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Chemistry of the $PC^{NHC}P$ Ligand: Silver and Ruthenium Complexes, Facial/Meridional Coordination, and Catalytic Transfer Hydrogenation

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The silver complex of $PC^{NHC}P$ was identified as $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)_2]Cl_2$ (**1**). Anion exchange of **1** with $AgNO_3$ affords a white compound, which crystallizes into two forms, $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)]_2(NO_3)_2$ (**2a**) and $[Ag_3(Cl)(NO_3)(0.5DMF)(PC^{NHC}P)_2]NO_3$ (**2b**), from different solvent combinations. Their structural determination reveals interesting structural features, including a short Ag⋯Ag interaction in both of them. Unlike the common preparation of ruthenium(II) NHC complexes in the literature, a novel silver carbene transfer reaction between **1** and $RuCl_2(PPh)_3$ produces *fac*-$[Ru_2(\mu\text{-}Cl)_3(PC^{NHC}P)_2]Cl$ (**3**) in good yield. The nonredox nature of the carbene transfer reaction is different from that of an earlier report and shows that the preparation of divalent ruthenium NHC complexes via silver carbene transfer is a feasible synthetic route. Significantly, complex **3** can also be prepared directly from $PC^{NHC}P{\cdot}HCl$ and $RuCl_2(PPh_3)_3$ in the absence of base. Reactions of **3** with CO, phenylacetylene, and pyridine afford mer complexes *mer*,*cis*-$RuCl_2(CO)(PC^{NHC}P)$ (**4**), *mer*-,*trans*-$RuCl_2({=}C{=}CHPh)(PC^{NHC}P)$ (**6**), and *mer*,*trans*-$[RuCl(py)_2(PC^{NHC}P)]Cl$ (**7**), respectively. The fac complex, *fac*,*cis*-$[RuCl(bipy)(PC^{NHC}P)]Cl$ (**8**), was produced in reaction of either **3** or **7** with 2,2′-bipyridine. Treatment of **4** with excess $NaBH_4$ produced the hydride complex *mer*-$RuHCl(CO)(PC^{NHC}P)$ (**5**). Complex **7** is slowly oxidized to *mer*-$[Ru^{III}Cl_3(PC^{NHC}P)]$ (**9**) in the air. The structures of **2a**, **2b**, **3**, **4**, **7**, **8**, and **9** have been confirmed by X-ray crystallography. The reactivity study shows that $PC^{NHC}P$ is capable of accommodating extra steric requirement by readily switching from facial to meridional coordination mode, and the preliminary catalytic study indicates that **3** is effective in transfer hydrogenation of ketones.

Introduction

Transition metal complexes with *N*-heterocyclic carbene (NHC) ligands are attracting a considerable amount of research interest because of their successful applications in diverse catalytic reactions.[1] We were interested in the preparation of transition metal complexes with functionalized *N*-heterocyclic carbene ligands and the study of their catalytic applicability.[2] The incorporation of the carbene functionality into ligand systems containing other “classical” donor groups offers vast opportunities for ligand design which promises the discovery of new efficient catalysts. Along this direction, we have recently reported a new tridentate phosphine/NHC pincer ligand, $PC^{NHC}P$.[2a] Catalytic studies showed that its corresponding palladium(II) complexes are robust Heck catalysts, capable of producing high TONs. There is much current interest in the preparation of ruthenium NHC complexes because of their catalytic properties in olefin metathesis.[1c,3] Other catalytic applications such as hydrogenation,[4] transfer hydrogenation,[5,6] and oxidation of olefins have also been investigated.[6] To further explore the utility of the $PC^{NHC}P$ ligand, we report new ruthenium complexes with $PC^{NHC}P$ and a preliminary catalytic application in hydrogen transfer reactions.

Similar to the preparation of $[Pd^{II}(PC^{NHC}P)Cl]Cl$,[2a] we also employed the silver carbene transfer reaction for the synthesis of the Ru(II) $PC^{NHC}P$ complex. In the course of investigation, we found that the silver compound of $PC^{NHC}P$ is indeed a trisilver complex contain-

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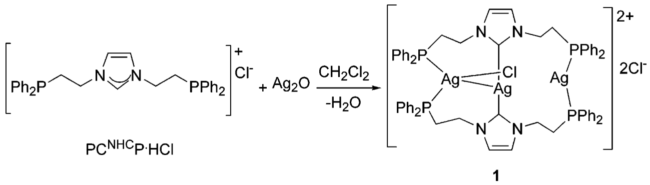
10.1021/om049070v CCC: $30.25

Scheme 1



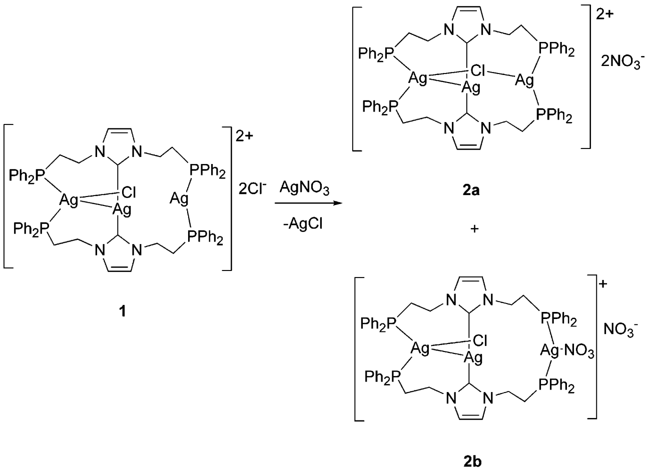
ing 2 equiv of PC^{NHC}P, [Ag$_3$(μ-Cl)(PC^{NHC}P)$_2$]Cl$_2$ (**1**). Reaction of **1** with RuCl$_2$(PPh$_3$)$_3$ cleanly produced a novel bimetallic ruthenium(II) NHC complex, *fac*-[Ru$_2$(μ-Cl)$_3$(PC^{NHC}P)$_2$]Cl, after simple workup procedure. This fac complex can also be produced from a direct reaction between PC^{NHC}P·HCl and RuCl$_2$(PPh$_3$)$_3$ without the need of base. Interestingly, the reactivity study of PC^{NHC}P complexes shows that the PC^{NHC}P ligand can coordinate either in facial or meridional mode depending on the steric environment around the ruthenium center. Catalytic study shows that *fac*-[Ru$_2$(μ-Cl)$_3$(PC^{NHC}P)$_2$]Cl is an effective catalyst in transfer hydrogenation of olefins.

Results and Discussion

Silver Compounds of PC^{NHC}P. The NHC/phosphine ligand precursor, PC^{NHC}P·HCl, has been reported by us recently.[2a] The reaction between a 1:1 molar mixture of Ag$_2$O and PC^{NHC}P·HCl in dichloromethane has been shown to produce a silver carbene complex (**1**), which is able to transfer its carbene moiety on to PdCl$_2$ very readily, producing the [Pd^{II}(PC^{NHC}P)Cl]Cl complex.[2a] However, the formulation of this solid compound was ambiguous, as it has been shown that formation of either Ag(NHC)X (**A**), which contains both NHC and chloride ligands coordinated to the silver, or [Ag(NHC)$_2$]X (**B**), which contains two trans coordinating NHC ligands, was possible in reactions of Ag$_2$O with imidazolium salt.[2d,7] In addition, structures **A** and **B** are indistinguishable by their NMR spectra. The initial formulation of **1** was Ag(PC^{NHC}P)Cl, containing dangling phosphine groups.[2a] However, in further utilization of this white solid as carbene transfer reagent, we noticed that the molecular weight of **1** should be much heavier. A reinvestigation on **1** dissolved in dichloromethane by electrospray mass spectrometry revealed unambiguously that **1** is a trinuclear silver compound containing three silver and three chloride atoms with two PC^{NHC}P ligands present. The peak at *m/z* 1114 corresponds to the molecular ion [Ag$_3$(PC^{NHC}P)$_2$Cl$_3$]$^+$. Peaks observed at *m/z* 1379, 1272, 1093, 743, and 599 correspond to molecular fragments [Ag$_3$(PC^{NHC}P)$_2$Cl$_2$]$^+$, [Ag$_2$(PC^{NHC}P)$_2$Cl$_2$]$^+$, [Ag$_2$(PC^{NHC}P)$_2$Cl]$^+$, [Ag(PC^{NHC}P)$_2$]$^+$, [Ag$_2$(PC^{NHC}P)Cl]$^+$, and [Ag(PC^{NHC}P)]$^+$, respectively. On the basis of the molecular structure of its derivatives (vide infra), the proposed structure of **1** is illustrated in Scheme 1. It is conceivable that the extra chloride present in the compound should come from the dichloromethane solvent during the reaction.

Despite our attempts, we were not able to obtain crystals of **1** with sufficient quality. We thought that by preparation of derivatives of **1**, X-ray structural determination may become possible, which would provide an ideal to the structure of **1**. Our strategy was proven to be successful. Reactions of **1** with 2 equiv of AgNO$_3$ in methanol produced a white solid (**2**). In contrast to the parent complex **1**, which exhibits only a single, broad ^{31}P{^{1}H} NMR signal at δ −10.0,[2a] the ^{31}P{^{1}H} NMR spectrum of **2** shows two broad signals centered at δ −3.1 and 0.6, indicating the presence of two types of chemically nonequivalent phosphorus atoms. The coupling of the ^{31}P nuclei with both ^{107}Ag and ^{109}Ag ($I = 1/2$) was unresolved. The two phosphorus signals coalesce into a single resonance on heating a CDCl$_3$ solution of the compound at 54 °C, indicating the fluxionality of the compound at elevated temperature.

Scheme 2



Colorless crystals can be obtained from the solid sample employing the solvent combinations of either acetonitrile/ether or DMF/ether. The X-ray structural determinations on the two batches of crystals afford two different structures (Scheme 2). The thermal ellipsoid plot of the cationic portion of **2a** obtained from the former solvent combination is shown in Figure 1. The crystallographic data are listed in Table 1. The structure, [Ag$_3$(μ-Cl)(PC^{NHC}P)$_2$]$_2$NO$_3$, consists of an unsymmetrical molecular dication in which three Ag$^+$ ions are spanned by two PC^{NHC}P ligands. Two of the Ag$^+$ ions are linked by a bridging Cl$^-$ anion, and the net +2 charge is balanced by two noninteracting nitrate ions. The central Ag$^+$ is bound to the two ligands via the NHC functionality, whereas the other two Ag$^+$ ions are bound via the phosphine groups. The Ag$^+$ ions are situated on a noncrystallographic mirror plane, which renders the two ligands chemically equivalent. As seen in Figure 1, the gauche conformation of the ethylene spacers (dihedral angles = 54.35° and 51.13°) on the right-hand side results in one short d^{10}−d^{10} Ag1−Ag2 distance of 2.9281(14) Å, whereas the anti conformation of the ethylene groups (dihedral angles = 159.22° and 159.29°) on the left-hand side precludes the formation of such short contact between Ag1 and Ag3 (nonbonding distance = 4.480 Å). The Ag2 and Ag3 are linked by the

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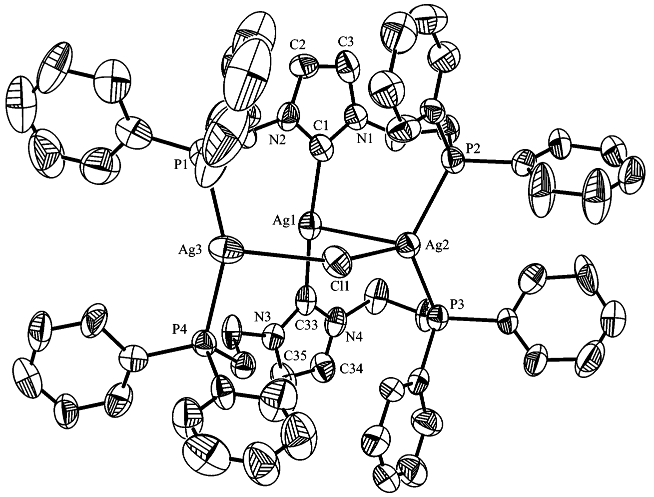


Figure 1. Thermal ellipsoid plot (30%) of cationic portion of **2a** with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ag1−C1, 2.117(14); Ag1−C33, 2.095(14); Ag1−Ag2, 2.9281(14); Ag2−P2, 2.472(4); Ag2−P3, 2.466(4), Ag2−Cl1, 2.664(3); Ag3−P1, 2.421(4); Ag3−P4, 2.418(4); Ag3−Cl1, 2.798(4); C1−Ag1−C33, 173.7(5), C1−Ag1−Ag2, 76.29(9); C33−Ag1−Ag2, 91.2(3); P2−Ag2−Ag1, 106.10(9); P2−Ag2−Cl1, 114.27 (12), P2−Ag2−P3, 124.08(12); P3−Ag2−Cl1, 119.37(12); P3−Ag2−Ag1, 100.72(9); Ag2−Cl1−Ag3, 145.53(15); Ag1−Ag2−Cl1, 76.27(9); P1−Ag3−P4, 154.18(13); P1−Ag3−Cl1, 111.23(13); P4−Ag3−Cl1, 94.31(12).

Table 1. Crystallographic Data for 2a and 2b

	2a	**2b**
empirical formula	$[C_{62}H_{60}Ag_3ClN_4P_4]2NO_3$	$[C_{62}H_{60}Ag_3ClN_4P_4\cdot NO_3\cdot 0.5DMF]NO_3\cdot DMF$
fw	1468.10	1577.45
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	18.543(8)	15.023(7)
b, Å	14.980(5)	15.734(8)
c, Å	23.226(8)	17.460(8)
α, deg	90	65.55(3)
β, deg	106.215(17)	66.36(2)
γ, deg	90	87.31(3)
V, Å^3	6195(4)	3406(3)
T, K	273(2)	273(2)
Z	4	2
D_{calcd}, Mg/m^3	1.574	1.538
μ, mm^{-1}	1.140	1.045
no. of data collected	34 462	21 227
no. of unique data	12 176	15 042
no. of params refined	715	901
R_1 [$I > 2\sigma I$]	0.0709	0.0505
wR_2 (all data)	0.2482	0.01420

bridging Cl1 anion asymmetrically with a Ag2−Cl1 distance of 2.664(3) Å, Ag3−Cl1 distance of 2.798(4) Å, and Ag−Cl−Ag angle of 145.53(15)°. The chemically nonequivalent phosphorus atoms in PC^{NHC}P are consistent with the solution NMR data, which exhibit two ^{31}P{^{1}H} NMR signals. Interestingly, in **2a**, each Ag$^+$ ion is in different coordination geometries. The Ag1 center is in a T-shaped coordination geometry with the three relevant angles 173.7(5)°, 86.3(3)°, and 91.2(3)°, whereas the Ag2 center is in a distorted tetrahedral geometry with the average of bond angles equal to 106.80°. The Ag3 center is in a distorted trigonal planar geometry with the sum of bond angles (154.18(13)°, 94.31(12)°, 111.23(13)°) of 359.72°.

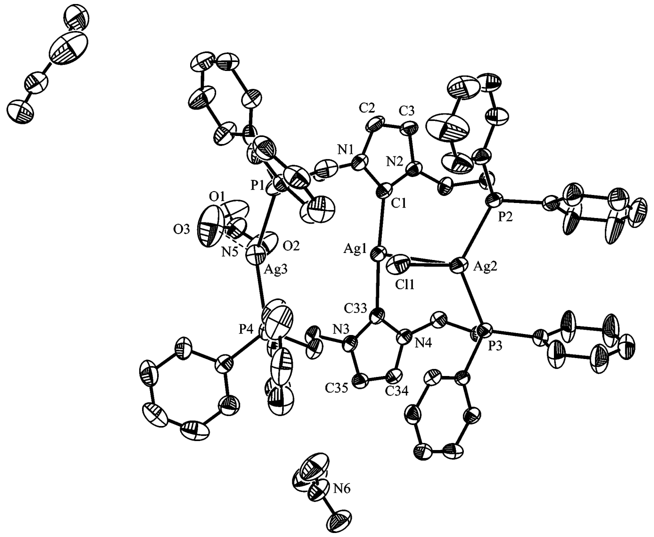
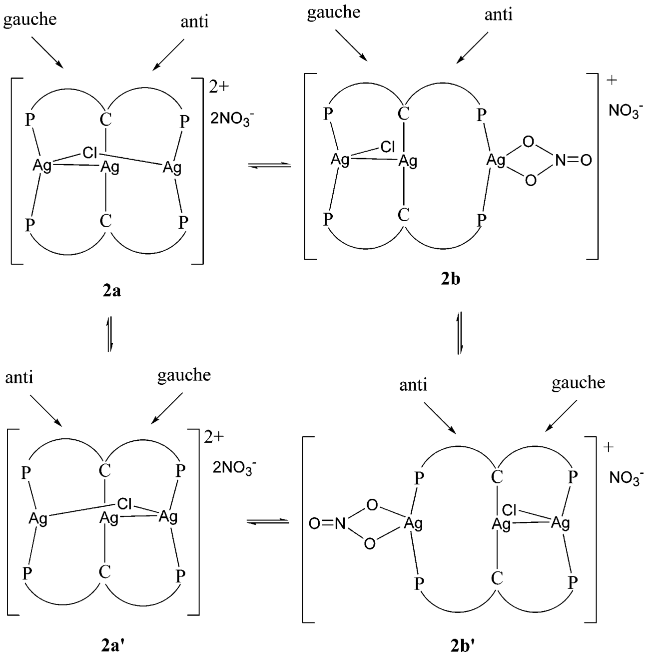


Figure 2. Thermal ellipsoid plot (30%) of **2b** with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ag1−C1, 2.110(5); Ag1−C33, 2.110(5); Ag1−Ag2, 3.0585 (15), Ag2−P2, 2.4571(18); Ag2−P3, 2.4432(16); Ag2−Cl1, 2.528(2); Ag3−P1, 2.428(2); Ag3−P4, 2.4194(19), C1−Ag1−C33, 173.07(19); C1−Ag1−Ag2, 90.98(13); C33−Ag1−Ag2, 88.81(14); P2−Ag2−Ag1, 102.32(5); P2−Ag2−Cl1, 117.44(6); P2−Ag2−P3, 122.16(6); P3−Ag2−Cl1, 119.74(6); P3−Ag2−Ag1, 104.67(5); Ag1−Ag2−Cl1, 69.47(6); P1−Ag3−P4, 139.62(6).

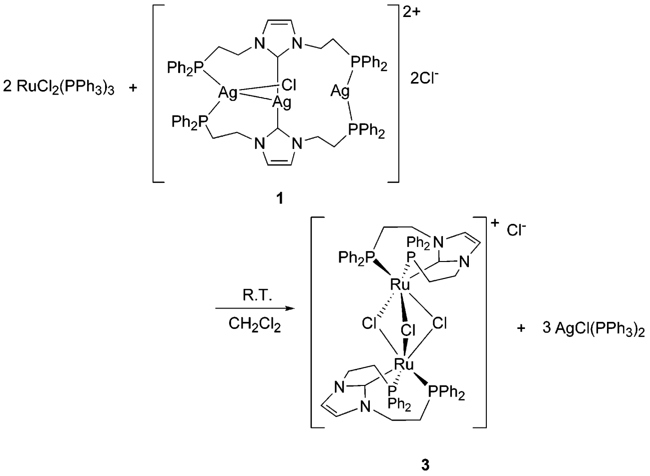
The structure obtained from the DMF/ether solvent system is depicted in Figure 2. The crystallographic data are listed in Table 1. The striking difference between structures **2a** and **2b** is the incorporation of DMF solvent molecules in the crystal lattice and one Ag$^+$ ion with coordinated phosphine groups is projected outward such that, unlike **2a**, the coordinating chloride is only ligated to one Ag$^+$ ion in **2b** with a Ag2−Cl1 distance of 2.528 (2) Å. The protruded Ag(3) is weakly coordinated to a chelating NO_3^- ligand (Ag3−O2 = 2.658 Å; Ag3−O3 = 2.701 Å) and a DMF molecule (Ag3−O7 = 2.624 Å) refined to have 50% occupancy factor. Therefore, the structure of the compound is described as a trinuclear silver monocation with a noncoordinating nitrate anion, $[Ag_3(Cl)(NO_3)(PC^{NHC}P)(0.5DMF)]NO_3\cdot DMF$. The nonbonding Ag1···Ag3 distance of 4.863 Å becomes much longer than that of 4.480 Å in **2a**. Similar to the structure **2a**, the gauche conformation of the ethylene spacers on the depicted right side of the cation (dihedral angles = 57.07° and 50.11°) affords a short Ag1−Ag2 distance of 3.0585(15) Å, which is, however, significantly longer than that in **2a**. In contrast, the dihedral angles of the ethylene linkage on the depicted left side are 173.54° and 172.38°, which are significantly greater than the corresponding angles of 159.22° and 159.29° in **2a**, as a consequence of the conformational flexibility of the ethylene spacer in projecting the Ag3 atom out and hence the absence of a μ-chloride bridge in **2b**.

The observation of only two broad singlets in the ^{31}P{^{1}H} NMR spectrum of **2** indicates that **2a** and **2b** are in rapid equilibrium at room temperature. At high temperature, these two signals coalesce, which can be explained by the fluxional interchange between **2a** and **2a′** (**2b** and **2b′**) due to the gauche/anti conformational interchange of the two ethylene spacers, which renders the two phosphorus atoms in PC^{NHC}P equivalent (Scheme

Scheme 3



Scheme 4



3). The two signals do not resolve at −35 °C, however. A similar trinuclear structure can be expected for **1**, and it is reasonable to suggest that the absence of the chelating anion in **1** renders the exchange much faster than in **2** and hence the observation of only a broad ^{31}P NMR signal at ambient temperature.[2a]

Synthesis and Characterization of *fac*-[Ru$_2$(μ-Cl)$_3$(PC^{NHC}P)$_2$]Cl (3). While silver carbene transfer reaction is a frequently used route for the preparation of NHC complexes of late transition metals, such as palladium,[8] the majority of ruthenium NHC complexes are typically prepared by trapping the NHC, preformed or generated in situ from an appropriate imidazolium salt in the presence of base, with a suitable Ru(II) precursor.[9] A recent article by Arnold et al. showed that the carbene transfer reaction between AgL [L = O$^-$CPh(CH$_2${1-C[NCHCHNBu^t]}$_2$) and RuCl$_2$(PPh$_3$)$_3$ afforded a Ru(III) complex, [Ru^{III}LCl$_2$(PPh$_3$)]. The coproducts of the reaction were PPh$_3$ and metallic silver.[10] We also conducted a similar reaction by stirring a 1:1 molar mixture of the silver carbene **1** and RuCl$_2$(PPh$_3$)$_3$ in dichloromethane at room temperature overnight (Scheme 4). In sharp contrast to the report by Arnold, a Ru(II) compound, subsequently identified by the X-ray structural analysis as a triply halide-bridged diruthenium complex, [Ru$_2$(μ-Cl)$_3$(PC^{NHC}P)$_2$]Cl (**3**), is produced. Also the coproduct is, instead of Ag^0, AgCl(PPh$_3$)$_2$.[11] This known compound is indentified by NMR spectra, which were the same as those of an authentic sample. Because of the ionic nature, complex **3** can easily be isolated from the reaction mixture by complete removal of DMF and then precipitation with THF, in which **3** is completely insoluble, whereas AgCl(PPh$_3$)$_2$ dissolves readily. Simple filtration affords the orange compound in good yields (72%). Complex **3** appears to be quite robust in both solution and solid state. In the ^{31}P{^{1}H} NMR spectrum, an AX spin splitting pattern having two sets of doublet at δ 43.4 and 48.5 is observed, reflecting the chemical nonequivalence of the two phosphorus nuclei in PC^{NHC}P. The magnitude of the coupling constant ($^2J_{PP}$ = 31.3 Hz) clearly suggests a cis disposition of phosphorus atoms and therefore facial coordination geometry in **3**. Only two phosphorus signals instead of four are observed, indicating the presence of a symmetry element in the diruthenium complex (vide infra). In the ^{31}C{^{1}H} NMR spectrum, the carbene resonance is observed at δ 174.5 as a virtual triplet with $^2J_{CP}$ = 21.6 Hz. Interestingly, in the ^{1}H NMR spectrum, seven different signals were observed for the ethylene protons, which span over a wide range of chemical shifts from δ 1.0 to 5.7. Also, a triplet corresponding to two phenyl protons is observed at δ 5.42, which resonates at a remarkably higher field than one of the CH signals at δ 5.72. The spectroscopic data strongly imply that, in solution, the PC^{NHC}P is coordinated in a sterically demanding facial fashion with some of the ethylene or phenyl protons localizing in the anisotropic shielding and deshielding regions of the phenyl rings.

An X-ray structural determination on single crystals of **3**, obtained by slow evaporation of an acetone/dichloromethane solution of **3**, was performed. A thermal ellipsoid plot of the molecular cation is shown in Figure 3 with crystallographic data and selected structural parameters in Tables 2 and 3, respectively. Complex **3** exists as a cationic triply μ-Cl-bridged diruthenium complex with an anionic chloride. The triply halide-bridged bioctahedral architecture is a recurring structure of remarkable stability and conceptual interest in ruthenium chemistry. Monodentate phosphines and tripodal and linear tridentate phosphines are common supporting ligands in these diruthenium complexes.[12] As predicted from the spectroscopic data, the two PC^{NHC}P ligands coordinate to the ruthenium centers in a facial mode. The two Ru(PC^{NHC}P) fragments are positioned across the μ-Cl bridges in a staggered conformation. A noncrystallo-

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Table 2. Crystallographic Data for 3, 4, 7, 8, and 9

	3	**4**	**7**	**8**	**9**
empirical formula	$[C_{62}H_{60}Cl_3N_4P_4\text{-}Ru_2]Cl$	$C_{32}H_{30}Cl_2N_2O\text{-}P_2Ru\cdot DMF$	$[C_{41}H_{40}ClN_4P_2Ru]Cl\cdot DMF$	$[C_{41}H_{38}ClN_4P_2Ru]Cl\cdot DMF\cdot 0.5(H_2O)$	$C_{31}H_{30}Cl_3N_2P_2Ru\cdot DMF$
fw	1328.96	765.59	895.78	902.77	765.59
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/c$	$P2_1/n$
a, Å	14.096(3)	13.332(7)	40.7001(14)	18.8238(7)	13.332(7)
b, Å	18.891(4)	12.287(6)	11.7146(4)	20.9699(8)	12.287(6)
c, Å	25.927(6)	20.891(10)	20.3929(7)	29.5630(10)	20.891(10)
α, deg	90	90	90	90	90
β, deg	92.846(4)	95.538(8)	105.996(2)	126.477(2)	95.535(8)
γ, deg	90	90	90	90	90
V, Å^3	6896(3)	3406(3)	9346.6(6)	9383.4(6)	3406(3)
T, K	298(2)	150(2)	150(2)	150(2)	298(2)
Z	4	4	8	8	4
D_{calcd}, Mg/m^3	1.280	1.493	1.273	1.278	1.493
μ, mm^{-1}	0.723	0.748	0.555	0.554	0.748
no. of data collected	37 974	18 584	77 235	13 2276	18 584
no. of unique data	13 512	7615	10 180	19 455	7615
no. of params refined	716	449	487	1072	449
R_1 [$I > 2\sigma I$]	0.0903	0.0390	0.0856	0.0842	0.0390
wR_2 (all data)	0.3160	0.1049	0.2992	0.2760	0.1049

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 3

Ru1−C1	1.993(11)	Ru2−C32	1.992(12)
Ru1−P1	2.269(3)	Ru2−P4	2.272(3)
Ru1−P2	2.272(3)	Ru2−P3	2.273(3)
Ru1−Cl1	2.528(3)	Ru2−Cl1	2.509(3)
Ru1−Cl2	2.515(3)	Ru2−Cl2	2.532(3)
Ru1−Cl3	2.497(3)	Ru2−Cl3	2.494(3)
C1−Ru1−P1	91.6(3)	C32−Ru2−P3	82.5(3)
C1−Ru1−P2	83.2(4)	P4−Ru2−P3	97.77(11)
P1−Ru1−P2	97.07(11)	C32−Ru2−Cl3	88.1(3)
C1−Ru1−Cl3	87.3(4)	P4−Ru2−Cl3	94.15(10)
P1−Ru1−Cl3	93.97(11)	P3−Ru2−Cl3	164.98(11)
P2−Ru1−Cl3	165.64(10)	C32−Ru2−Cl1	169.8(3)
C1−Ru1−Cl2	168.0(4)	P4−Ru2−Cl1	93.25(10)
P1−Ru1−Cl2	92.90(11)	P3−Ru2−Cl1	105.79(11)
P2−Ru1−Cl2	107.17(11)	Cl3−Ru2−Cl1	82.53(9)
Cl3−Ru1−Cl2	81.33(10)	C32−Ru2−Cl2	97.9(3)
C1−Ru1−Cl1	98.2(3)	P4−Ru2−Cl2	169.25(10)
P1−Ru1−Cl1	169.22(11)	P3−Ru2−Cl2	88.65(11)
P2−Ru1−Cl1	88.57(10)	Cl3−Ru2−Cl2	81.04(10)
Cl3−Ru1−Cl1	82.10(9)	Cl1−Ru2−Cl2	76.65(9)
Cl2−Ru1−Cl1	76.62(9)	Ru2−Cl1−Ru1	83.74(8)
C32−Ru2−P4	91.5(4)	Ru1−Cl2−Ru2	83.53(8)
		Ru2−Cl3−Ru1	84.68(9)

graphic C_2 axis orthogonal to the Ru−Ru axis renders the two halves chemically equivalent. The presence of only a C_2 rotation axis in the molecule means that **3** is chiral and it crystallizes in the centrosymmetric space group $P2_1/n$ so that the two enantiomers are situated across a center of inversion in the crystal lattice. Venanzi et al. has shown that the binuclear complex $[Ru_2(\mu\text{-}Cl)_2(ETP)_2]Cl$ (ETP = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$) is a mixture in solution in which the central phosphorus atoms of the linear triphosphine ligand can be either eclipsed or staggered, producing the symmetric isomer having C_s symmetry (*ec*-form) and the chiral isomer having C_2 symmetry (*st*-form), respectively.[12b] Crystal structures of the *ec*-form were obtained, whereas the *st*-form was only inferred by NMR spectroscopy. In contrast, NMR spectroscopy and structural determination show that **3** exists only in the chiral *st*-form in both solution and solid state. It is conceivable from the structure that steric repulsion between the phenyl rings prevents the formation of the sterically demanding *ec*-form. Each ruthenium is in a distorted octahedral geometry. All of the six Cl−Ru−P and Cl−Ru−C angles (average 167.8°) are deviated significantly from the ideal 180°. The nonbonding $Ru^{II}\cdots Ru^{II}$ distance of 3.362 Å is in the usual range of $Ru^{II}(\mu\text{-}Cl)_3Ru^{II}$ complexes.[12,13] The Ru−carbene distance is 1.99 Å, which is comparable to that of a reported ruthenium complex with the same donor set (2.02 Å).[14] Notably, short intramolecular CH/π hydrogen bonds are present in the structure, which are consistent with the NMR data. The CH/π hydrogen bond, a kind of hydrogen bond operating between a soft acid CH and a soft base π-system, plays a significant role in intramolecular interaction and supramolecular

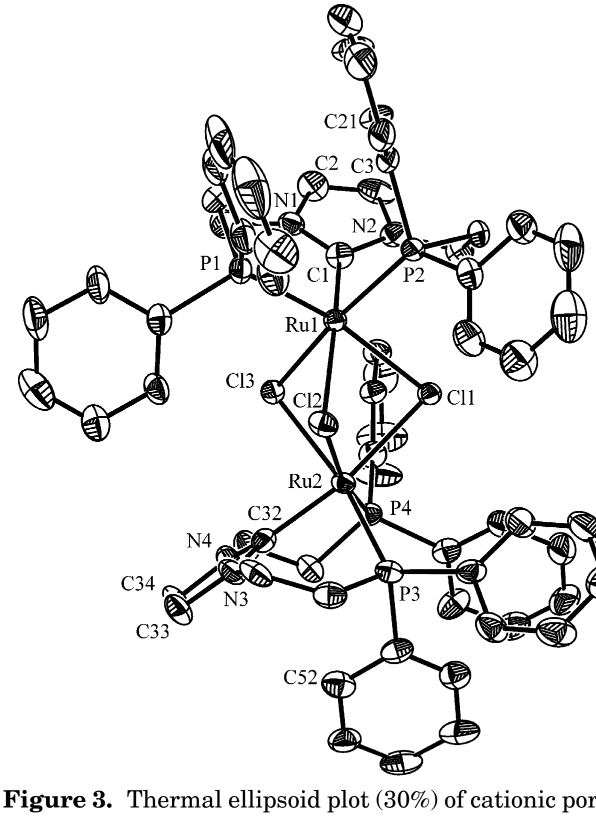

Figure 3. Thermal ellipsoid plot (30%) of cationic portion of **3** with hydrogen atoms omitted for clarity.

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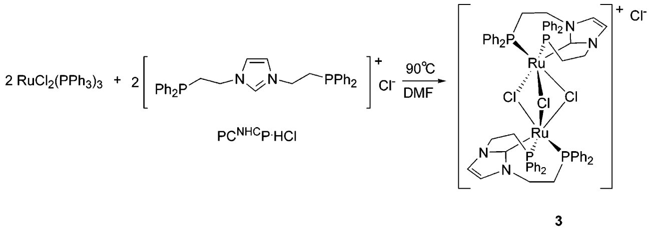
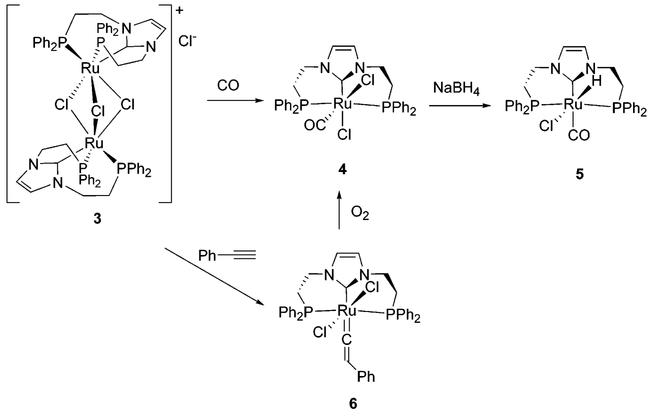
Scheme 5



Scheme 6



chemistry.[15] The phenyl proton on C52 points toward the face of the central imidazole ring, making short CH/π hydrogen contacts (N3, 2.546 Å; C32, 2.686 Å; N4, 2.880 Å; C33, 2.957 Å; C34, 2.716 Å). Similarly, the hydrogen on C21 makes short CH/π hydrogen contacts with the other imidazole ring (N1, 3.002 Å; C1, 2.747 Å; N2, 2.553 Å; C3, 2.764 Å; C2, 3.054 Å). Indeed these two hydrogen atoms are located only 2.49 and 2.46 Å above the best plane of the neighboring imidazole rings, respectively. The localization of the two chemically equivalent hydrogen atoms over the π-cloud results in an upfield shift of its NMR resonance. Hence, the signal at δ 5.42 can be safely assigned to these hydrogen atoms. For comparison, in the crystal structures of *cis*-1,4-dihydro-4-tritylbiphenyl and its bromo derivative, the short contacts between an aromatic CH and the best plane of a phenyl ring were 2.55 and 2.48 Å, respectively.[16] The two corresponding CH protons were observed at δ 6.3 and 6.15. It should be noted that the NMR data and structural determination clearly indicate that the crystal conformation of **3** is kept in solution.

We have shown that for the preparation of [Pd(PC^{NHC}P)Cl]Cl the ligand precursor, PC^{NHC}P·HCl, can react with PdCl$_2$ without the need of base.[2a] Consistent with this previous finding, PC^{NHC}P·HCl can similarly react with RuCl$_2$(PPh$_3$)$_3$ without base at 90 °C in DMF, affording **3** (Scheme 5). However, this synthetic route is not as clean as the silver carbene transfer reaction because in situ NMR study shows that minor unidentified coproducts with phosphorus signals δ 10−22 were produced. Nevertheless, recrystallization of the crude product with dichloromethane/THF gives pure **3** in 62% of yield.

Reactivity of *fac*-[Ru$_2$(μ-Cl)$_3$(PC^{NHC}P)$_2$]Cl (3). On refluxing a 1,2-dichloroethane solution of **3** under CO atmosphere, RuCl$_2$(CO)(PC^{NHC}P) (**4**) was obtained (Scheme 6). In sharp contrast to **3**, the ^{31}P{^{1}H} NMR spectrum of **4** consists of only a singlet at δ 10.9, indicating the equivalence of the two phosphorus atoms in the PC^{NHC}P ligand by the presence of symmetry. It has been shown that the chemical shifts of the phosphorus atoms are diagnostic for the coordination modes of linear tridentate phosphine ligands.[17,18] Because of the remarkable trans influence of the phosphine ligands, the phosphorus nuclei of the mer complex typically resonate at higher field than those of the facial isomers. The high-field resonance of the ^{31}P signal compared with those in **3** strongly indicates a meridional chelation mode of PC^{NHC}P in **4**. Also, in its ^{1}H NMR spectrum, three broad signals corresponding to the eight CH$_2$ protons are observed at δ 2.67, 4.11, and 4.81 with a 2:1:1 integration ratio. The broadening of these signals can be similarly attributed to the involvement of a dynamic interconversion between left- and right-twisted forms in solution observed in Pd(PC^{NHC}P) complexes.[2a] Similar to what we have observed for the Pd(PC^{NHC}P) complexes, the fluxionality is not resolved down to −60 °C. In its ^{13}C{^{1}H} NMR spectrum, the coordinating C≡O ligand gives a triplet at δ 199.6 with a $^2J_{CP}$ coupling constant of 13.2 Hz, which indicates that the carbonyl ligand is cis to the two phosphorus atoms. The carbene signals also appear as a triplet at δ 169.1 with the $^2J_{CP}$ coupling constant of 11.0 Hz, the magnitude of which is significantly smaller than the corresponding value of 21.6 Hz in **3** (vide supra). The question whether the carbonyl ligand is trans or cis to the carbene donor was answered by structural determination. Crystals of **4** were readily obtained by vapor diffusion of diethyl ether into a DMF solution. The crystallographic data are summarized in Table 2. The molecular structure of **4** is shown in Figure 4. The ruthenium center is in an

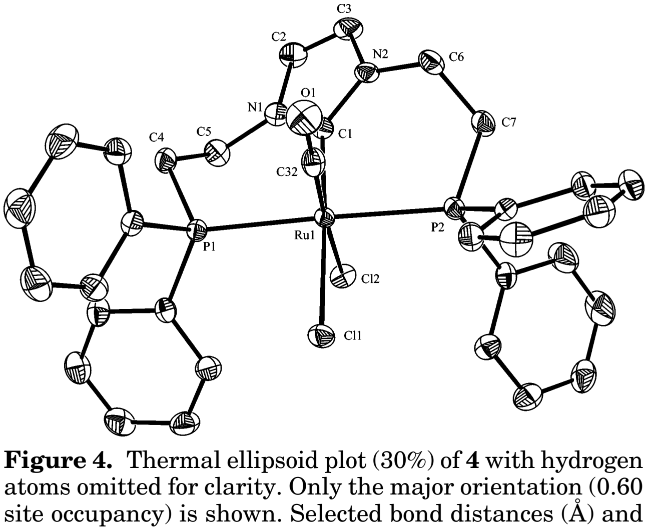


Figure 4. Thermal ellipsoid plot (30%) of **4** with hydrogen atoms omitted for clarity. Only the major orientation (0.60 site occupancy) is shown. Selected bond distances (Å) and angles (deg) of the major orientation: Ru1−C1, 2.038(3); Ru1−C32, 1.792(9); Ru1−Cl1, 2.4846(12); Ru1−Cl2, 2.432(3); Ru1−P1, 2.3737(13); Ru1−P2, 2.3780(13); C32−Ru1−Cl2, 175.3(4); C1−Ru1−Cl1, 177.35(9); P1−Ru1−P2, 178.20(3); C1−Ru1−P1, 91.02(9); C1−Ru1−P2, 90.55(9); C1−Ru1−C32, 89.4(4); C1−Ru1−Cl2, 94.77(9); Cl1−Ru1−P1, 86.34(3); Cl1−Ru1−P2, 92.10(3); Cl1−Ru1−C32, 89.4(4); Cl1−Ru1−Cl2, 94.77(9).

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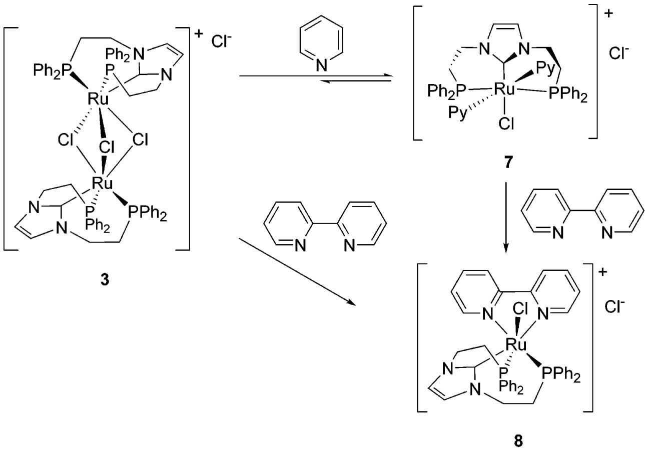
octahedral geometry with the PC^{NHC}P ligand chelating in a meridional fashion. One of the chloride ligands is trans to the carbene moiety, whereas the other chloride (C≡O) is disordered between the two apical sites in a 60:40 ratio. Hence, the two chlorides are cis to each other with the carbonyl ligand also cis to the carbene moiety. Similar to the reported palladium complexes of PC^{NHC}P,[2a] the ligand is twisted to one side, forming an overall chiral environment of the complex. The twist angle between the best planes defined by the imidazole ring and the equatorial plane is 28.9°. Notably, the disorder model implies that there are two overlapping diastereomers present in the asymmetric unit of the centrosymmetric $P2_1/n$ unit cell. Their corresponding enantiomers are present about centers of inversion in the crystal lattice. In solution, it is the rapid interconversion between the left- and right-twisted forms that leads to the broadening of ethylene signals and single phosphorus resonance observed. In the major orientation, the Ru−carbene distance is 2.038(3) Å, which is longer than that of 1.99 Å in **3**, whereas the Ru−CO distance is significantly shorter (1.792(9) Å). The Ru−Cl distance trans to the carbene (2.4846(12) Å) is slightly longer than that trans to Cl (2.432(3) Å), which can be attributed to the bigger trans influence exerted by the NHC moiety.

Recently, a number of ruthenium hydride complexes with NHC as supporting ligand have been reported.[4,19] But it is rather surprising that they are generally prepared by reactions between preformed ruthenium hydride precursors and NHC ligands. So far, none of them are prepared from reactions of ruthenium halide complexes with hydride transfer reagent, such as $NaBH_4$, which is a common synthetic route for other ruthenium hydride complexes.[20] We carried out a reaction by stirring a mixture of **4** with excess $NaBH_4$ in ethanol, which results in the isolation of the ruthenium hydride RuHCl(CO)(PC^{NHC}P) (**5**). The $^{31}P\{^1H\}$ NMR spectrum reveals a single resonance at δ 9.56, indicating the meridional chelation of PC^{NHC}P. The presence of the hydride ligand is clearly indicated by the high-field triplet at δ −14.8 ($^2J_{HP}$ = 19.3 Hz). The integral ratio indicates **5** is a monohydride compound. Although the poor solubility of **5** precludes the acquisition of its ^{13}C NMR spectrum, the presence of the C≡O ligand is confirmed by the presence of an intense IR absorption at 1928.6 cm^{-1}. This lower frequency number compared with that in **4** is in accord with the more electron-donating nature of hydride than chloride. On the basis of the NMR data, three possible structures of complex **5** can be proposed. The possibility of the hydride trans to the C≡O is precluded first because such a hydride would be significantly upfield shifted and appear in the range δ −3 to −8. For example, the hydride signal is at δ −3.75 for $Ru(IMes)_2(CO)_2(OH)H$,[19a] δ −5.15 for $RuHCl(CO)_2(P(i\text{-}Pr)_3)_2$,[21] and δ −3.68 to −7.25 for $[RuH(CO)(PP)_2]^+$ (PP = dppm, dppe, dppp).[22] The hydride in **5** should be trans to the chloride, rather than trans to the carbene, as its chemical shift (δ −14.8) is close to those of related hydride structures; δ = −13.65 for RuHCl(CO)(PMP) (PMP = $2,6\text{-}(Ph_2PCH_2)_2C_5H_3N$)[20b] and δ = −13.5 to −15.4 for $RuHCl(CO)(PPh_3)(PP)$ (PP = dppm, dppp).[22]

Scheme 7



On refluxing a 1,2-dichlorethane solution of **3** with excess phenylacetylene, a vinylidene complex, $RuCl_2(=C=CHPh)$(PC^{NHC}P) (**6**), is produced. There is only a single ^{31}P resonance observed at δ 7.00, indicating the meridional chelation of PC^{NHC}P. The presence of a vinylidene ligand is characterized by the presence of the vinylidene proton observed as a triplet at δ 3.52 ($^4J_{HP}$ = 3.8 Hz), the low-field metal bonded vinylidene carbon signal at δ 348.1 ($^2J_{CP}$ = 16.1 Hz), and its β-carbon signal at δ 108.3. The Ru−carbene signal is observed as a triplet with a smaller coupling constant of $^2J_{CP}$ = 10.6 Hz. Similar to **4**, three broad signals for the ethylene protons at δ 2.64, 4.18, and 4.70 (integration ratio = 2:1:1) are observed, indicating the fluxionality of the complex. Unfortunately, we were not able to obtain crystals for the structural determination. But based on related vinylidene structures of linear tridentate phosphine complexes,[18,23] presumably the vinylidene ligand in **6** is trans to the carbene moiety with two mutually trans chloride ligands. Similar to other reported vinylidene complexes,[24] complex **6** is air-stable in the solid state but slowly undergoes oxidative cleavage (4−5 days) to give the carbonyl complex **4** and benzaldehyde. The transformation can be speeded up by refluxing a solution of **6** in the air overnight.

Complex **3** reacts with excess pyridine in DMF to produce a cationic ruthenium bis(pyridine) compound, $[RuCl(py)_2$(PC^{NHC}P)] (**7**) (Scheme 7). The $^{31}P\{^1H\}$ NMR spectrum of the yellow solid in $CDCl_3$ shows a major single resonance at δ 9.56, suggesting a meridional chelation of the PC^{NHC}P ligand around the metal center. However, even with a prolonged reaction time, the set

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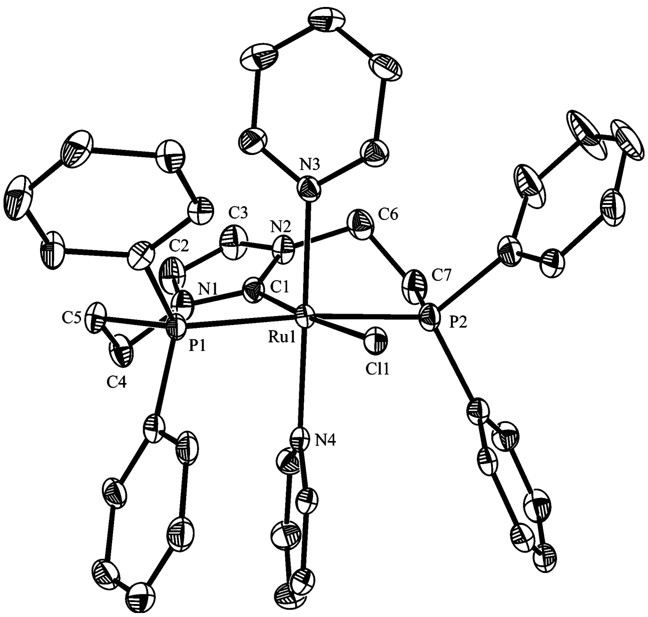

Figure 5. Thermal ellipsoid plot (30%) of cationic portion of **7** with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1–C1, 2.027(7); Ru1–Cl1, 2.4996(18); Ru1–N3, 2.136(6); Ru1–N4, 2.131(6); Ru1–P1, 2.3458(18); Ru1–P2, 2.3948(19); C1–Ru1–Cl1, 175.9(2); N3–Ru1–N4, 177.8(2); P1–Ru1–P2, 175.43(7); C1–Ru1–P1, 91.0(2); C1–Ru1–P2, 90.5(2); C1–Ru1–N3, 86.6(3); C1–Ru1–N4, 91.2(3); Cl1–Ru1–P1, 88.93(6); Cl1–Ru1–P2, 89.90(6); Cl1–Ru1–N3, 89.26(17); Cl1–Ru1–N4, 92.89(17).

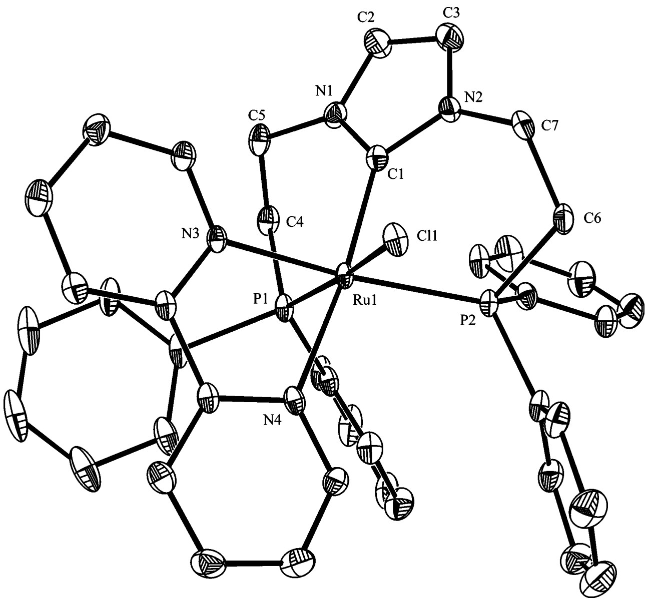

Figure 6. Thermal ellipsoid plot (30%) of cationic portion of **8** (one of the two independent molecules in the asymmetry unit) with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1–C1, 2.040(6); Ru1–Cl1, 2.4791(14); Ru1–P1, 2.2785(15); Ru1–P2, 2.3155(15); Ru1–N3, 2.127(5); Ru1–Cl1, 2.4791(14); C1–Ru1–N4, 173.4(2); N3–Ru1–P2, 167.97(13); P1–Ru1–Cl1, 171.00(5); C1–Ru1–N3, 97.5(2); C1–Ru1–P2, 81.53(16); C1–Ru1–P1, 89.75(17); C1–Ru1–Cl1, 94.84(17); N4–Ru1–N3, 75.96(18); N4–Ru1–P2, 104.72(13); N4–Ru1–Cl1, 83.53(13); N4–Ru1–P1, 91.03(13).

of two doublets due to the starting complex **3** always remains about 8% according to the integral ratio. Proton signals due to the free pyridine are also observed. Interestingly, with addition of a few drops of pyridine inside the NMR tube, the phosphorus signals due to **3** disappear completely, resulting in a clean spectrum of **7**. The observation is consistent with an equilibrium existing between **3** and **7**. When dissolved in solution, a small fraction of **7** undergoes pyridine dissociation to re-form **3**. Complex **7** is quite air-sensitive in chlorinated solvent. When exposed to air, a dichloromethane solution of **7** will be oxidized to a $Ru^{III}Cl_3$ complex (vide infra). Crystals of **7** were successfully obtained by vapor diffusion of diethyl ether into a DMF solution. The crystallographic data are reported in Table 2. The ruthenium center is in an octahedral geometry with the $PC^{NHC}P$ ligand coordinating in meridional mode (Figure 5). The two pyridine ligands are in trans positions to each other. The complex is symmetry-related by the presence of a noncrystallographic C_2 along the C···Ru···Cl axis. The twist angle between the imidazole ring and the equatorial plane is 27.9°, which is similar to that in **4**. The two pyridine rings are staggered, making an interplanar angle of 53.6°. Interestingly, while examples of *trans*-$Ru(py)_2$ complexes with tridentate/tetradentate nitrogen donors are known,[25] complex **7** appears to be the first *trans*-$Ru(py)_2$ containing tridentate phosphorus donors.

It appears that $PC^{NHC}P$ can adopt both fac and mer chelation modes. The trans disposition of pyridines in **7** prompts us to react **3** with 2,2′-bipyridine because it will enforce a cis chelation of the two pyridine rings, which may lead to a structural change from meridional to facial geometry. Reaction of **3** with 2,2′-bipyridine produces cleanly the red complex $[RuCl(bipy)(PC^{NHC}P)]Cl$ (**8**). Similar to **3**, the $^{31}P\{^1H\}$ NMR display an AX splitting pattern of two doublets at δ 38.5 and 42.3 with a $^2J_{pp}$ coupling constant of 29.4 Hz. The CH protons of the ethylene spacers are also spread out into six signals spanning a range from δ 2.58 to 5.72. Obviously, similar to **3**, the $PC^{NHC}P$ also adopts a facial chelation. In situ NMR experiments shows that **8** can also be formed by reacting the mer complex **7** with excess 2,2′-bipyridine at elevated temperature.

The stereochemistry of **8** was confirmed by structural determination. Crystals were obtained by vapor diffusion of diethyl ether into a DMF solution of **8**. The crystallographic data are reported in Table 2. The structure is solved in the space group $P2_1/c$ with the presence of two independent molecules in the asymmetric unit. The geometric parameters of the two molecules are almost identical, and so only one set will be discussed in the following text. As depicted in the Figure 6, which shows the thermal ellipsoid plot of the cationic portion, the ruthenium center is coordinated to a $PC^{NHC}P$, a 2,2′-bipyridine, and a chloride ligand. The $PC^{NHC}P$ ligand is chelated in facial mode, consistent with the NMR data, and the coordinated chloride is trans to a PPh_2 group. The resultant coordination environment around the ruthenium center is, similar to that in **3**, a distorted octahedral geometry with the

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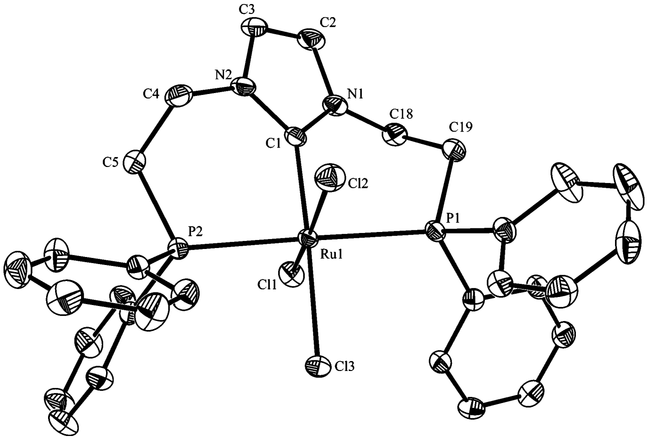

Figure 7. Thermal ellipsoid plot (30%) of **9** with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Selected bond distances (Å) and angles (deg): Ru1−C1, 2.050(4); Ru1−Cl1, 2.3604(14); Ru1−Cl2, 2.3751(15); Ru1−Cl3, 2.4387(14); Ru1−P1, 2.3964(14); Ru1−P2, 2.3893(14); C1−Ru1−Cl3, 177.62(12); Cl1−Ru1−Cl2, 171.36(5); P1−Ru1−P2, 178.50(4); C1−Ru1−P1, 90.39(12); C1−Ru1−P2, 91.03(12); C1−Ru1−Cl1, 86.38(13); C1−Ru1−Cl2, 85.26(12); Cl3−Ru1−P1, 91.94(4); Cl3−Ru1−P2, 96.64(4); Cl3−Ru1−Cl1, 93.10(5); Cl3−Ru1−Cl2, 95.33(5).

average Cl1−Ru1−P1, N3−Ru1−P2, and N4−Ru1−C1 angle equal to 170.79°. The Ru−N bond trans to the carbene (2.178(5) Å) is slightly longer than that trans to a phosphorus (2.127(5) Å). The Ru−P bond trans to a nitrogen (2.3155(15) Å) is longer compared with that trans to a chloride (2.2785(15) Å). A noticeable feature of the structure is that one of the phenyl rings of the PPh_2 group is parallel to the 2,2′-bipyridine. The interplanar distance of 3.22 Å suggests an intramolecular $\pi-\pi$ stacking. A comparison of **7** and **8** clearly indicates that the cis chelation of the rigid 2,2′-bipyridine causes a larger steric effect than two free pyridines and $PC^{NHC}P$ is able to accommodate the additional steric requirement by switching from the sterically demanding meridional to the less demanding facial chelation mode.

Crystal Structure of *mer*-[Ru^{III}Cl$_3$(PC^{NHC}P)] (9). As mentioned above, *mer,trans*-[RuCl(py)$_2$(PC^{NHC}P)] in solution is sensitive to air. In fact, an attempted crystallization of **7** from DMF in air resulted in sole production of green crystals, *mer*-[Ru^{III}Cl$_3$(PC^{NHC}P)] (**9**), which was successfully determined by X-ray diffraction. The crystal data are listed in Table 2. The ruthenium is in an octahedral geometry with $PC^{NHC}P$ chelating in meridional mode (Figure 7). The twist angle between the imidazole ring and the equatorial plane is 28.6°, essentially the same as those in **4** and **7**. The longer Ru−Cl distance trans to the carbene (2.4387(14) Å) compared with those of the two mutually trans chlorides (2.3751(15) and 2.3604(14) Å) is due to the bigger trans influence of carbene donor. Ru(II) NHC complexes, because of their importance in catalysis,[1c,3−6] are receiving much attention, and numerous crystal structures of Ru(II) NHC complexes have been reported. In contrast, only until recently has the first example of a Ru(III) NHC complex been prepared.[10] To the best of our knowledge, complex **9** appears to be the first structurally characterized Ru(III) complex bearing a NHC moiety. Despite the smaller ionic radius of Ru(III), the Ru−carbene bond distance in **9**, 2.050(4) Å, is similar to those found in **4**, **7**, and **8**.

Table 4. Catalytic Transfer Hydrogenation of Ketones with 2-Propanol Catalyzed by 3[a]

entry	cat. mol %	base	substrate	time, h	yield, %
1	0.1	KOBu^t	cyclohexanone	0.5	91
2	0.1	KOBu^t	cyclohexanone	1	90
3	0.1	KOBu^t	cyclohexanone	2	98
4	0.1	KOH	cyclohexanone	2	96
5	0.01	KOBu^t	cyclohexanone	2	trace
6	0.01	KOBu^t	cyclohexanone	24	77
7	0.1	KOBu^t	acetophenone	3	85
8	0.1	KOBu^t	acetophenone	4.5	100
9	0.01	KOBu^t	acetophenone	3	5
11	0.01	KOBu^t	acetophenone	24	51
12	0.1	KOBu^t	benzophenone	12	58
13	0.1	KOBu^t	benzophenone	24	94
14	0.01	KOBu^t	benzophenone	24	trace

[a] Conditions: ketone, 1 mmol; base, 10 mol %; catalyst, 0.1 or 0.01 mol %; 2-propanol, 10 mL; temp, 80 °C. Yield determined by ^{1}H NMR spectroscopy.

Catalytic Transfer Hydrogenation of Ketones. Ruthenium complexes of both NCN and PCP pincer ligands have been shown to be efficient catalysts in the transfer hydrogenation of ketones.[26] Recently, new catalysts of ruthenium CNC-pincer bis(NHC) complexes are reported.[5,6] On the other hand, bimetallic ruthenium compounds, such as [{RuX(μ-X)(CO)(PP)}$_2$] (PP = dppf, dippf; X = Cl, Br)[27] and [Ru$_2$(μ-Cl)$_3$(η^4-1,2,3,4-Me$_4$-NUPHOS)$_2$]X (X = Cl, SbF$_6$),[28] are also shown to be highly active in the catalytic reaction. Inspired by these reports, we were interested in investigating whether the bimetallic ruthenium NHC/phosphine complex **3** is also an efficient catalyst. A preliminary investigation (unoptimized conditions) was carried out, which shows that **3** catalyzes the hydrogenation of ketones via hydrogen transfer from 2-propanol in the presence of base (Table 4). Entry 1 shows that a 0.1 mol % of **3** can catalyze the conversion of cyclohexanone to cyclohexanol with KOBu^t as base in 30 min, affording a 91% yield. Replacement with KOH as base gives identical results (entries 3 and 4). Prolongation of reaction time is needed if the catalyst loading is reduced to 0.01 mol % (entries 5 and 6). With acetophenone as substrate, a 0.1 mol % catalyst loading gives quantitative conversion in 4.5 h (entry 8); a much longer reaction time (24 h) is needed for benzophenone to produce a 94% yield (entry 13).

Conclusions

The silver $PC^{NHC}P$ complex **1** is identified by electrospray mass spectroscopy as a trinuclear compound, [Ag$_3$(μ-Cl)(PC^{NHC}P)$_2$]Cl$_2$. Anion exchange of **1** with AgNO$_3$ affords **2**, which crystallizes into two forms, [Ag$_3$(μ-Cl)(PC^{NHC}P)]$_2$NO$_3$ (**2a**) and [Ag$_3$(Cl)(NO$_3$)(0.5DMF)(PC^{NHC}P)]NO$_3$·DMF (**2b**), from different solvent combinations. In both forms, short Ag···Ag interactions are present. In **2a**, a μ-Cl bridging two silver centers exists, whereas in **2b**, such μ-Cl bridge is absent because of a weak coordination of NO$_3^-$ ion to one of the silver ions. In solution, fast interconversion between **2a** and **2b**

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occurs. Although the structure of **1** is not available, it can be anticipated that **1** should adopt a structure similar to **2a** and **2b**. The exchange of chloride anions in **1** with nitrate anions apparently slows the fluxional exchange, which renders the two halves of $PC^{NHC}P$ in **2a** and **2b** nonequivalent.

Unlike the common preparation of ruthenium(II) NHC complexes, we successfully employ a silver carbene transfer reaction between **1** and $RuCl_2(PPh)_3$, affording the pure diruthenium(II) complex **3** in good yield. The nonredox nature of this transfer reaction is remarkably different from the reported reaction in which the carbene transfer is coupled with oxidation of ruthenium(II).[10] This shows that the preparation of divalent ruthenium NHC complexes via silver carbene transfer is also a feasible synthetic route. Consistent with our previous findings, **3** can be produced by reaction of $PC^{NHC}P$ with $RuCl_2(PPh)_3$ without the necessity of base. The structural analysis on **3** reveals the formation of a novel triply μ-Cl-bridged diruthenium complexes in which the $PC^{NHC}P$ ligands coordinate to the Ru centers in a facial manner. Obviously, the formation of the μ-Cl bridge enables each ruthenium center to have a formally 18e configuration. However, because of the steric bulkiness, the formation of such diruthenium complexes is not possible if the $PC^{NHC}P$ ligand is in meridional mode. Among the two possible facial chelating isomers, *ec*-form and *st*-form, and because of steric reasons, **3** adopts solely the latter structure both in solution and in the solid state.

The ability of $PC^{NHC}P$ to accommodate the steric requirement is demonstrated in reactions of fac complexes **3** with CO, phenylacetylene, and pyridine, which result in the formation of mononuclear mer complexes **4**, **6**, and **7**. The structural determinations show that the central imidazole rings in the mer complexes are twisted from the equatorial planes. We have previously shown that in Pd($PC^{NHC}P$) complexes a wide range of twisting of the imidazole ring from the equatorial plane (twist angle = 27−49°) is possible, and theoretical calculation has shown that the rotation barrier about the Pd−carbene bond is indeed very small.[2a] However, in Ru($PC^{NHC}P$) complexes, the twist angles observed are limited to 28−29°, which can be attributed to the fact that the presence of axial ligands obscures the twisting to a limited extent. The relatively sharp NMR signals for the ethylene protons observed in fac complexes, **3** and **8**, indicate that the facial coordination mode is conformationally more rigid, whereas in mer complexes **4**−**7**, the broad NMR signals indicate that the ethylene spacers are flexible, which enables fast interconversion between the left- and right-twist forms. Reactions of **3** or **4** with 2,2′-bipyridine further confirm that $PC^{NHC}P$ can accommodate the extra steric requirement by switching readily from facial to meridional coordination mode.

Experimental Section

General Procedures. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified according to standard procedures.[29] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 and 75.48, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to residual protons of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.0) and DMSO-d_6 (^1H: δ 2.50; ^{13}C: δ 39.5). Elemental analyses were performed on a Heraeus CHN-OS-Rapid elemental analyzer at Instrument Center, National Chung Hsing University, Taiwan.

Preparation of $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)_2]Cl_2$ (1). 1 was prepared according to the literature procedure.[2a] MS (ES+): *m/z* 1414 $[Ag_3(PC^{NHC}P)_2Cl_3]^+$ (M), 1379 $[Ag_3(PC^{NHC}P)_2Cl_2]^+$, 1272 $[Ag_2(PC^{NHC}P)_2Cl_2]^+$, $[Ag_2(PC^{NHC}P)_2Cl]^+$, 1093 $[Ag(PC^{NHC}P)_2]^+$, 743 $[Ag_2(PC^{NHC}P)Cl]^+$, 599 $[Ag(PC^{NHC}P)]^+$.

Preparation of $[Ag_3Cl(PC^{NHC}P)_2](NO_3)_2$ (2). To a mixture of **1** (140 mg, 0.12 mmol) and $AgNO_3$ (36 mg, 0.21 mmol) was added 10 mL of methanol. The solution was heated under reflux for 4 h and was then passed through a small plug of Celite. The solvent was pumped dry under vacuum. Upon addition of diethyl ether, a colorless precipitate was formed, which was filtered on a frit and dried under vacuum. Yield: 52 mg, 33%. Anal. Calcd for $C_{62}H_{60}Ag_3ClN_6O_6P_4$: C, 50.72; H, 4.12; N, 5.72. Found: C, 50.75; H, 4.21; N, 5.70. Mp: 170−172 °C. ^1H NMR ($CDCl_3$): δ 3.06 (br s, 8H, CH_2), 4.61 (br s, 8H, CH_2), 6.42 (br s, 4H, imi-CH), 7.18−7.45 (m, 40H, Ph-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.4 (CH_2), 49.5 (CH_2), 121.6 (imi-CH); 129.0, 130.6, 130.7, 132.8 (Ph-CH), the carbene carbon was not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −3.1 (br s), 0.6 (br s). Single crystals of **2a** and **2b** were obtained by slow diffusion of diethyl ether into an acetonitrile and DMF solution of **2**, respectively.

Preparation of *fac*-$[Ru_2(\mu\text{-}Cl)_3(PC^{NHC}P)_2]Cl$ (3). Method A. Complex **1** (366 mg, 0.26 mmol) was dissolved in dichloromethane (10 mL), and to this solution was added $RuCl_2(PPh_3)_3$ (552 mg, 0.58 mmol). The solution was allowed to stir overnight at ambient temperature, which was then passed through a small plug of Celite. The solvent was pumped dry under reduced pressure. Upon addition of THF, an orange solid was formed, which was filtered on a frit and dried under vacuum. Yield: 249 mg, 72%. Anal. Calcd for $C_{62}H_{60}Cl_4N_4P_4Ru_2$: C, 56.03; H, 4.55; N, 4.22. Found: C, 56.00; H, 4.53; N, 4.30. Mp: 228−230 °C. ^1H NMR ($CDCl_3$): δ 1.00 (t, J = 13.0 Hz, 1H, CH), 2.44 (t, J = 13.0 Hz, 1H, CH), 2.65 (m, 1H, CH), 2.79 (m, 1H, CH), 4.26−4.41 (m, 2H, CH), 4.37 (q, J = 13.4 Hz, 1H, CH). 5.42 (t, J = 7.5 Hz, 2H, Ph-H), 5.72 (br, 1H, CH), 6.81−7.30 (m, 16H, Ph-H and imi-H), 7.40 (t, J = 7.1 Hz, 2H, Ph-H), 7.67 (t, J = 8.9 Hz, 2H, Ph-H), 8.19 (t, J = 9.2 Hz, 2H, Ph-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.5 (d, $^1J_{CP}$ = 31.6 Hz, PCH_2), 31.9 (d, $^1J_{CP}$ = 35.1 Hz, PCH_2), 46.6 (d, $^2J_{CP}$ = 58.8 Hz, NCH_2), 122.0−140.7 (aromatic), 174.5 (virtual t, $^2J_{CP}$ = 21.6 Hz, RuC). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.4 (d, $^2J_{PP}$ = 31.3 Hz), 48.5 (d, $^2J_{PP}$ = 31.3 Hz). Single crystals were obtained by slow evaporation of an acetone/dichloromethane solution of **3**.

Method B. A mixture of $PC^{NHC}P\cdot HCl$ (188 mg, 0.35 mmol) and $RuCl_2(PPh_3)_3$ (340 mg, 0.35 mmol) in 10 mL of DMF was heated at 90 °C overnight. After the reaction, the solvent was removed completely under vacuum. To the residue was added 20 mL of dichloromethane, and the solution was then filtered through a plug of Celite. The solvent was removed again under vacuum. Upon addition of THF, a solid was formed, which was filtered and collected on a frit. Recrystallization of this crude product with dichloromethane/THF gave pure **3**. Yield: 146 mg, 62%.

Preparation of *mer,cis*-$RuCl_2(CO)(PC^{NHC}P)$ (4). A solution of **3** (250 mg, 0.19 mmol) in 20 mL of 1,2-dichloroethane was bubbled with CO and heated under reflux overnight. The solution was then allowed to pass through a small plug of Celite. The solvent was pumped dry under reduced pressure. Upon addition of *n*-hexane, a white solid was formed, which was filtered on a frit and dried under vacuum. Yield: 200 mg, 77%. Anal. Calcd for $C_{32}H_{30}Cl_2N_2OP_2Ru_2$: C, 55.50; H, 4.37; N, 4.05. Found: C, 55.48; H, 4.31; N, 4.00. Mp: 205−207 °C. ^1H NMR ($CDCl_3$): δ 2.67 ((br s, 4H, CH_2), 4.11 (br, 2H, CH_2),

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4.81 (br, 2H, CH_2), 6.87 (s, 2H, imi-*H*), 7.24−7.40 (m, 14H, Ph-*H*), 7.97−8.06 (m, 6H, Ph-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.9 (t, $^1J_{CP}$ = 13.5 Hz, CH_2), 46.4 (CH_2), 122.3 (imi-*C*H), 127.4 (t, J_{CP} = 4.8 Hz, C_{orth} or C_{meta}), 128.3 (t, J_{CP} = 4.5 Hz, C_{orth} or C_{meta}), 129.6 (C_{para}), 130.0 (C_{para}), 131.9 (t, $^1J_{CP}$ = 23.0 Hz, C_{ipso}), 133.3 (t, J_{CP} = 5.2 Hz, C_{orth} or C_{meta}), 134.2 (t, $^1J_{CP}$ = 22.0 Hz, C_{ipso}), 134.4 (t, J_{CP} = 4.8 Hz, C_{orth} or C_{meta}), 169.1 (t, $^2J_{CP}$ = 11.0 Hz, Ru*C*), 199.6 (t, $^2J_{CP}$ = 13.2 Hz, *C*≡O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 10.9 (s). IR (KBr): ν(C≡O) = 1948.23 cm^{-1}. Single crystals were obtained by slow diffusion of diethyl ether into a DMF solution of **4**.

Preparation of *mer*-RuHCl(CO)(PC^{NHC}P) (5). A mixture of **4** (38 mg, 0.055 mmol) and $NaBH_4$ (20 mg, 0.550 mmol) in 10 mL of ethanol was heated at 70 °C until all solids dissolved (ca. 30−90 min). The solvent was then removed completely under vacuum. The residue was extracted with toluene. The solution was then passed through a plug of Celite. The solvent was then pumped dry again under vacuum. Upon addition of diethyl ether, a white solid was formed, which was filtered on a frit and dried under vacuum. Yield: 18 mg, 50%. Anal. Calcd for $C_{32}H_{31}ClN_2OP_2Ru$: C, 58.40; H, 4.75; N, 4.26. Found: C, 58.48; H, 4.70; N, 4.26. Mp: 178−180 °C. ^1H NMR (C_6D_6): δ −14.8 (t, $^2J_{HP}$ = 19.3 Hz, Ru-H), 2.03 (m, 2H, CH_2), 2.34 (m, 2H, CH_2), 3.54 (br, 2H, CH_2), 4.38 (br, 2H, CH_2), 6.08 (s, 2H, imi-*H*), 6.90−7.23 (m, 14H, Ph-*H*), 7.89−8.14 (m, 6H, Ph-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.5 (s). IR (KBr): ν(C≡O) = 1928.6 cm^{-1}.

Preparation of *mer,trans*-$RuCl_2$(=C=CHPh)(PC^{NHC}P) (6). A mixture of **3** (100 mg, 0.075 mmol) and phenylacetylene (1 mL. 9.03 mmol) in 10 mL of 1,2-dichloroethane was heated under reflux overnight. The solution was pumped dry under vacuum. Upon addition of diethyl ether, a reddish-brown solid was formed, which was filtered on a frit and pumped dry under vacuum. Yield: 93 mg, 80%. Anal. Calcd for $C_{39}H_{36}Cl_2N_2P_2Ru$: C, 61.10; H, 4.73; N, 3.65. Found: C, 61.20; H, 4.80; N, 3.70. Mp: 218−220 °C. ^1H NMR ($CDCl_3$): δ 2.64 (br, 4H, CH_2), 3.52 (t, $^4J_{HP}$ = 3.8 Hz, 1H, Ru=C=C*H*Ph), 4.18 (br, 2H, CH_2), 4.70 (br, 2H, CH_2), 5.88 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ph-*H*), 6.70−7.70 (m, 19H, imi-C*H*, Ph-*H*), 7.66−8.14 (m, 6H, Ph-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.7 (unresolved t, CH_2), 46.3 (CH_2), 108.3 (C=*C*HPh), 122.2−135.1 (Ph-*C*, imi-*C*), 166.4 (t, $^2J_{CP}$ = 10.6 Hz, Ru*C*), 348.1 (t, $^2J_{CP}$ = 16.1 Hz, Ru=*C*=C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 7.00.

Oxidative Cleavage of Complex 6. A solution of **6** (45 mg, 0.059 mmol) in 10 mL of 1,2-dichloroethane was heated under reflux in the air overnight. The solvent was then pumped dry under vacuum. The residue was washed with diethyl ether. The white solid formed was pure *mer,cis*-$RuCl_2$(CO)(PC^{NHC}P). Yield: 39 mg, 97%.

Preparation of *mer,trans*-[RuCl$(py)_2$(PC^{NHC}P)]Cl (7). To a solution of **3** (150 mg, 0.11 mmol) in DMF (10 mL) was added pyridine (3.0 mL, 36.7 mmol). The solution was heated at 110 °C overnight. The solution was then pumped dry under reduced pressure. Upon addition of diethyl ether, a yellow solid was formed, which was filtered on a frit and dried under a stream of nitrogen. Yield: 162 mg, 87%. Anal. Calcd for $C_{41}H_{40}Cl_2N_4P_2Ru$: C, 59.86; H, 4.90; N, 6.81. Found: C, 59.90; H, 4.95; N, 6.85. Mp: 136−138 °C. ^1H NMR ($CDCl_3$): δ 4.23 (br, 4H, CH_2), 6.20 (br, 4H, CH_2), 6.97−7.99. (m, 32H, imi-C*H*, Py-*H*, Ph-*H*). Because of the re-formation of **3** and free pyridine in solution, its $^{13}C\{^1H\}$ NMR spectrum was not determined. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.56 (s). Single crystals were obtained by slow diffusion of diethyl ether into a DMF solution of **7**.

Preparation of *fac,cis*-[RuCl(bipy)(PC^{NHC}P)]Cl (8). Method A. To a solution of **3** (50 mg, 0.038 mmol) in DMF (10 mL) was added 2,2′-bipyridine (705 mg, 4.51 mmol). The solution was heated at 100−110 °C overnight. The solution was then pumped dry under reduced pressure. Upon addition of diethyl ether, a reddish-brown solid was formed, which was filtered on a frit and dried under a stream of nitrogen. Yield: 47 mg, 76%. Anal. Calcd for $C_{41}H_{38}Cl_2N_4P_2Ru$: C, 60.00; H, 4.76; N, 6.83. Found: C, 60.05; H, 4.70; N, 6.90. Mp: 150−152 °C. ^1H NMR ($CDCl_3$): δ 2.58 (m, 2H, CH_2), 3.28 (m, 1H, CH_2), 3.52 (m, 1H, CH_2), 4.05 (m, 1H, CH_2), 4.83 (m, 1H, CH_2), 5.72 (m, 2H, CH_2), 6.00 (t, *J* = 9.0 Hz, 2H, Ph-*H*), 6.53−8.68. (m, 28H, imi-C*H*, 2,2′-bipy-*H*, Ph-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.9 (d, $^1J_{CP}$ = 33.2 Hz, CH_2), 31.6 (d, $^1J_{CP}$ = 36.2 Hz, CH_2), 47.9 (d. $^2J_{CP}$ = 81.7 Hz, CH_2), 128.7−156.7 (aromatic), 174.4 (virtual t, $^2J_{CP}$ = 18.0 Hz, Ru*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.5 (d, $^2J_{PP}$ = 29.4 Hz), 42.3 (d, $^2J_{PP}$ = 29.4 Hz). Single crystals were obtained by slow diffusion of diethyl ether into a DMF solution of **8**.

Method B. Solid **7** (ca. 5 mg) and 2,2′-bipyridine (ca. 5 mg) were dissolved in $CDCl_3$ and transferred into a 5 mm NMR tube, which was sealed and heated in an oil bath. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After overnight, **7** completely disappeared to give **8** without formation of other phosphorus-containing species.

Preparation of *mer*-$RuCl_3$(PC^{NHC}P) (9). A 10 mg sample of **7** in 0.2 mL of DMF was left in the air for about a week. The green crystalline solid was *mer*-$RuCl_3$(PC^{NHC}P), as confirmed by the X-ray structural analysis. Anal. Calcd for $C_{31}H_{30}Cl_3N_2P_2Ru_2$: C, 46.48; H, 3.77; N, 3.50. Found: C, 46.36; H, 3.35; N, 3.51.

General Procedure for Catalytic Transfer Hydrogenation of Ketones. Appropriate amounts of **3** (0.01 or 0.1 mol %), base (10 mol % of $KOBu^t$ or KOH), and the ketone (1.00 mmol) were dissolved in 10 mL of 2-propanol inside a Schlenk tube, which was then heated at 80 °C for the required time (0.5−24 h). After the reaction, the solvent was removed under reduced pressure. Water and dichloromethane (20 mL each) were added. The organic layer was then separated and the solvent was removed under reduced pressure. The residue was then analyzed by ^1H NMR spectroscopy.

X-ray Data Collection. Typically, the crystal was removed from the vial with a small amount of mother liquor and immediately coated with silicon grease on a weighting paper. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the cold stream of either a Bruker SMART 1000 CCD or APEX II with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 273(2) or 150(2) K, respectively. Calculations for the structures were performed using SHELXS-97 and SHELXL-97. Tables of neutral atom scattering factors, *f*′ and *f*″, and absorption coefficients are from a standard source.[30] All atoms except hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated using a riding model. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 255830−255836. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: Full crystallographic data for compounds **2a**, **2b**, **3**, **4**, **7**, **8**, and **9** are provided as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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