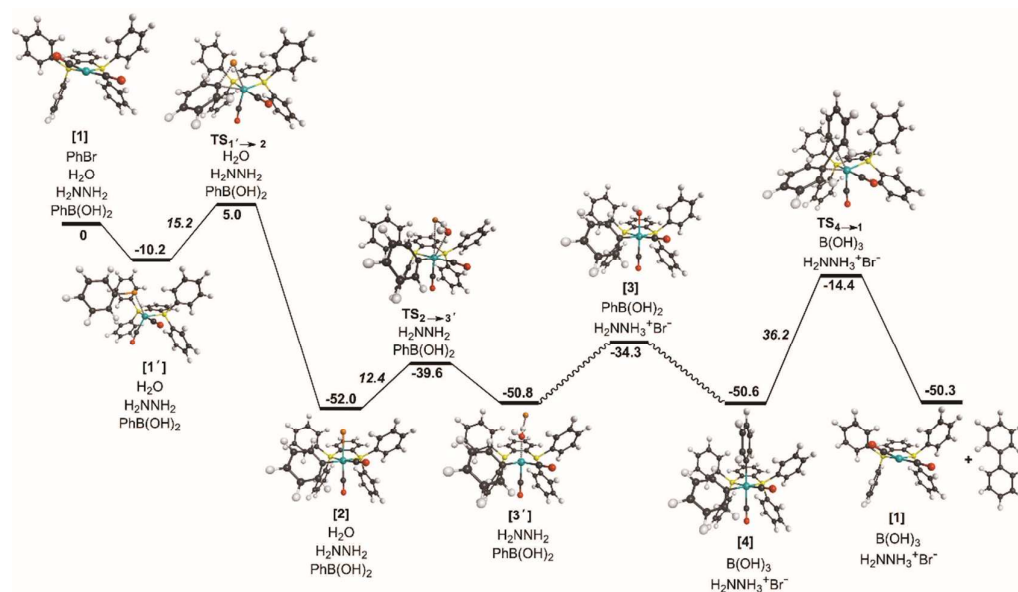


Figure 3 B3LYP-D3/6-31+G(2d,p)/SDD[Ru] relative energies, corrected for differences in zero-point energies, calculated at B3LYP/6-31+G(d')/SDD[Ru] optimized geometries. Relative energy values (ΔE + ΔZPE) in kcal/mol with respect to the reactants depicted in **Scheme 2**.

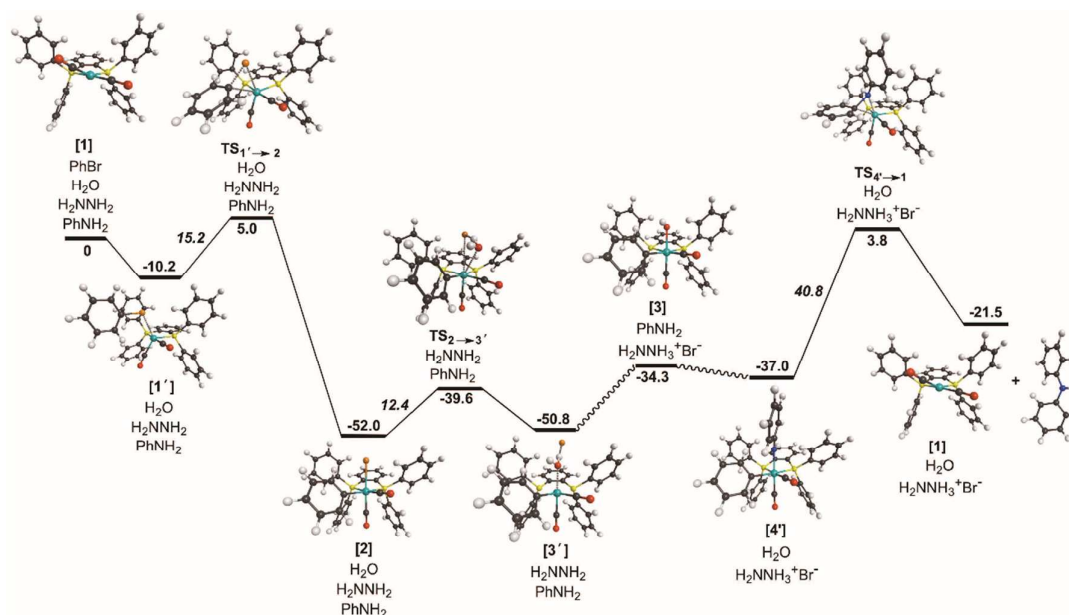


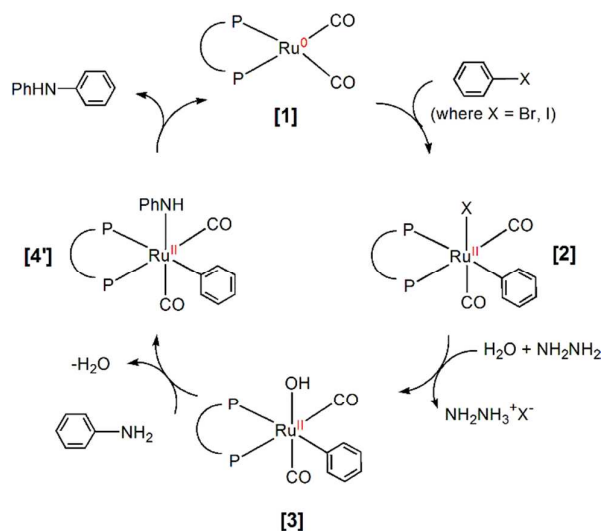
Figure 4 B3LYP-D3/6-31+G(2d,p)/SDD[Ru] relative energies, corrected for differences in zero-point energies, calculated at B3LYP/6-31+G(d')/SDD[Ru] optimized geometries. Relative energy values (ΔE + ΔZPE) in kcal/mol with respect to the reactants depicted in **Scheme 4**.



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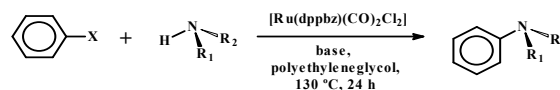
Drawing from the published work of Barder and Buchwald,²³ we propose the mechanism in Scheme 3 for our observed C-N bond coupling reactions. Here the *in situ* generation of ruthenium(0) species [1], the oxidative addition product [2], and the ruthenium hydroxide species [3], represent common species to both bond coupling reactions. Complex [4'] is produced upon reaction of aniline with [3] to give the anilide species [4'] and HBr (scavenged by hydrazine). C-N bond coupling in [4'] occurs by a reductive elimination and gives the amine product and regenerates the active catalyst [1]. Though Ru-catalyzed C-N bond formation reactions are reported in the literature,^{9,24} examples of Buchwald-type C-N coupling catalyzed by Ru(0) are, to our knowledge, unprecedented.



Scheme 3. Probable mechanism for the observed C-N cross-coupling reactions. P-P represents the coordinated dppbz ligand

The thermodynamics for the formation of diphenylamine from bromobenzene and aniline in hydrazine hydrate is exothermic by 21.5 kcal/mol (Scheme 4). The C-N bond formation sequence depicted in Scheme 3 shares commonality to Scheme 1 with respect to the reaction steps up to species [3] in the catalytic cycle. This premise is reasonable, and apart from the exchange of the phenylboronic acid for the amine reactant, the reaction conditions optimized in the Buchwald-type C-N coupling are identical to those employed in the Suzuki-type C-C coupling reactions here. The branch point in the amine functionalization occurs at species [3], and this involves the amine-promoted hydrolysis step, which furnishes the amide species [4'] and water. Reductive elimination from [4']

Table 2 C-N cross-coupling reaction of aryl halides with amines^a



Entry	X	Amine	Yield ^b , %
1	I		76 (64) ^c
2	I		67
3	I		70 (57) ^c
4	I		56 (46) ^c
5	I		69
6	I		63 (52) ^c
7	I		61 (53) ^c
8	Br		49 (38) ^c
9	Br		42
10	Br		43
11	Br		35
12	Br		39
13	Br		41 (35) ^c
14	Br		40

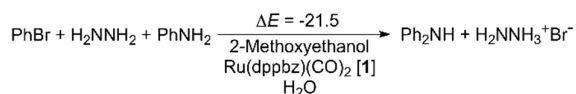
^aReaction conditions: aryl halide (1.0 mmol), amines (1.2 mmol), hydrazine hydrate (1.0 mmol), Ru catalyst (2 mol%), polyethylene glycol (5 mL). ^bDetermined by GCMS. ^c Isolated yield.



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represents the rate-limiting step and $TS_4 \rightarrow 1$ exhibits a barrier of 40.8 kcal/mol; Figure 4 illustrates this reaction.



Scheme 4. B3LYP-D3/6-31+G(2d,p)/SDD[Ru]/B3LYP/6-31+G(d')/SDD[Ru] computed thermodynamics for the Buchwald-type C-N bond coupling reaction (ΔE in kcal/mol).

Conclusions

The present study confirms that 1,2-bis(diphenylphosphino)benzene readily reacts with polymeric $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ to afford the new complex $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$. We have demonstrated that the stereochemically rigid nature of the P-C-C-P platform in the dppbz ligand promotes intramolecular chelation of the ruthenium center as opposed to the intermolecular ligation of multiple ruthenium centers as exemplified by the more flexible diphosphines dppe, dppp, and dppb. We have demonstrated $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ to be an excellent pre-catalyst for Suzuki-type C-C coupling and Buchwald-type C-N coupling reactions. In both catalytic reactions, the catalysis proceeds through the intermediacy of the Ru(0) species, $[\text{Ru}(\text{dppbz})(\text{CO})_2]$, that is generated *in situ* from the parent complex by a solvent-promoted reduction process.

Experimental

Materials and methods

Ruthenium trichloride was purchased from Arora Matthey, Kolkata, India. The diphosphine ligand (dppbz) was procured from Aldrich and used as received. $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ was prepared by following the reported procedure.²⁵ All solvents were reagent grade commercial materials and were used as received. Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. GC-MS analyses were performed using a Perkin Elmer CLARUS 680 instrument. The ^1H NMR spectra were recorded in CDCl_3 solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. IR spectra were obtained on a Perkin Elmer Spectrum Two IR spectrometer as KBr a pellet.

Synthesis of *ct*- $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$

To a solution of $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ (0.10 g, 0.44 mmol)¹² in methanol (20 mL) was added 1,2-bis(diphenylphosphino)benzene

(0.20 g, 0.44 mmol) dissolved in dichloromethane (20 mL). The mixture was stirred for 6 h, whereby a yellow solution was obtained. The solvent was then evaporated under reduced pressure and the resulting solid was subjected to purification by thin-layer chromatography on a silica plate. With 1:1 dichloromethane-chloroform as the eluant, two yellow bands were separated, the faster of the two corresponded to the desired product.²⁶ Removal of the eluent under vacuum gave *ct*- $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ as a yellow crystalline solid. Yield: (45 mg) 15%. Anal. Calc. for $\text{C}_{32}\text{H}_{24}\text{O}_2\text{P}_2\text{Cl}_2\text{Ru}$: C, 56.97; H, 3.56. Found: C, 57.13; H, 3.54. ^1H NMR (300 MHz, CDCl_3):²⁷ δ 6.67–7.64 (24H)*. IR (KBr, cm^{-1}): 492, 511, 523, 557, 618, 668, 692, 745, 844, 998, 1027, 1091, 1114, 1157, 1187, 1265, 1482, 1570, 1584, 2060, and 2009.

Crystallography

Single crystals of *ct*- $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$ were obtained by slow diffusion of hexane into a dichloromethane solution containing the complex. Table S4 (ESI[†]) shows the X-ray data processing and collection parameters for the data that were collected on a Bruker SMART CCD diffractometer. X-ray data reduction, structure solution, and refinement were done using the *SHELXL-2016* and *Olex-2* packages.²⁸ The reported structure was solved by the direct methods. The lattice solvent molecules of the crystal could not be modeled satisfactorily due to severe disorder problem. Therefore, the *Olex-2* program was utilized to mask the disordered solvent molecules, which showed total 83.6 electrons per unit cell. This corresponds to 41.8 electrons per molecule ($Z=2$) and can be tentatively assigned to one molecule of dichloromethane.

Computational modeling details

The DFT calculations on the optimized ground-state structures and energy calculations for the data reported in Figure 2 were carried out using the Gaussian 09.¹⁴ The DFT calculations for the optimized structures in the catalytic cycles presented in Figures 3 and 4 were performed using the Gaussian 16 package of programs,²⁹ employing the B3LYP hybrid functional. This functional is comprised of Becke's three-parameter hybrid exchange functional (B3)³⁰ and the correlation functional of Lee, Yang, and Parr (LYP).³¹ The ruthenium atom was described with the Stuttgart-Dresden effective core potential (ECP) and SDD basis set,³² and the 6-31+G(d') basis set³³ was employed for all remaining atoms. The effect of the solvent on the reaction was taken into account through the polarizable continuum model (PCM) using 2-methoxyethanol ($\epsilon = 17.2$) to approximate the polyethylene glycol solvent employed in the catalytic reactions. The effect of dispersion

and polarization on the energetics was addressed through single-point calculations using the B3LYP functional with Grimmes empirical dispersion correction³⁴ (i.e. B3LYP-D3) and the 6-31G(2d,p)³⁵ basis set for the main group atoms. The ECP and valence basis set on the ruthenium atom remained unchanged. The relative energies reported in Schemes 2 and 4, and Figures 3 and 4 were calculated from the B3LYP-D3/6-31+G(2d,p) PCM single-point energies and corrected for differences in zero-point energies obtained at the B3LYP/6-31+G(d') optimized geometries.

All reported geometries were fully optimized, and the analytical Hessian was evaluated at each stationary point to determine whether the geometry was an energy minimum (no negative eigenvalues) or a transition structure (one negative eigenvalue). Unscaled vibrational frequencies were used to make the zero-point energy corrections. Intrinsic reaction coordinate (IRC) calculations were performed on reported transition states in order to establish the reactant and product species associated with this transition-state structure. The geometry-optimized structures have been drawn with the *MacMolPlt* molecular visualization and manipulation program.³⁶ The cartesian coordinates for the optimized geometries of all the molecules in Figures 3 and 4 are deposited in Table S5 (ESI⁺) along with the computed electronic and zero-point energies.

Application as catalysts

General procedure for C-C coupling reactions. In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of the catalyst, K₃PO₄ (1.5 mmol), phenylboronic acid (1.2 mmol), aryl halide (1 mmol), and polyethylene glycol as solvent (5 mL). The flask was placed in a preheated oil bath at required temp. For aryl bromide hydrazine hydrate (1.0 mmol) was used instead of K₃PO₄. After the specified time had been reached, the flask was removed from the oil bath, and water (20 mL) added, followed by extraction with ether (4 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na₂SO₄, and filtered. The solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GCMS. In selected cases, the product was isolated via purification by thin-layer chromatography on a silica plate.

General procedure for C-N coupling reactions. In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of the catalyst, hydrazine hydrate (1.0 mmol), amine (1.2 mmol), aryl halide (1.0 mmol), and polyethylene glycol as solvent (5 mL). The flask was placed in a preheated oil bath at required temp. After the specified time, the flask was removed from the oil bath, water (20 mL) was added, and extraction with ether (4 × 10 mL) was done. The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na₂SO₄, and filtered. The solvent was removed under vacuum. The residue was dissolved in acetonitrile and analyzed by GCMS. In selected cases, the product was isolated via purification by thin-layer chromatography on a silica plate.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Helpful comments from the reviewers are acknowledged. Financial assistance received from the Department of Science and Technology, Government of West Bengal, Kolkata [Sanction No. 746(Sanc.)/ST/P/S&T/2G-4/2013], University Grants Commission, New Delhi [Sanction No. F.19-122/2014(BSR)] and Council of Scientific and Industrial Research, New Delhi [Grant No. 01(2788)/14/EMR-II] is gratefully acknowledged. The authors thank Dr. Saurabh Das (Department of Chemistry, Jadavpur University) for his help in recording the electronic spectra. MGR thanks The Robert A. Welch Foundation through Grant B-1093 for research support. We also wish to acknowledge the computational resources at UNT that are housed in CASCaM and supported by NSF (CHE-1531468).

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A new diphosphine-carbonyl complex of ruthenium: An efficient precursor for C-C and C-N bond coupling catalysis

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Graphical Abstract

Reaction of 1,2-bis(diphenylphosphino)benzene (dppbz) with $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ affords $[\text{Ru}(\text{dppbz})(\text{CO})_2\text{Cl}_2]$, which serves as an excellent pre-catalyst for Suzuki-type C-C coupling and Buchwald-type C-N coupling reactions.

