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Bimetallic Catalysis Involving Dipalladium(I) and Diruthenium(I) Complexes

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Dedicated to Professor Pierre H. Dixneuf on the occasion of his 70th birthday

Abstract: Dipalladium(I) and diruthenium(I) compounds bridged by two [{(5,7-dimethyl-1,8-naphthyridin-2-yl)-amino}carbonyl]ferrocene (L) ligands have been synthesized. The X-ray structures of $[Pd_2L_2][BF_4]_2$ (**1**) and $[Ru_2L_2(CO)_4][BF_4]_2$ (**2**) reveal dinuclear structures with short metal–metal distances. In both of these structures, naphthyridine bridges the dimetal unit, and the site *trans* to the metal–metal bond is occupied by weakly coordinating oxygen from the amido fragment. The catalytic utilities of these bimetallic compounds are evaluated. Compound **1** is an excellent catalyst for phosphine-free, Suzuki cross-coupling reactions of aryl bromides with arylboronic acids and provides high yields in short reaction times. Compound **1** is also found to be catalytically active for aryl chlorides, although the corresponding yields are lower. A bimetallic mechanism is proposed, which involves the oxidative addition of aryl bromide across the Pd–Pd bond and the bimetallic reductive elimination of the product. Compound **1** is also an efficient catalyst for the Heck cross-coupling of aryl bromides with styrenes. The mechanism for aldehyde olefination with ethyl diazoacetate (EDA) and PPh_3, catalyzed by **2**, has been fully elucidated. It is demonstrated that **2** catalyzes the formation of phosphorane utilizing EDA and PPh_3, which subsequently reacts with aldehyde to produce a new olefin and phosphine oxide. The efficacy of bimetallic complexes in catalytic organic transformations is illustrated in this work.

Keywords: catalysis · C–C coupling · cooperative effects · palladium · ruthenium

Introduction

Bimetallic catalysis is based on the premise that sequential or cooperative participation of two metal components might lead to an enhanced reaction rate, better selectivity, and in some cases new types of reactions.[1] Several bimetallic complexes have been exploited as catalysts in organic transformations. Sequential participation of Pd- and Sn-based reagents is demonstrated in the C–C bond-forming Stille reaction.[2] The dicopper(I) active site in metallaenzyme tyrosinase exhibits bimetallic cooperativity towards the conversion of catechol to benzoquinone.[3] In our continuing effort to examine cooperative bimetallic reactivity, we have explored organometallic chemistry on a diruthenium(I) platform. Room temperature activation of the C–H bond,[4] and formation of the C–C bond[5] have been performed at the axial site of the metal–metal singly bonded '$Ru_2(CO)_4$' core. In a recent report, we have described bimetallic water–gas shift (WGS) chemistry executed on a diruthenium platform.[6] These stoichiometric reactions have provided valuable insight on fundamental organometallic processes on a dimetal unit. The present work seeks to evaluate the catalytic activity of metal–metal bonded dimetal compounds in organic transformations.

The challenging task in designing a bimetallic catalyst is the selection of ligands that are capable of accommodating geometrical and electronic reorganization of the dimetal core during the course of the catalytic cycle. The demonstrated ability of 1,8-naphthyridine (NP) to stabilize a host of dimetal cores prompted the utilization of the NP-based ligand.[7] A donor appendage (such as pyridyl, thiazolyl, pyrollyl) at the 2 position of the NP unit enables additional chelate-ring formation and allows axial modulation of the metal–metal bond.[8] Coordination of 2-(2-thiazolyl)-1,8-naphthyridine (tzNP) to a dimetal unit is shown in Scheme 1a, as an illustrative example. To access axial sites

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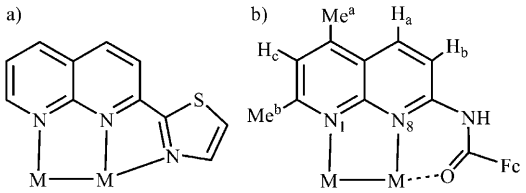


Scheme 1. Coordination of a) tzNP and b) L to a dimetal unit.

for substrate coordination, we proposed to incorporate hemilabile amido group.[9] The NP derivative [{(5,7-dimethyl-1,8-naphthyridin-2-yl)amino}carbonyl]ferrocene (L) bridges the dimetal core through the N-C-N unit and the oxygen atom occupies the site trans to the metal–metal axis, as shown in Scheme 1b. Introduction of ferrocenyl group metal complexes dramatically improves their solubility.

Dipalladium(I) and diruthenium(I) complexes supported by two L ligands have been synthesized, the catalytic activity of [Pd^I–Pd^I] complex towards Suzuki and Heck coupling reactions has been examined and the [Ru^I–Ru^I] complex has been evaluated as a catalyst for aldehyde olefination reactions.

Results and Discussion

$[Pd_2L_2][BF_4]_2$ (1): The room temperature reaction of L with $[Pd(CH_3CN)_4][BF_4]_2$ in acetonitrile affords $[Pd_2L_2][BF_4]_2$ (**1**) in high yield (75%). Analysis of the X-ray structure and spectroscopic data reveals a dipalladium(I) compound. The IR absorption of the carbonyl group ($\tilde{\nu}=1684\ cm^{-1}$) does not shift by a significant value when compared to the free ligand ($\tilde{\nu}=1680\ cm^{-1}$). This indicates a weak coordination of carbonyl to the metal. In comparison, the corresponding shift in $[CuL_2][ClO_4]_2$ is 37 cm^{-1} in which L forms a chelate involving carbonyl oxygen and napththyridine nitrogen.[9]

Compound **1** is diamagnetic and analysis of the ^1H NMR spectrum indicates the equivalence of two ligands on the NMR time scale. The naphthyridine protons appear at $\delta=$ 8.60 (H_a), 8.50 (H_b), and 7.56 ppm (H_c). Two singlets at $\delta=$ 2.77 and 3.38 ppm are assigned to two methyl groups. Four protons in the substituted Cp ring appear at $\delta=4.62$, 4.68, 5.04, and 5.13 ppm. The second Cp protons resonate at $\delta=$ 4.35 ppm. The signal at $\delta=9.49$ ppm is assigned to the NH proton. The ESI-MS spectrum of complex **1** reveals a signal at m/z 492 ($z=2$) assigned for the molecular ion $[Pd_2L_2]^{2+}$ on the basis of the mass and isotopic distribution pattern (see Figure S5 in the Supporting Information).

*X-ray structure of **1***: The molecular structure of **1** consists of a dipalladium unit spanned by two ligands. The ORTEP diagram of the dicationic unit in **1** is shown in Figure 1 and the relevant parameters are provided in the corresponding caption. The X-ray structure confirms that two ligands are in a *trans* arrangement. The NP unit bridges the dimetal, and the site *trans* to Pd–Pd axis is occupied by the O atom of the amido unit. The Pd–N bond lengths vary within a small

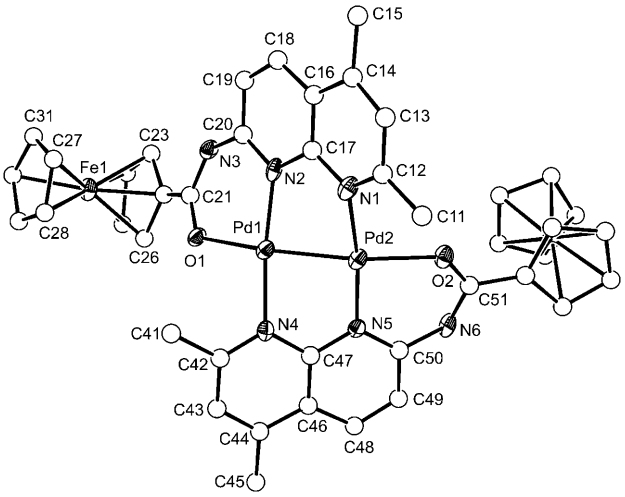


Figure 1. ORTEP diagram (50% probability thermal ellipsoids) of the $[Pd_2L_2]^{2+}$ unit in compound **1** with important atoms labelled. Carbon atoms are shown as circles of arbitrary radius. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles [°]: Pd1–Pd2 2.3952(8), Pd1–N2 2.045(5), Pd1–N4 2.050(5), Pd2–N1 2.052(5), Pd2–N5 2.039(5), Pd1–O1 2.149(4), Pd2–O2 2.171(4), O1–C21 1.249(7), O2–C51 1.259(7), N3–C21 1.364(8); N2-Pd1-N4 172.6(2), N5-Pd2-N1 172.9(2), N2-Pd1-Pd2 88.02(14), N5-Pd2-Pd1 87.81(14), N1-Pd2-Pd1 85.15(14), N4-Pd1-Pd2 85.07(15), C21-O1-Pd1 123.4(4), C51-O2-Pd2 121.6(4), N2-Pd1-O1 90.95(18), N5-Pd2-O2 90.23(18), O1-Pd1-Pd2 163.52(12), O2-Pd2-Pd1 159.92(12). Dihedral angles [°]: O1-Pd1-Pd2-O2 15.9(6), N4-Pd1-Pd2-N5 27.3(2), N1-Pd2-Pd1-N2 25.8(2), N2-C20-N3-C21 21.7(10), N5-C50-N6-C51 17.1(10).

range (2.039(5)–2.052(5) Å) and the Pd–O bond lengths are comparatively longer (2.149(4) and 2.171(4) Å). The C–O bond lengths (1.249(7), 1.259(7) Å) are marginally elongated compared to the unbound ligand (1.225(5) Å). The trans nitrogens exhibit N-Pd–N bond angles 172.9(2) and 172.6(2)°. The N4-Pd1-Pd2-N5, N1-Pd2-Pd1-N2 torsional angles 27.3(2) and 25.8(2)° signify distortion of the $Pd_2(NP)_2$ framework from planarity.

The most remarkable finding of this structure is the Pd–Pd bond length. To the best of our knowledge, compound **1** exhibits the shortest Pd–Pd distance (2.3952(8) Å) among dipalladium(I) compounds known in literature.[10] A selected list of dipalladium(I) compounds along with their Pd–Pd distances are collected in Table 1. The Pd–Pd distance in unsupported $[Pd_2(CH_3CN)_6](BF_4)_2$ is 2.486(1) Å. It increases when the coordinated acetonitrile molecules are replaced by stronger ligands, such as halides, isocyanides or phosphines (Table 1, entries 2–4). Most of the bridged dipalladium(I) compounds contain phosphine-based ligands. The Pd–Pd separations vary within the range 2.55–2.70 Å.[10e–n] Ortho-functionalized triazenido ligands have afforded dipalladium(I) compounds in which the Pd–Pd bond lengths are comparatively smaller (2.416(1)–2.431(1) Å; see entry 15). The shortest metal–metal distance in **1** is the result of a constrained ligand bite and weak axial coordination.

It is evident that the Pd^{II} precursor converts to Pd^I during the course of the reaction. Reduction of Pd^{II} to Pd^0 with phosphine has been postulated in cross-coupling reactions.[11] Tertiary amines have been implicated for the transformation

Table 1. Comparison of Pd–Pd bond lengths in selected dipalladium(I) complexes.[a]

No	Complex	d_{Pd-Pd} [Å]	Ref.
1	$[Pd_2(MeCN)_6]^{2+}$	2.486(1)	[10a]
2	$[Pd_2(MeNC)_4I_2]$	2.533(1)	[10b]
3	$[Pd_2(t\text{BuNC})_4Cl_2]$	2.532(2)	[10c]
4	$[Pd_2(t\text{BuNC})_4(PPh_3)_2]$	2.556(1)	[10d]
5	$[Pd_2(dppm)_2Br_2]$	2.699(5)	[10e]
6	$[Pd_2(dppm)_2(t\text{BuNC})_2]^{2+}$	2.619(1)	[10f]
7	$[Pd_2(dppm)_2(OCOCF_3)_2]$	2.594(2)	[10g]
8	$[Pd_2(dmpm)_2Br_2]$	2.603(1)	[10h]
9	$[Pd_2Cl_2(dpmMe)_2]$	2.664(1)	[10i]
10	$[Pd_2(dppa)_2Cl_2]$	2.638(1)	[10j]
11	$[Pd_2[PhN\{P(OPh)_2\}_2]_2Cl_2]$	2.620(1)	[10k]
12	$[Pd(etp)]_2^{2+}$	2.617(1)	[10l]
13	$[Pd_2(Ph_2PC_5H_4N)_2(OAc)_2]$	2.579(1)	[10m]
14	$[Pd_2\{(Ph_2P)_2py\}_2]^{2+}$	2.552(1)	[10n]
15	$[Pd_2(o\text{-}MeO_2C\text{-}C_6H_4\text{-}NNN\text{-}p\text{-}C_6H_4\text{-}CH_3)_2]$	2.416(1)	[10o]
16	$[Pd_2L_2]^{2+}$	2.395(1)	[b]

[a] Abbreviations: dppm = bis(diphenylphosphino)methane, dmpm = bis-(dimethyl-phosphino)methane, dpmMe = bis(diphenylphosphino)ethane, dppa = bis-(diphenylphosphino)amine, etp = bis(Diphenylphosphino)-ethyl)phenylphosphine and L = [{(5,7-dimethyl-1,8-naphthyridin-2-yl)amino}carbonyl]ferrocene. [b] This work.

of Pd^{II} to dipalladium(I) compounds.[12,10o] Compound **1** was obtained in absence of either of these. The presence of redox active ferrocenyl moiety ($E_{1/2}(ox) = 0.65(100)$ V) in L certainly raises the possibility of ligand-promoted reduction with concomitant formation of the corresponding ferrocenium salt. However, isolation of **1** in yields exceeding 70%, by employing strictly one equivalent of L, does not support this premise. Furthermore, the use of excess ligand did not improve the yield by any significant number, thereby contradicting the role of sacrificial ligand for the reduction. Notably, the reaction of the solvated dipalladium(I) precursor $[Pd_2(CH_3CN)_6][BF_4]_2$ with L did not provide **1** in a detectable amount, as revealed from ESI-MS spectra analysis. It is likely that the solvent acetonitrile and possibly a trace impurity of water in the reaction mixture are responsible for the reduction of $[Pd_2]^{4+}$ to a $[Pd_2]^{2+}$ core under the influence of L, although we have no direct experimental evidence to prove this point.

$[Ru_2L_2(CO)_4][BF_4]_2$ (2): The reaction of L with $[Ru_2(CO)_4(MeCN)_6][BF_4]_2$ in dichloromethane provided $[Ru_2L_2(CO)_4][BF_4]_2$ (**2**) in high yield (82%). ESI-MS spectrum revealed a signal at a mass-to-charge ratio of 1173, attributed to $[\{M\}^{2+} + BF_4^-]^+$ in which $\{M\}$ is $[Ru_2(CO)_4L_2]$. In addition, signals corresponding to $[M]^{z+}$ ($z = 1$ and 2) were observed at m/z 1086 and 543, respectively. The IR spectrum of **2** exhibits carbonyl absorptions at $\tilde{\nu} = 2042$, 1998 and 1954 cm^{-1} and the aminocarbonyl absorption appears at $\tilde{\nu} = 1633\ cm^{-1}$, a drop of 47 cm^{-1} compared to the free ligand indicating its coordination to the metal. This is further supported by analysis of the $^{13}C\{^1H\}$ NMR spectrum, which exhibits a amido carbonyl resonance at $\delta = 176.1$ ppm, significantly downfield shifted from the free ligand ($\delta = 169.7$ ppm). The ^1H NMR spectrum exhibits three resonances for the aromatic protons, indicating the equivalence of two ligands on the NMR time scale. The aromatic protons appear as two doublets at $\delta = 8.58$ (H_a) and 7.43 ppm (H_b) and a singlet at $\delta = 7.20$ ppm (H_c). Two methyl groups resonate at $\delta = 2.81$ and 3.04 ppm. The protons of the functionalized Cp ring appear at $\delta = 4.77$ and 5.29 ppm, whereas the second Cp ring protons are observed at $\delta = 4.21$ ppm. The signal at $\delta = 9.36$ ppm is attributed to NH proton.

X-ray structure of ***2***: Two independent molecules are observed in the asymmetric unit. The metrical parameters of these two structures are very similar and we restrict our discussion to one molecule. Complete data for both molecules are provided in the Supporting Information. The ORTEP diagram of the dicationic unit in **2** is shown in Figure 2 and

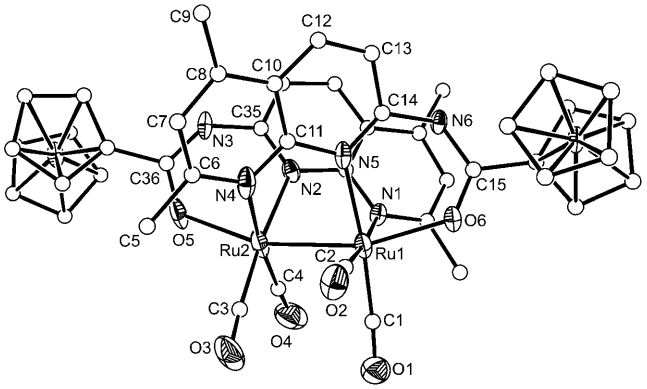


Figure 2. ORTEP diagram (50% probability thermal ellipsoids) of the $[Ru_2L_2(CO)_4]^{2+}$ unit in compound **2** with important atoms labelled. Carbon atoms are shown as circles of arbitrary radius. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Ru2–Ru1 2.5825(9), Ru1–N1 2.176(7), Ru1–N5 2.191(5), Ru2–N2 2.174(6), Ru2–N4 2.182(5), Ru1–O6 2.213(5), Ru2–O5 2.181(4) , O5–C36 1.250(7), O6–C15 1.241(10), N3–C36 1.366(8), N6–C15 1.316(10), N1-Ru1-N5 85.4(2), N2-Ru2-N4 85.69(19), C1-Ru1-N5 174.5(3), C2-Ru1-N1 173.7(3), C4-Ru2-N4 174.2(3), C3-Ru2-N2 174.4(3), N2-Ru2-O5 83.50(19), N5-Ru1-O6 82.5(2), N1-Ru1-O6 86.2(2), O6-Ru1-Ru2 161.89(17), O5-Ru2-Ru1 161.39(13) Dihedral angles [°]: C1-Ru1-Ru2-C4 40.5(5), C2-Ru1-Ru2-C3 39.2(4), N1-Ru1-Ru2-N2 33.0(2), N4-Ru2-Ru1-N5 33.6(2), N2-C35-N3-C36 38.7(9), N5-C14-N6-C15 22.6(12).

the relevant parameters are provided in the corresponding caption. The molecular structure of **2** consists of a diruthenium unit spanned by two cis-coordinating ligands. The coordination motif of the ligand is similar to that observed in **1**. The NP fragment bridges two ruthenium centres, and the site *trans* to the Ru–Ru bond is occupied by the O atom of the amido unit. Each ruthenium is additionally bonded to two CO ligands in a cis fashion.

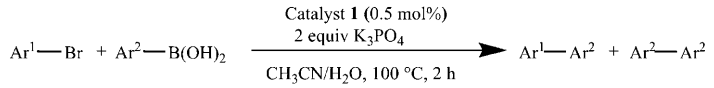
The effects of axial coordination on the Ru–Ru bond length has been examined in a series of $[Ru_2(CO)_4(NP\text{-}R)_2]$ compounds.[8] Experimental and computational studies revealed that the variation in metal–metal distances is the direct consequence of the interaction of different axial donors with the diruthenium unit. The stronger the axial ligand, the longer the Ru–Ru bond length. The shortest

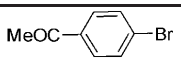
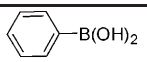
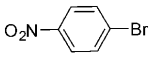
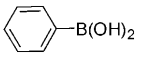
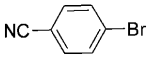
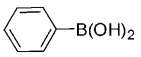
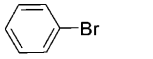
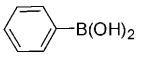
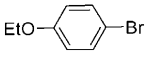
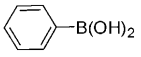
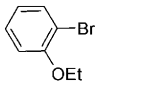
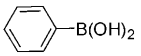
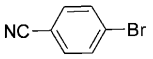
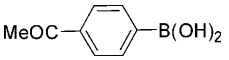
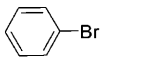
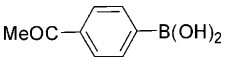
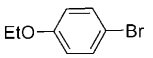
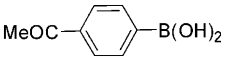
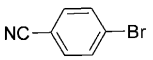
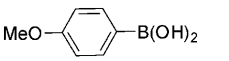
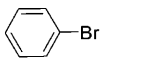
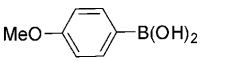
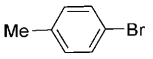
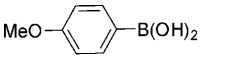
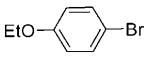
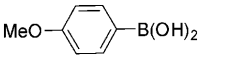
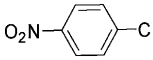
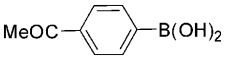
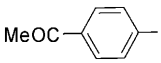
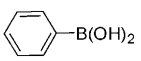
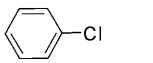
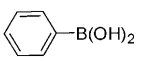
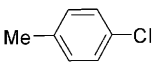
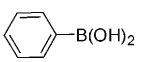
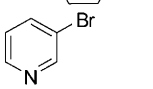
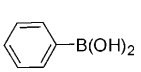
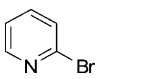
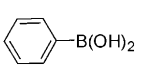
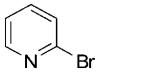
Ru–Ru bond length 2.6071(9) Å was observed for $[Ru_2(3\text{-MeNP})_2(CO)_4(OTf)_2]$ (3-MeNP = 3-methyl-1,8-naphthyridine) in which triflates are coordinated at the axial sites. It is rather remarkable that the Ru–Ru bond length (2.5825(9) Å) in **2** is even shorter! The Ru1–O6 and Ru2–O5 bond lengths (2.213(5) and 2.181(4) Å, respectively) are shorter than the corresponding Ru–O bond length 2.267(14) Å in the triflate-bound complex. The Ru-Ru-O angles (161.9(1) and 161.4(1)°) deviate from linearity. The N1-Ru1-Ru2-N2 and N5-Ru1-Ru2-N4 torsional angles are 33.0(2) and 33.6(2)°, respectively, indicating deviation from planarity. The carbonyl ligands are staggered along the Ru–Ru axis with C1-Ru1-Ru2-C4 and C2-Ru1-Ru2-C3 torsion angles of 40.5(5) and 39.2(4)°, respectively.

Catalysis using complex 1

Suzuki cross-coupling reactions: To evaluate the catalytic efficacy of dimetal complexes in organic transformations, we performed Suzuki reactions with **1**.[13] Under the optimized reaction conditions (vide infra), cross coupling of a number of aryl bromides with arylboronic acids were investigated and the results are tabulated in Table 2. In a typical experiment, 1 mmol aryl bromide was reacted with 1.2 mmol arylboronic acids in the presence of 0.5 mol% catalyst **1** and 2 mmol K_3PO_4 at 100 °C for 2 h. Electron-poor aryl bromides, as well as bromo benzene, could be efficiently converted to the desirable products in high yields (Table 2, entries 1–4), but moderate yields were observed for electron-rich aryl bromides (Table 2, entries 5 and 6). *para*-Substituted aryl bromides generally undergo faster cross-coupling reactions compared to corresponding ortho-substituted aryl bromides (Table 2, entries 5 and 6). The substitution effect on the arylboronic acid was also explored in our study. Although electron-rich arylboronic acids were in general active (Table 2, entries 10–13), electron-poor arylboronic acids provided greater yields (Table 2, entries 7–9). Selectivity of the catalyst towards desired cross-coupled product is good, although some homo-coupled product was also observed (less than 10%) when the reaction is slow.[14]

Table 2. Suzuki cross-coupling of aryl bromides with boronic acids catalyzed by **1**.[a]



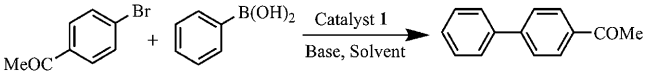
Entry	Aryl halide Ar^1–Br	Coupling partner Ar^2–$B(OH)_2$	Conversion[b] [%] Ar^1–Ar^2	Yield[c] [%] Ar^1–Ar^2
1			100	96
2			100	96
3			96	90
4			100	100
5			84	80
6			65	60
7			100	94
8			98	94
9			88	84
10			85	80
11			76	70
12			70	65
13			70	65
14			45	40
15			44	36
16			42	40
17			37	30
18			68	60
19			0	0
20			0	0

[a] Reaction conditions: 1 mmol aryl bromide, 1.2 mmol aryl boronic acid, 2 mmol base and 0.5 mol% **1**; solvent mixture is CH_3CN/H_2O (v/v = 4:1); $T = 100$ °C; $t = 2$ h. [b] Determined by using GC-MS after the reaction. [c] Yield of isolated product.

Encouraged by Hor and co-workers work[15a] on the coupling of aryl chlorides employing $[Pd_2(CH_3CN)_6](SbF_6)_2$ and ferrocenyl phosphine ligands, we subjected catalyst **1** to cross-coupling reactions between aryl chlorides and arylboronic acids. Reactions with 1 mol% catalyst loading, and heating at 100°C for 2 h in CH_3CN/H_2O solvent mixture, afforded nearly 45% conversion for the electron-poor aryl chlorides (Table 2, entries 14 and 15). However, yields exceeding 80% could be achieved with 5 mol% catalyst loading and 8 h of prolonged heating at 100°C. Electron-rich chlorides provided lower yields under identical reaction conditions.

The screening of solvents and various bases was performed by using the model coupling reaction between 4-bromoacetophenone and phenyl boronic acid (Table 3). Reaction in acetonitrile gave better yields compared to DMF or THF (Table 3, entries 1–3). The effect of base was studied and K_3PO_4 (2 equiv) turned out to be the best choice as it provided higher yields. A mixed solvent combination of CH_3CN/H_2O (4:1) (Table 3, entries 6 and 8) gave better results than any other organic solvents we attempted. The positive effects of water have been attributed to several factors, including the suppression of the trimerization of aryl boronic acid and the better solubility of inorganic bases.[15]

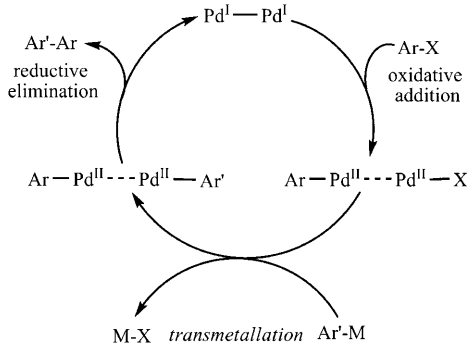
Table 3. Influence of solvent and base on the coupling reaction.



Entry	Base	Solvent	Conversion[a] [%]
1	K_2CO_3	CH_3CN	51
2	K_2CO_3	DMF	49
3	NaOAc	THF	44
4	K_3PO_4	DMF	68
5	K_2CO_3	CH_3CN	72
6	K_2CO_3	CH_3CN/H_2O	92
7	K_3PO_4	DMF/H_2O	88
8	K_3PO_4	CH_3CN/H_2O	100

[a] Determined by using GC-MS.

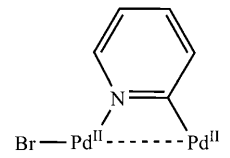
We propose a bimetallic mechanism for catalyst **1** (Scheme 2). The first step is the oxidative addition of aryl bromide across the Pd^I–Pd^I single bond. Substrate addition via oxidative pathway to a variety of dimetal unit has been reported.[16] In particular, dipalladium(I) compounds have been reported to undergo oxidative addition to a variety of substrates including dioxygen and RSH.[17] Transmetalation of the oxidative-addition product [Ar-Pd^{II}···Pd^{II}-Br] with aryl(Ar′)-boronic acid produces [Ar-Pd^{II}···Pd^{II}-Ar′], which undergoes bimetallic reductive elimination to provide the coupled product Ar–Ar' with the regeneration of the catalyst to initiate the next catalytic cycle (Scheme 2).



Scheme 2. Proposed bimetallic catalytic mechanism for a Suzuki cross-coupling reaction.

Metal dimers are unique in their mode of bonding to small molecules and can trigger facile activation.[18] Furthermore, dinuclear elimination of product has been invoked to rationalize the enhanced reaction rate in homogeneous metal-cluster catalysis.[19] Evidently, the presence of a second metal causes the rate enhancement of hydrogen elimination from a metal hydride, which exhibits sluggish intramolecular elimination otherwise.[20] Nocera has demonstrated the bimetallic cooperativity for the dihydrogen addition and elimination on a diiridium core.[21] There are strong indications to propose that the substrate activation, in addition to the product elimination steps, are more efficient on a dimetal platform. The ability of **1** to catalyze the coupling of aryl chlorides is linked to the superior activity of dipalladium(I) core compared to mononuclear Pd^{II} compounds, which show poor activity towards aryl chlorides.[22]

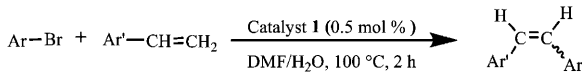
To establish the bimetallic reactivity, we performed reactions with bromo pyridines. In general, the presence of a heteroatom reduces the reactivity, as it binds to the metal centre, thereby suppressing oxidative addition. We observed a 68% conversion with 3-bromo pyridine (Table 2, entries 18). Remarkably, no cross-coupled product was detected for the ortho isomers (Table 2, entries 19, 20) even after prolonged heating. It is our assertion that the oxidation addition of 2-bromopyridine leads to a bridged cyclometalated product, as shown in Scheme 3, which prohibits subsequent reactions. Structural precedence of similar cyclometalated products $[Pd_2Cl_2(PPh_3)_2(\mu_2\text{-}C^2N\text{-}py)_2]$ and $[Pd_2Cl_2(PPh_3)_2(\mu_2\text{-}C^2N\text{-}^i\text{quinoline})_2]$ gives credence to this pathway.[23]

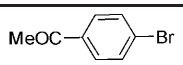
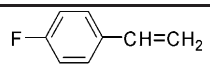
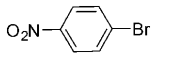
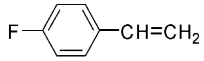
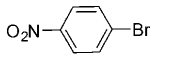
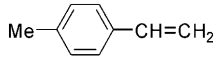
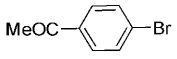
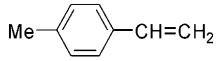
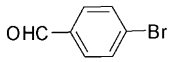
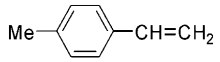
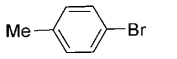
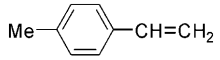
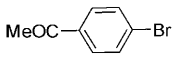
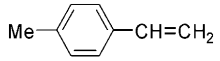
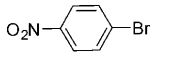
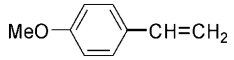
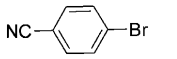
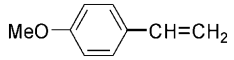
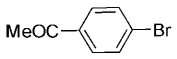
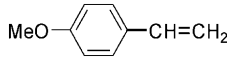


Scheme 3. Schematic representation of the proposed bridged-cyclometalated product.

Heck coupling reaction: The Heck reaction is a powerful and efficient method for the C–C bond formation in which haloarenes couple with alkenes in the presence of a Pd catalyst to form a new alkene.[24] Phosphine ligands have been used extensively along with Pd^{II} salts for the in situ generation of the Pd^0 catalysts. The cost and air/moisture sensitivity of phosphine is a major drawback. We have examined the utility of **1** as catalyst in phosphine-free Heck-coupling reactions. In a typical reaction, aryl bromide and styrene are reacted at 100°C for 2 h with 0.5 mol% catalyst (Table 4). For electron poor aryl bromides (Table 4, entries 1–5), quantitative conversions were achieved, whereas slightly lower

Table 4. Heck cross coupling of aryl bromides with substituted styrenes catalyzed by **1**.



Entry	Aryl halide Ar–Br	Coupling partner Ar′–CH=CH_2	Conversion[b] [%]	*E*/*Z*[b] [%]	Yield[c] [%]
1			100	96/4	96
2			100	96/4	96
3			98	96/4	94
4			96	96/4	90
5			96	96/4	90
6			92	96/4	88
7			90	96/4	86
8			96	96/4	92
9			94	96/4	90
10			94	96/4	90

[a] Reaction conditions: 1 mmol aryl bromide, 1.5 mmol substituted styrene and 0.5 mol% **1**, temp. 100°C, time 2 h. [b] Determined by using GC-MS. [c] Combined yields of *E* and *Z* isomers after chromatography.

yields were noted for electron-rich counterparts (Table 4, entries 6,7). Identical trends are noted for different styrene derivatives. An excellent *trans* to *cis* ratio (96:4) is observed for each case.

Catalysis using diruthenium(I) complex 2

Aldehyde olefination: Metal–metal singly bonded dirhodium(II) carboxylate and carboxamide have been used for a wide range of synthetic transformations, such as cyclopropanation,[25] C–H insertions[26] and aromatic substitution.[27] The critical intermediate, which unifies this body of chemistry, is an electrophilic dirhodium carbenoid in which a carbene occupies the site trans to the Rh–Rh axis in a linear fashion.[28] Compound **2** is isoelectronic with dirhodium(II) compounds and offers access to axial sites for substrate coordination. These features prompted us to examine the prospect of **2** as a carbene transfer catalyst. The catalytic potential was evaluated for aldehyde olefination reaction by using 1.5 mmol ethyl diazoacetate (EDA), 1.2 mmol of PPh_3 and 1 mol% catalyst in toluene. Treatment of benzaldehyde with EDA/PPh_3/**2** in toluene at 80°C provided ethyl cinnamate in 82% conversion after 6 h (Table 5). Purification of the product by silica gel column chromatography with petroleum ether/ethyl acetate (9:1 v/v) afforded 75% isolated yield (Table 5, entry 7). Ethyl maleate and fumarate were also observed in the GC-MS spectra, as side products resulting from the dimerization of carbene with a combined yield of less than 10%. Incorporation of electron-withdrawing nitro groups on the aromatic ring provided higher yields and *E*-selectivity. Quantitative conversion was achieved for 2,4-dinitrobenzaldehyde at ambient temperature in 1 h with excellent selectivity (99:1). Similar conversion and selectivity values were also observed for *p*- and *o*-nitro benzaldehyde (Table 5, entries 2 and 3). Introduction of trifluoromethyl, cyano and bromo groups afforded marginal improvements in the yields compared to benzaldehyde (Table 5, entries 4–6).

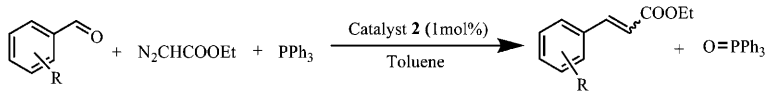
Electron-rich aldehydes exhibited reduced reactivity. Lower conversions were observed for *o*-hydroxy, *p*-methyl and *p*-methoxy benzaldehyde after 6 h (Table 5, entries 8–10). *p*-(Dimethyl)amino benzaldehyde was found to be the least reactive (Table 5, entry 11), however, after a prolonged reaction time (10 h) the reaction could be completed.

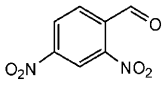
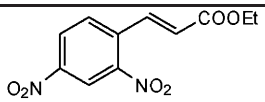
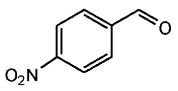
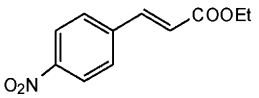
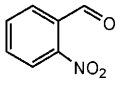
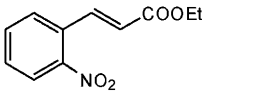
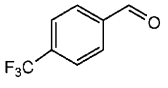
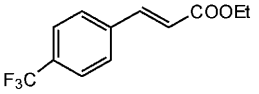
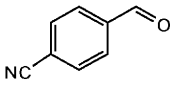
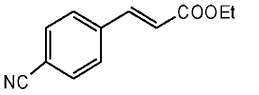
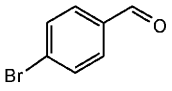
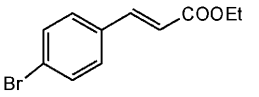
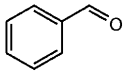
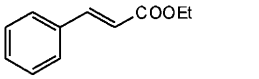
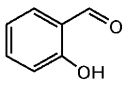
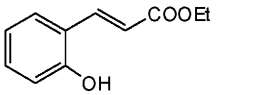
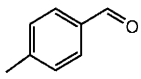
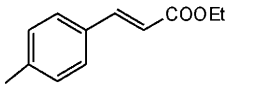
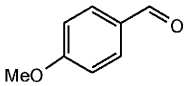
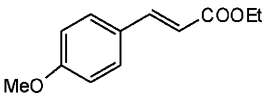
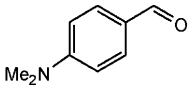
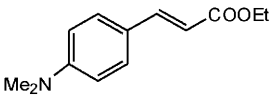
The reaction is catalytic, as no olefination product was observed without the application of catalyst **2** under identical reaction conditions. In the absence of catalyst, the azine Ph-CH=N–N=CHCOOEt was observed in the GC-MS spectra when the reaction was allowed to continue for 1 day. The presence of triphenylphosphine was found to be essential for this reaction and no olefination product was observed in its absence. We made attempts to optimize the amount of PPh_3 and it was found that 1.2 equivalents with respect to the catalyst provides maximum conversion. Invariably, the formation of triphenylphosphine oxide was observed in the GC-MS spectra.

To evaluate the effect of catalyst loading, the olefination of benzaldehyde was investigated at different catalyst loadings. On increasing the catalyst amount from 1% to 5%, a marginal increase in the conversion was observed with no significant change in the selectivity.

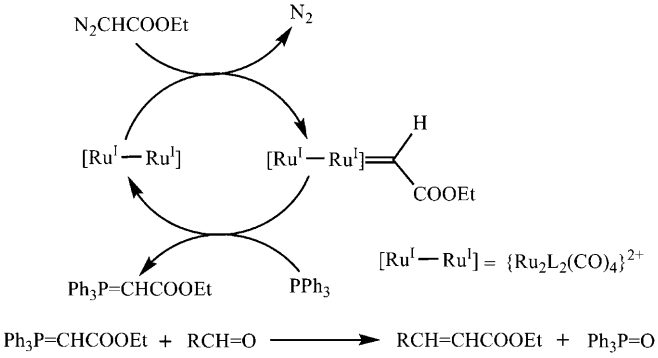
We propose a catalytic cycle as shown in Scheme 4. In the initial step, ethyl diazoacetate reacts with the diruthenium(I) catalyst **1** and forms a dimetal-carbene intermediate. To establish the intermediacy of the [Ru^{I}–Ru^{I}=CH(COOEt)] species, styrene was added to the reaction mixture and the cyclopropanation product ethyl-2-phenylcyclopropylcarboxylate, which was detected by using GC-MS, was subsequently isolated and characterized by using NMR spectroscopy. Gerhard Maas has noted the formation of axial carbenes in cyclopropanation reactions with diazo compounds catalyzed

Table 5. Olefination of aldehyde with ethyl diazoacetate catalyzed by **2**.[a]



Entry	Aldehyde	Product	*T* [°C]	*t* [h]	Conversion [%][b]	*E*/*Z* [%][b]	Yield [%][c]
1			25	1	100	99/1	95
2			25	2	98	99/1	92
3			25	2	98	99/1	92
4			25	2	87	93/7	79
5			25	2	86	94/6	78
6			80	6	84	92/8	77
7			80	6	82	92/8	75
8			80	6	74	98/2	65
9			80	6	68	93/7	60
10			80	6	61	91/9	55
11			80	6	52	91/9	45

[a] Reaction conditions: 1 mmol aldehyde, 1.2 mmol PPh_3, 1.5 mmol of EDA, 1 mol% catalyst **2**. [b] Determined by using GC-MS after reaction. [c] Combined yields of *E* and *Z* isomers after chromatography.



$Ph_3P{=}CHCOOEt + RCH{=}O \longrightarrow RCH{=}CHCOOEt + Ph_3P{=}O$

Scheme 4. Mechanism of aldehyde olefination catalyzed by **2**.

by $[Ru^{I}_2(CO)_4(OAc)_2]$.[29] This is also in line with the mechanism suggested for dirhodium(II) carboxylates.[25] Thus, there is a strong indication for the formation of a linear diruthenium-carbenoid intermediate in this reaction. The next step is the transfer of carbene to PPh_3 resulting in the phosphorane. The ylide reacts with aldehyde to produce new olefin and phosphine oxide (Scheme 4). In a controlled experiment, the phosphorane $Ph_3P{=}CHCOOEt$ was identified by using ^{31}P NMR spectroscopy in the absence of aldehyde.[30] Furthermore, it has been established that the stoichiometric reaction of $Ph_3P{=}CHCOOEt$ with benzaldehyde produce ethyl cinnamate in high yield. Notably, it is the formation of ylide that is catalyzed and not the subsequent Wittig reaction.

The pathway proposed here is akin to the process described for a Fe^{II}-porphyrin catalyst.[31] An alternate mechanism has been suggested for the methyltrioxorhenium (MTO)-catalyzed aldehyde olefination, which involves a metallaoxetane intermediate (see Scheme S1 in the Supporting Information).[32] The metallaoxetane intermediate is formed in the reaction of an aldehyde with a metal carbene and fragmentation of the metallaoxetane provides the new olefin and the MTO. Subsequently, the PPh_3 abstracts oxygen atom from MTO generating a Re^{V}–dioxo species. The latter reacts with diazo reagent to produce a metal carbene, which initiates the next catalytic cycle. To check this possibility in the aldehyde olefination reaction for catalyst **2**, cyclohexene was used instead of PPh_3 under the same catalytic conditions and neither the olefin nor the cyclohexene epoxide is detected in the GC-MS. It is, therefore, unlikely that the diruthenium(I)-catalyzed aldehyde olefination proceeds by means of the metallaoxetane route. Moreover, the naphthyridines and carbonyls afford a single site for the catalysis, which is not conducive for metallaoxetane formation.

Conclusion

Dipalladium(I) and diruthenium(I) compounds bridged by two amide-linked naphthyridine-ferrocene hybrid ligands have been synthesized. Both compounds exhibit short metal–metal distances aided by a ligand framework. The dipalladium(I) compound (**1**) is an excellent catalyst for phosphine-free, Suzuki cross-coupling and Heck-coupling reactions. A cooperative bimetallic mechanism is proposed for the Suzuki reaction in which the substrate addition and product elimination occur on the dipalladium platform. The diruthenium(I) compound (**2**) is shown to be an efficient catalyst for selective olefination of aldehydes. The mechanism has been fully elucidated. Compound **2** catalyzes the formation of phosphorane from ethyl diazoaceate and PPh_3. Subsequently the phosphorane reacts with aldehyde to produce new olefin. The efficacy of bimetallic complexes in catalytic organometallic transformation reactions is demonstrated in this work. Further work is in progress to extend this chemistry to other dimetal compounds and to apply them in more challenging organic reactions.

Experimental Section

General procedures: All reactions with metal complexes were carried out under an atmosphere of purified nitrogen by using standard Schlenk-vessel and vacuum-line techniques. The ^{1}H NMR spectra were obtained by using JEOL JNM-LA 400 MHz and 500 MHz spectrometers. The ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed by using a Thermoquest EA1110 CHNS/O analyzer. Recrystallized compounds were powdered, washed several times with dry ether and dried in vacuum for at least 48 h prior to elemental analyses. ESI-MS were recorded by using a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. The ESI-MS of all complexes were recorded in acetonitrile. The Infrared spectra were recorded by using a Bruker Vertex 70 FTIR spectrophotometer in the range $\tilde{\nu}=400$ to 4000 cm^{-1} using KBr pellets. The GC-MS experiments were performed by using an Agilent 7890 A GC and 5975C MS system.

Materials: Solvents were dried by using conventional methods, distilled under nitrogen and deoxygenated prior to use. $RuCl_3{\cdot}xH_2O$ and Pd sponge were purchased from Arora Matthey, India. Compounds $[Ru_2(CH_3CN)_6(CO)_4][BF_4]_2$,[33] $[Pd(CH_3CN)_4][BF_4]_2$[34] and [{(5,7-dimethyl-1,8-naphthyridin-2-yl)amino}carbonyl]ferrocene (L) were synthesized according to the literature procedure.[9]

Synthesis of $[Pd^I_2(L)_2][BF_4]_2$ (1): A sample of L (38 mg, 0.098 mmol) was added to an acetonitrile solution (30 mL) of $[Pd(CH_3CN)_4][BF_4]_2$ (36 mg, 0.081 mmol), and the mixture was stirred overnight at room temperature. The solution was concentrated, and diethyl ether (15 mL) was added with stirring to induce precipitation. The resulting dark-red solid residue was washed with diethyl ether (3×10 mL), and dried in a vacuum to afford **1**. Yield: 35 mg (75%). X-ray quality crystals were grown by layering petroleum ether onto a saturated dichloromethane solution of **1** inside an 8 mm o.d. vacuum-sealed glass tube. ^{1}H NMR (CD_3CN): $\delta=$ 9.49 (br. 1H, NH), 8.60 (d, $J=10$ Hz, 1H, NP-H_a), 8.50 (d, $J=10$ Hz, 1H, NP-H_b), 7.56 (s, 1H, NP-H_c), 4.62 (s, 1H, Cp), 4.68 (s, 1H, Cp), 5.04 (s, 1H, Cp), 5.13 (s, 1H, Cp), 4.35 (s, 5H, Cp) 3.38 (s, 3H, NP-Me), 2.77 ppm (s, 3H, NP-Me); ^{13}C NMR (125 MHz, CD_3CN, 294 K): $\delta=169.9$ (NHCO), 166.1 (NCN_{NP}), 154.8 (NCC_{NP}), 153.9 (NCC_{NP}), 152.8 (CCC_{NP}), 137.2 (CH_{NP}), 125.8 (CH_{NP}), 124.4 (CCC_{NP}), 120.2 (CH_{NP}), 72.4 (CCC_{Cp}), 70.9 (CH_{Cp}), 70.2 (CH_{Cp}), 69 (CH_{Cp}), 25.9 (CH_3), 18 ppm (CH_3); IR (KBr): $\tilde{\nu}=\nu$(CONH) 1684 (s), ν(NP) 1599 (m), 1504(vs), 1406 (m), 1322(s), 1292(s), 1264(s), $\nu(BF_4^-)$ 1069 cm^{-1} (br); ESI-MS: m/z: 492 $[M]^{2+}$; elemental analysis (%) calcd for $C_{42}H_{38}N_6O_2F_8B_2Fe_2Pd_2$: C 43.6, H 3.31, N 7.26; found: C 43.04, H 3.25, N 7.09.

Synthesis of $[Ru^I_2(L)_2(CO)_4][BF_4]_2$ (2): A dichloromethane solution (10 mL) of L (44 mg, 0.11 mmol) was added drop wise to a dichloromethane solution (15 mL) of $[Ru_2(CO)_4(MeCN)_6][BF_4]_2$ (40 mg, 0.054 mmol), and the reaction mixture was stirred overnight at room temperature. Solution was concentrated, and diethyl ether (15 mL) was added with stirring to induce precipitation. The resulting dark-red solid residue was washed with diethyl ether (3×10 mL), and dried in a vacuum to afford **2**. Yield: 56 mg (82%). X-ray quality crystals were grown by layering diethyl ether onto a saturated dichloromethane solution of **2** inside an 8 mm o.d. vacuum-sealed glass tube. ^{1}H NMR ($CDCl_3$): $\delta=9.36$ (br. 1H, NH), 8.58 (d, $J=9$ Hz, 1H, NP-H_a), 7.43 (d, $J=9$ Hz, 1H, NP-H_b), 7.2 (s, 1H, NP-H_c), 5.29 (s, 2H, Cp), 4.77 (s, 2H, Cp), 4.21 (s, 5H, Cp), 3.04 (s, 3H, NP-Me), 2.81 ppm (s, 3H, NP-Me); ^{13}C NMR (125 MHz, $CDCl_3$, 294 K): $\delta=202.6$ (CO), 200.6 (CO), 176.1 (NHCO), 169 (NCN_{NP}), 157 (NCC_{NP}), 154.5 (NCC_{NP}), 150.6 (CCC_{NP}), 141 (CH_{NP}), 125.9 (CH_{NP}), 121.3 (CCC_{NP}), 117.4 (CH_{NP}), 74.9 (CCC_{Cp}), 71.1 (CH_{Cp}), 70.8 (CH_{Cp}), 70 (CH_{Cp}), 27.9 (CH_3), 18.5 ppm (CH_3); IR (KBr): $\tilde{\nu}=$ ν(CO) 2042 (vs), 1998 (s), 1954 (s), ν(CONH) 1633 (m), ν(NP) 1610 (m), 1415 (s), 1294 (s), $\nu(BF_4^-)$ 1083 cm^{-1} (br). ESI-MS: m/z: 1173 $[\{M\}^{2+}+BF_4^-]^+$, 1086 $[M]^+$, 543 $[M]^{2+}$; elemental analysis (%) calcd for $C_{46}H_{38}N_6O_6F_8B_2Fe_2Ru_2$: C 43.91, H 3.04, N 6.68; found: C 43.48, H 2.91, N 6.50.

X-ray data collection and refinement: Single-crystal X-ray studies were completed by using a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. All the data were collected at 100(2) K using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). The frames were indexed, integrated, and scaled by using the SMART and SAINT software packages,[35] and the data were corrected for absorption by using the SADABS program.[36] The structures were solved and refined by using the SHELX suite of programs.[37] All hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. Structure solution

Table 6. Crystallographic data and pertinent refinement parameters for compounds **1**·2CH_2Cl_2 and **2**.

	1·2CH_2Cl_2	**2**
empirical formula	$C_{44}H_{42}B_2Cl_4F_8Fe_2N_6O_2Pd_2$	$C_{46}H_{35}B_2F_8Fe_2N_6O_6Ru_2$
formula weight	1326.76	1255.26
crystal system	triclinic	tetragonal
space group	$P\bar{1}$	$P\bar{4}$
a [Å]	10.266(2)	28.309(5)
b [Å]	13.121(3)	28.309(5)
c [Å]	19.318(4)	14.629(4)
α [°]	82.634(4)	90.00
β [°]	82.136(3)	90.00
γ [°]	69.561(3)	90.00
V [Å^3]	2406.4(9)	11724(4)
Z	2	8
ρ_{calcd} [g cm^{-3}]	1.831	1.422
μ [mm^{-1}]	1.625	1.061
$F(000)$	1316	4984
reflections collected	21260	106056
independent	11438	29126
observed [$I>2\sigma(I)$]	7454	18657
no. of variables	635	1303
GooF	1.055	0.963
R_{int}	0.0476	0.1063
final R indices [$I>2\sigma(I)$][a]	$R1=0.0637$ $wR2=0.1567$	$R1=0.0605$ $wR2=0.1142$
R indices (all data)[a]	$R1=0.1069$ $wR2=0.1892$	$R1=0.1010$ $wR2=0.1327$

[a] $R_1=\Sigma\ ||F_o|-|F_c||/\Sigma|F_o|$ with $F_o^2>2\sigma(F_o^2)$. $wR_2=[\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$.

and refinement details for compounds **1** and **2** are provided in the Supporting Information. The "SQUEEZE" option in PLATON program[38] was used to remove a disordered solvent molecule from the overall intensity data of compound **2**. All non-hydrogen atoms were refined with anisotropic thermal parameters. Pertinent crystallographic data for compounds **1** and **2** are summarized in Table 6. ORTEP-32[39] was used to produce the diagrams. CCDC-782940 (**1**) and CCDC-782941 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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