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Bis(bipyridine) ruthenium(II) bis(phosphido) metalloligand: synthesis of heterometallic complexes and application to catalytic (*E*)-selective alkyne semi-hydrogenation†

Shin Takemoto, * Manami Kitamura, Shuhei Saruwatari, Atsutaka Isono, Yoko Takada, Rie Nishimori, Mina Tsujiwaki, Naoki Sakaue and Hiroyuki Matsuzaka

The first phosphido derivative of the bis(bipyridine) ruthenium(II) fragment, *cis*-[(bpy)$_2$Ru(PPh$_2$)$_2$] ([RuP$_2$]), has been developed and applied as a P-donor metalloligand to form new Ru–Rh, Ru–Ir and Ru$_2$Cu$_2$ heterometallic complexes. The Ru–Ir hydride complex [([RuP$_2$])IrH(NCMe)$_3$][BF$_4$]$_2$ exhibits significant catalytic activity for (*E*)-selective semi-hydrogenation of alkynes.

The development of new metal-containing phosphorus donor ligands is an active area of current catalysis research,[1] aiming at exploring ways to use functions of metal elements in the ligand framework to realize new reactivity at catalytic metal centres.[2] Among ligands in this category, metallophosphines L$_n$M-PR$_2$, or transition metal phosphido complexes, have attracted considerable attention, as they have ligand characteristics significantly influenced by the directly attached L$_n$M unit yet retaining the versatility of tertiary phosphines.[3] It has been shown that metallophosphines can exhibit very high basicity at phosphorus when a sufficiently electron rich L$_n$M fragment is introduced.[4] Catalytic application of metallophosphine ligands has already met with some notable success.[4a,5–8] For example, Gladysz *et al.* employed electron-rich ruthenium and rhenium phosphido complexes as effective P-donor ligands for palladium-catalysed Suzuki–Miyaura coupling reactions.[4a,5] Metallophosphines that act as chelating κ^2-P,P′ and κ^2-P,N ligands have also been developed and applied to catalytic reactions such as olefin hydroformylation,[6] hydrosilylation[7] and asymmetric olefin hydrogenation.[8] Despite these advances, the catalytic application of metallophosphines is still at the early stage of its development.

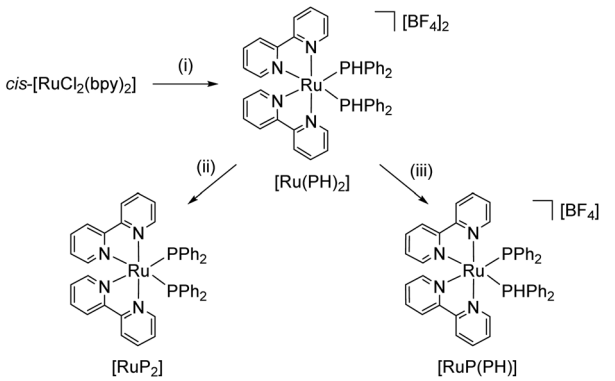
Recently, metalloligands based on polypyridyl ruthenium(II) fragments have drawn considerable attention as building blocks for multimetallic catalysts with wide range of applications.[9] In particular, polypyridyl ruthenium(II) complexes containing nitrogen-based metal-binding sites have been extensively developed.[9] In contrast, those ligands containing phosphorus-based metal binding units have received much less attention[10] despite the proven utility of P-donor ligands in homogeneous catalysis. Given our interest in metal-containing ligands and their applications,[11] we specifically targeted the bis(phosphido) complex *cis*-[(bpy)$_2$Ru(PPh$_2$)$_2$] (bpy = 2,2′-bipyridine), which represents the first phosphido derivative of the archetypal (bpy)$_2$Ru(II) fragment. Here we report the successful synthesis of this species and its derivatization to Ru–Rh, Ru–Ir and Ru$_2$Cu$_2$ heterometallic complexes with an initial proof-of-concept demonstration that the Ru–Ir complex quite efficiently catalyses the (*E*)-selective semi-hydrogenation of alkynes.[12]

We first prepared the dicationic bis(phosphine) precursor *cis*-[(bpy)$_2$Ru(PHPh$_2$)$_2$][BF$_4$]$_2$ ([Ru(PH)$_2$]) by adopting the method for the synthesis of analogous tertiary phosphine derivatives (Scheme 1).[13] The product [Ru(PH)$_2$] is isolated as an air-stable yellow solid in typically 60% yield. NMR data for [Ru(PH)$_2$] are consistent with the C_2 symmetric *cis* structure, showing eight distinct pyridinic proton resonances and an AA′XX′ pattern for the P–H protons from which $^1J_{P-H}$ of 368 Hz can be extracted; the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 36.3 ppm.

Deprotonation of [Ru(PH)$_2$] with 2 equiv. of NaN(SiMe$_3$)$_2$ cleanly afforded the desired bis(phosphido) complex [RuP$_2$] (Scheme 1), which also shows NMR features consistent with C_2 symmetry with a ^{31}P NMR signal (31.4 ppm) slightly shifted upfield relative to that of [Ru(PH)$_2$]. Treatment of [Ru(PH)$_2$] with a weaker base K$_2$CO$_3$ resulted in the formation of the mono-deprotonated complex [RuP(PH)] in 95% yield. The isolation of these deprotonated species was hampered by their high susceptibility to oxidation.[14] However, as described below, the [RuP$_2$] unit can be conveniently delivered to other

Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan. E-mail: takemoto@c.s.osakafu-u.ac.jp

†Electronic supplementary information (ESI) available: Synthetic procedure, spectroscopic data and crystallographic details. CCDC 1870127 and 1870128. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt04646h



Scheme 1 (i) $AgBF_4$ (2 equiv.), acetone, r.t.; then, $PHPh_2$ (4 equiv.), DMF, 100 °C. (ii) $NaN(SiMe_3)_2$ (2 equiv., 1.1 M in THF), DMSO-d_6, r.t. (iii) K_2CO_3 (10 equiv.), DMSO-d_6, r.t.

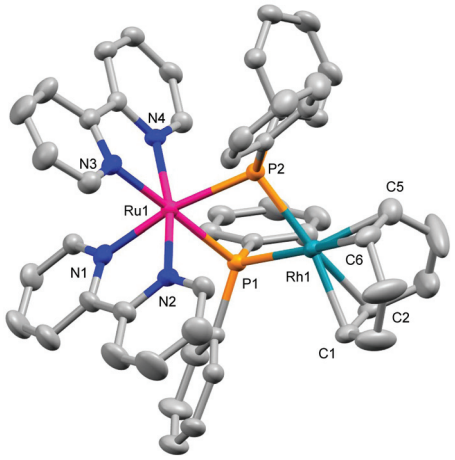
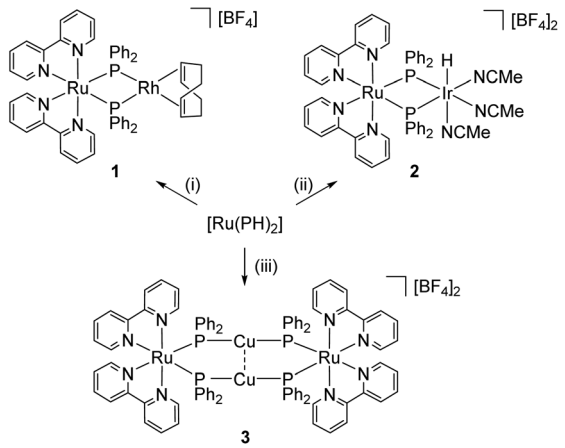


Fig. 1 Thermal ellipsoid plot for the cationic part of [([RuP_2])Rh(cod)][OTf] (**1′**) at 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Rh1–P1 2.3727(13), Rh1–P2 2.3486(13), Ru1–P1 2.3894(14), Ru1–P2 2.3573(13), Rh1–C1 2.211(5), Rh1–C2 2.205(5), Rh1–C5 2.163(6), Rh1–C6 2.195(5), Ru1–N1 2.097(5), Ru1–N2 2.073(4), Ru1–N3 2.122(4), Ru1–N4 2.098(4), Ru1···Rh1 3.596, C1–C2 1.373(9), C5–C6 1.367(10), P1–Rh1–P2 76.29(5), P1–Ru1–P2 75.81(5).

transition metal centres by deprotonating $[Ru(PH)_2]$ in the presence of appropriate metal sources.

The Ru–Rh complex [([RuP_2])Rh(cod)][BF_4] (**1**; cod = 1,5-cyclooctadiene) was prepared in 93% yield *via* deprotonation of $[Ru(PH)_2]$ with K_2CO_3 in the presence of $[Rh(cod)_2][BF_4]$ (Scheme 2). Single-crystal X-ray analysis performed on the triflate salt [([RuP_2])Rh(cod)][OTf] (**1′**) established the chelate coordination of the [RuP_2] ligand to form the square-planar rhodium(I) centre (Fig. 1). The Ru–P and Rh–P bond lengths are similar to each other (2.35–2.39 Å) and comparable to those found in known ruthenium(II) and rhodium(I) complexes with a μ-PPh_2 ligand.[15] The P–Rh–P bond angle of 76.29(5)° places the bite angle of the [RuP_2] chelate in between those of dppm (72°) and dppe (85°) (*i.e.*, $Ph_2P(CH_2)_nPPh_2$; n = 1, 2, respectively).[16]

In contrast to the formation of the rhodium(I) complex **1**, the corresponding reaction between $[Ru(PH)_2]$ and $[Ir(cod)_2][BF_4]$ in the presence of K_2CO_3 afforded an iridium(III) hydride complex [([RuP_2])$IrH(NCMe)_3$][BF_4]$_2$ (**2**) in 74% yield (Scheme 2). The presence of the hydride ligand is evidenced by the ^{1}H NMR signal at −18.44 ppm, whose appearance as a double doublet and the associated $^2J_{P-H}$ coupling constants (16.8 and 11.6 Hz) indicated the facial arrangement of the hydride and two inequivalent phosphido ligands. The ^{1}H NMR spectrum of **2** also shows three distinct signals ascribed to the acetonitrile ligands. It is likely that the initial coordination of the *in situ* generated [RuP(PH)] to an Ir(I) centre is followed by P–H oxidative addition rather than deprotonation of the second P–H bond.



Scheme 2 (i), (ii) [$M(cod)_2$][BF_4] ((i) M = Rh, (ii) M = Ir), K_2CO_3 (10 equiv.), MeCN, r.t., (iii) $[Cu(NCMe)_4][BF_4]$, K_2CO_3 (10 equiv.), MeCN, r.t.

Bridging coordination of [RuP_2] ligands to a dicopper(I) unit was seen in the tetranuclear complex $[Cu_2([RuP_2])_2][BF_4]_2$ (**3**), which was prepared in 94% yield from the reaction of $[Ru(PH)_2]$ with $[Cu(NCMe)_4][BF_4]$ in the presence of K_2CO_3 (Scheme 2). The X-ray structure of **3** (Fig. 2) features the non-chelate μ-κ^1,κ^1-P,P′ coordination of the [RuP_2] ligands and a short Cu1···Cu1* distance (2.4932(9) Å) attributable to a d^{10}–d^{10} closed-shell attraction. Large steric hindrance imposed by the [RuP_2] ligands is indicated by the absence of any coordination of either BF_4^- counter anion or acetonitrile solvent to the unsaturated copper centres in **3**. This feature parallels the R = *t*-Bu case[17a] in the $[Cu_2(\mu\text{-}R_2PCH_2PR_2)_2]^{2+}$ series (R = *t*-Bu, Cy, Ph); the less hindered R = Cy and Ph derivatives are known to give adducts with acetonitrile.[17b,c]

To evaluate the electron donor ability of the [RuP_2] ligand, complex **1** was converted to the dicarbonyl derivative [([RuP_2])$Rh(CO)_2$][OTf] (**4**). As shown in Fig. 3, the CO stretching frequencies of **4** are considerably lower than those of analogous rhodium(I) diphosphine and bis(NHC) complexes,[18] establishing stronger electron donor power of [RuP_2] than those of these organic ligands. The effect may be explained by the resonance structures of **4** shown in Fig. 3.[7b] The electropositive $(bpy)_2Ru(II)$ unit will accommodate the positive charge of the

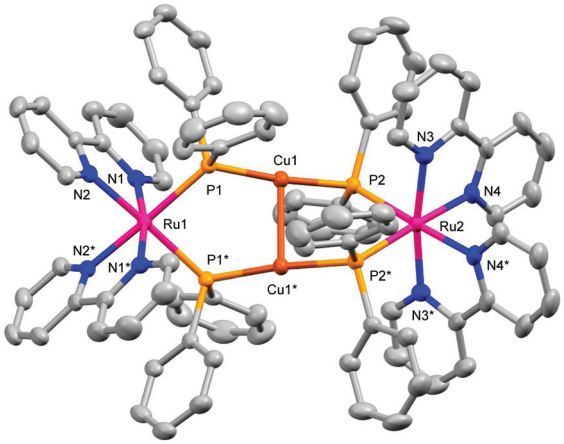


Fig. 2 Thermal ellipsoid plot for the cationic part of $[Cu_2([RuP_2])_2][BF_4]_2$ (**3**) at 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu1–P1 2.2513(10), Cu1–P2 2.2529(10), Cu1···Cu1* 2.4932(9), Ru1–P1 2.4137(9), Ru2–P2 2.4045(10), Ru1–N1 2.080(3), Ru1–N2 2.098(3), Ru2–N3 2.085(3), Ru2–N4 2.104(3), P1–Cu1–P2 174.10(4).

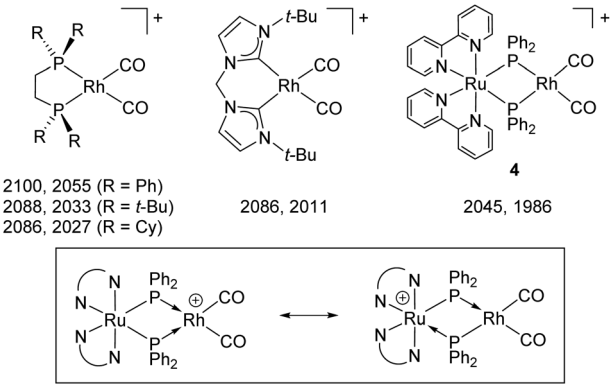


Fig. 3 CO stretching frequencies (cm^{-1}) for rhodium(I) dicarbonyl complexes. Values for organodiphosphine complexes taken from ref. 18*a* (R = Ph), 18*b* (R = *t*-Bu) and 18*c* (R = Cy), and those for the bis-NHC complex from ref. 18*b*.

entire complex to a greater extent than do backbones of organic diphosphine ligands, facilitating the back-donation to the CO moieties.

Finally, the Ru–Ir complex **2** was found to be an efficient catalyst for (*E*)-selective semi-hydrogenation of alkynes. The stereoselective semi-hydrogenation of alkynes is an important atom-economical route to configurationally defined alkenes. The (*E*)-selective alkyne semi-hydrogenation is complementary to the classical (*Z*)-selective hydrogenation protocol using the Lindlar's catalyst.[19] Recently, several homogeneous catalysts have been developed that are active for the (*E*)-selective semi-hydrogenation of alkynes (Fig. 4).[12] Although these catalysts show good functional group tolerance, they exhibit moderate catalyst activity and need elevated reaction temperature or H_2 pressure to reach good conversions.

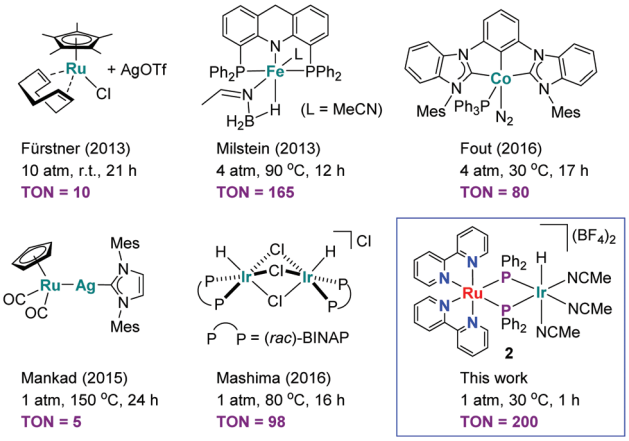
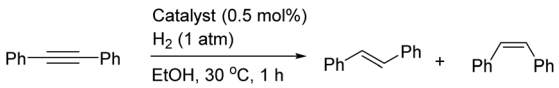


Fig. 4 Catalysts for (*E*)-selective semi-hydrogenation of alkynes (ref. 12). The reaction conditions and turnover numbers (TON) are those reported for the hydrogenation of diphenylacetylene to (*E*)-stilbene. Mes = 1,3,5-trimethylphenyl.

Table 1 Catalyst screening



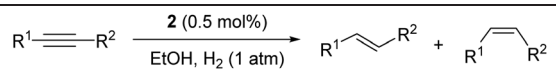
Entry	Catalyst	Conv.[a] (%)	Yield[a] (%) (*E*)	(*Z*)
1	**2**	>99	>99	0
2	**2** (0.1 mol%)	17	12	5
3	$[Ru(PH)_2]$	0	0	0
4	[Ir(cod)((*S*)-BINAP)][BF_4]	37	2	35
5	[Ir(cod)(dppe)][BF_4]	11	1	8
6[b]	[Ir(cod)(dcype)][BF_4]	33	0	22
7[b]	[Ir(cod)(dcype)][BF_4] + HBF_4	2	0	2

[a] Determined by GC. [b] dcype = $Cy_2PCH_2CH_2PCy_2$.

As shown in Table 1, 0.5 mol% of catalyst **2** is sufficient to effect the quantitative conversion of diphenylacetylene into (*E*)-stilbene in 1 h under 1 atm H_2 at 30 °C in EtOH (entries 1 and 2). The result corresponds to a turnover frequency (TOF) of 200 h^{-1}, which is the highest one reported for this reaction. No reaction occurred when $[Ru(PH)_2]$ was used as catalyst (entry 3), indicating that the iridium unit is an essential catalytic component. Iridium(I) organodiphosphine precatalysts (entries 4–6) gave (*Z*)-stibene as the main product and were much less active than **2**, even in the presence of HBF_4 (entry 7) which could generate an iridium(III) hydride.

Having established the catalytic competence of **2**, we tested semi-hydrogenation of various alkyne substrates. Besides diphenylacetylene, phenyl *n*-butyl and phenyl trimethylsilyl acetylenes, 4-octyne and *p*-methoxy- and *p*-hydroxymethyl-substituted diphenylacetylenes were smoothly hydrogenated to give the corresponding (*E*)-alkenes at 30 °C in good yields and stereoselectivity (Table 2, entries 1–6), although alkane byproducts were formed in some cases (entries 2 and 3). The

Table 2 Substrate Scope

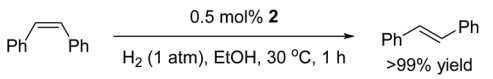


Entry	R^1	R^2	t (h)	T (°C)	Yield[a,b] (%)	$E:Z$[c]
1	Ph	Ph	1	30	>99	100 : 0
2	Ph	*n*-Bu	10	30	91 (9)	94 : 6
3	Ph	$SiMe_3$	1	30	87 (12)	100 : 0
4	*n*-Pr	*n*-Pr	2	30	>99	85 : 15
5	Ph	*p*-C_6H_4OMe	2	30	>99	100 : 0
6	Ph	*p*-$C_6H_4CH_2OH$	2	30	>99	100 : 0
7	Ph	*p*-$C_6H_4NH_2$	15	70	95	90 : 10
8	Ph	*p*-C_6H_4Br	3	70	>99	98 : 2
9	Ph	*p*-C_6H_4COMe	89	70	67	72 : 28
10	Ph	*p*-$C_6H_4NO_2$	39	70	90 (6)	65 : 35
11	Ph	*p*-C_6H_4CN	73	70	66 (15)	27 : 73

[a] Determined by ^{1}H NMR. [b] Yield in parenthesis is the yield of the corresponding alkane. [c] Determined by ^{1}H NMR and/or GC.

p-amino-substituted diphenylacetylene was also hydrogenated to (*E*)-*p*-amino-stilbene in good yield and selectivity (entry 7); the higher temperature (70 °C) and a longer reaction time required for the conversion of this substrate might be due to competitive coordination of the amino group to the cationic iridium(III) centre. The reactions involving electron-withdrawing *p*-acetyl-, *p*-nitro- and *p*-cyano-substituted diphenylacetylenes were slow and exhibited low $E:Z$ selectivity (entries 9–11), which might be due to poor coordination ability of these electron-deficient alkynes (and *Z*-alkene intermediates derived therefrom; see below) to the cationic iridium(III) catalyst.

Complex **2** catalysed isomerization of (*Z*)-stilbene to (*E*)-stilbene under 1 atm H_2 at 30 °C in EtOH (eqn (1)). In addition, (*Z*)-stilbene was detected at the initial stage of the hydrogenation of diphenylacetylene and converted to (*E*)-stilbene (Fig. S27†). These observations suggest that the alkyne semi-hydrogenation by catalyst **2** proceeds *via* initial hydrogenation to (*Z*)-alkenes followed by their isomerization to (*E*)-akenes.[12b,d,e]



(1)

In conclusion, we have synthesized the first phosphido derivative of the $(bpy)_2Ru(II)$ fragment, $[RuP_2]$, and established its coordination behaviour as a bulky and strongly electron-donating bidentate P-donor metalloligand. The potential utility of this ligand in homogeneous catalysis has been demonstrated by the efficient (*E*)-selective alkyne semi-hydrogenation catalysed by the Ru–Ir complex **2**. Future work will focus on the synthesis of other $[RuP_2]$-ligated transition metal complexes and further elucidation of the functions of the $[RuP_2]$ ligand.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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