A Stable Hydrido Amido Ruthenium Complex Bearing a Tridentate Iminophosphorane−Phosphine−Amine Ligand

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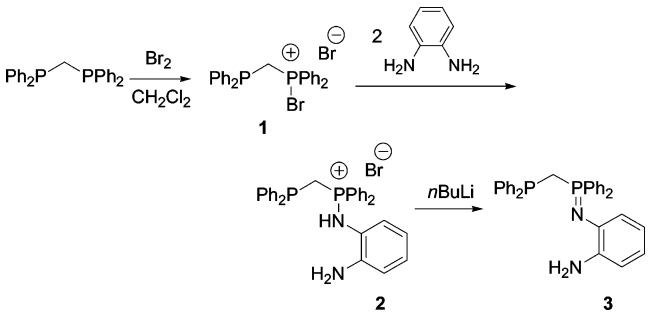
Summary: A heterotridentate (P,N,N′) ligand featuring phosphine, iminophosphorane, and amine groups has been prepared in high yield. The corresponding dichlororuthenium(II) complex reacts with base in 2-propanol to give a stable hydrido amido complex. The lack of hydrogens that are α to the amine allowed for the isolation and structural characterization of this hydrido amido species by X-ray diffraction.

Among the most studied catalytic processes, the reduction of polar double bonds is one of the most fundamental transformations in organic synthesis.[1,2] In the catalytic hydrogenation of ketones, Noyori and co-workers have shown the crucial role played by the ligand in enhancing the activity of the catalyst ("NH effect").[3] Following these pioneering works, numerous groups developed ligands bearing both soft P-donor and hard N-donor moieties. A multitude of highly chemo- and enantioselective ruthenium systems have thus been reported. However, few examples of nonsymmetrical heterotridentate or tetradentate ligands have been designed.[4]

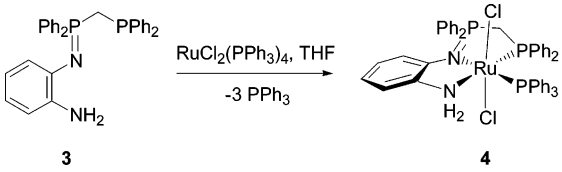
In this communication the synthesis of a new mixed (P,N,N′) tridentate ligand bearing phosphine, iminophosphorane, and amine functions and its coordination to the $[RuCl_2(PPh_3)]$ fragment are reported. Additionally, we also show that the use of an aromatic amine is the key point in the isolation of a rare hydrido amido ruthenium complex postulated to be involved as an intermediate in the Ru-catalyzed transfer hydrogenation of ketones.

We recently reported an efficient synthesis of mixed bidentate phosphine−iminophosphorane ligands from the commercially available diphosphine dppm (1,2-bis(diphenylphosphino)-methane).[5] This method, which was previously applied to aliphatic, benzylic, and aromatic primary amines (chiral or not), could be extended here to a primary diamine. The synthetic approach employed is depicted in Scheme 1. The selective monobromination of the symmetrical diphosphine dppm using 1 equiv of bromine, followed by reaction with 2 equiv of *o*-diaminobenzene, yielded the aminophosphonium salt **2** in an excellent yield (92% after isolation). This salt was characterized by conventional NMR techniques, elemental analysis, and X-ray diffraction (see Supporting Information). As expected, the ^{31}P NMR spectrum exhibits two doublets (AX spin system) at 38.8 and −30.2 ppm ($^2J_{PP}$ = 74 Hz), which were respectively assigned to the aminophosphonium moiety and the phosphine. The new unsymmetrical tridentate salt **2** was then deprotonated quantitatively to yield the desired heterotridentate (P,N,N′) ligand **3** (phosphine−iminophosphorane−amine). As previously noted, the formation of the iminophosphorane ligand results in a significant upfield shift and the ^{31}P NMR spectrum of **3** showed two doublets at 4.1 and −27.1 ppm ($^2J_{PP}$ = 48 Hz, $\Delta\delta \cong -35$ ppm for the iminophosphorane moiety).

Scheme 1



The coordination behavior of this potentially tridentate ligand was then studied. Reaction of **3** with $[Ru(PPh_3)_4Cl_2]$ readily led to the formation of complex **4** through the displacement of three PPh_3 ligands (eq 1).



(1)

Complex **4**, which was isolated as a brown solid in 84% yield, was characterized by the usual NMR techniques and elemental analyses.[6] The ^{31}P NMR spectrum of **4** displays three doublets of doublets at 32.4, 41.5, and 52.3 ppm that were respectively assigned, on the basis of 2D (^{31}P, ^1H) correlation, to the iminophosphorane, phosphine PPh_2, and phosphine PPh_3 moieties. In the ^1H NMR spectrum, the resonances corresponding to methylenic protons and the NH_2 hydrogen atoms were found at 4.22 and 5.10 ppm, respectively ($\Delta\delta$ = 0.88 ppm with respect to free ligand **3**). Altogether, these data suggest the coordination of the ligand to the ruthenium center in a tridentate fashion. The pseudo-octahedral geometry was confirmed by an X-ray diffraction study (Figure 1). It is noteworthy that the Ru(1)−P(2) and Ru(1)−P(3) bond distances at 2.269(1) and 2.288(1)

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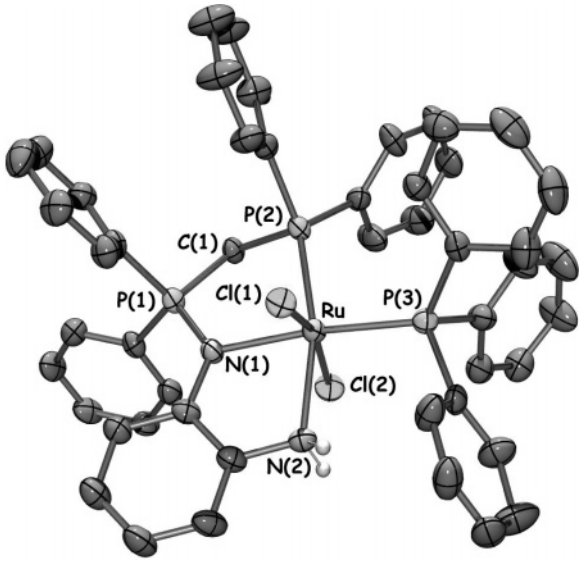
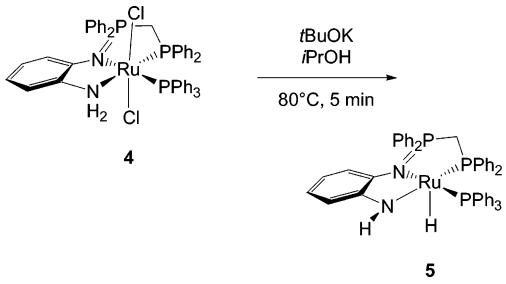


Figure 1. Molecular structure of complex **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ru(1)−P(2), 2.269(1); Ru(1)−P(3), 2.288(1); Ru(1)−N(1), 2.144(3); Ru(1)−N(2), 2.181(4); Ru(1)−Cl(1), 2.421(1); Ru(1)−Cl(2), 2.425(1); C(1)−P(1), 1.803(4); C(1)−P(2), 1.859(4); N(1)−Ru(1)−N(2), 77.5(1); N(1)−Ru(1)−P(2), 87.2(1); P(3)−Ru(1)−N(2), 96.0(1); N(2)−Ru(1)−P(2), 164.1(1); N(1)−Ru(1)−Cl(2), 84.1(1); N(1)−Ru(1)−Cl(1), 87.0(1); P(2)−Ru(1)−Cl(1), 101.89(4); P(2)−Ru(1)−Cl(2), 92.00(4); Cl(1)−Ru(1)−Cl(2), 163.10(4).

Å, respectively, reflect the higher trans effect of the iminophosphorane moiety compared to the amine moiety.

The ruthenium-catalyzed transfer hydrogenation of ketones has been thoroughly studied, both experimentally and mechanistically. In terms of activity, Noyori and co-workers have developed remarkably efficient catalysts. These complexes bear an amine moiety which is able to assist the hydrogenation (outer-sphere mechanism, "NH effect"). In this mechanism, the in situ formation of a hydrido amido complex has been proposed.[1,7] Such types of complexes have been proven to be very difficult to isolate and characterize because the formation of a dihydrido imine complex is usually favored when a β-hydrogen is accessible. Only two complexes have been fully characterized by Morris and co-workers. One could be isolated because of the lack of such a hydrogen atom,[8] while for the other, the equilibrium (hydrido amido ↔ dihydrido imine) could be shifted in favor of the hydrido amido species.[9] The presence of an aromatic diamine in the design of our ligand allowed us to expect the possible formation of a hydrido amido species under typical reaction conditions.

As expected, reaction of the dichloro complex **4** with 2 equiv or more of *t*BuOK in 2-propanol led to the quantitative formation of complex **5** (by ^{31}P NMR), which precipitated from the reaction medium as a red solid (60% isolated yield) (eq 2).



(2)

This complex, which proved to be very reactive toward dioxygen in solution as well as in the solid state, was fully characterized by NMR techniques and X-ray diffraction.[10] The ^{31}P NMR spectrum consists of three sets of signals at 29.7, 57.9, and 74.5 ppm assigned to the iminophosphorane, PPh_3, and PPh_2 fragments, respectively. The coupling constant $^2J_{PP} = 26$ Hz indicates the two phosphorus atoms to be in cis positions.[11] On the other hand, the ^{1}H NMR spectrum reveals the presence of a doublet of doublets ($^2J_{HP} = 31.2$ and 41.5 Hz) at −22.9 ppm (1H), which is a typical chemical shift for a terminal hydride.[12] Moreover, the signal for the NH proton appears at 5.56 ppm (1H) as a broad singlet. Together these data pointed to the formation of the desired hydrido amido species. Due to a different electronic environment, the two methylenic protons are split in the ^{1}H NMR spectrum into two multiplets at 3.87 and 4.19 ppm, which appear as two doublets ($^2J_{HH} = 14.3$ Hz) in the ^{1}H{^{31}P} NMR spectrum. Finally, the structure of the hydrido amido complex was confirmed by an X-ray diffraction study. A view of one molecule of **5** is presented in Figure 2.

The P(3)−Ru(1)−N(1) (170.54(4)°) and N(2)−Ru(1)−P(2) (157.91(5)°) angles suggest that the geometry of **5** is better described as a distorted square-based pyramid. The quality of the X-ray data allowed the refinement of the hydrogen atoms

(6) [Ru(PPh$_3$)$_4$Cl$_2$] (1.40 g, 1.15 mmol) was added to a solution of **3** (565 mg, 1.15 mmol) in 10 mL of THF. The solution turned from yellow to brown immediately. After 30 min the solvent was removed under vacuum and the residue dissolved in toluene. After 15 min a brown solid precipitated. The latter was isolated by filtration on a frit, washed with toluene and then hexanes, and dried under vacuum. Yield: 84% (894 mg). Anal. Calcd for $C_{49}H_{43}Cl_2N_2P_3Ru$: C, 63.64; H, 4.69. Found: C, 63.25; H, 4.70. ^{31}P{^{1}H} NMR (THF-d_8): 32.4 (dd, $^2J_{PP} = 22$ Hz, $^3J_{PP} = 6$ Hz, P═N), 41.5 (dd, $^2J_{PP} = 22$ Hz, $^2J_{PP} = 36$ Hz, PPh_2), 52.3 (dd, $^2J_{PP} = 36$ Hz, $^3J_{PP} = 6$ Hz, PPh_3). ^{1}H NMR (THF-d_8): 4.22 (dd, A_2XY, 2H, $^2J_{P^VH} = {}^2J_{P^{III}H} = 10.0$ Hz, PCH_2P), 5.10 (s, 2H, NH_2), 6.08−6.17 (m, 1H, CH_2), 6.40−6.45 (m, 2H, $C(H_3)$ and $C(H_4)$), 6.76−6.95 (m, 5H), 6.97−7.24 (m, 10H), 7.25−7.39 (m, 5H), 7.40−7.62 (m, 12H), 7.85−8.06 (m, 4H, Ph_2P). ^{13}C{^{1}H} NMR (THF-d_8): 44.0 (dd, AXY, $^1J_{CP} = 90$ Hz, $^1J_{CP} = 10$ Hz, PCH_2P), 117.6 (s, C_3), 120.7 (d, $J_{CP} = 10$ Hz, C_2), 126.3 (s, C_4), 127.0 (C^{IV}−P), 127.5 (d, $J_{CP} = 9$ Hz), 127.6 (d, $J_{CP} = 10$ Hz, C_5), 128.8, 129.0, 129.4, 129.5, 133.1 (d, $J_{CP} = 3$ Hz), 134.4 (d, $J_{CP} = 10$ Hz), 134.6 (d, $J_{CP} = 10$ Hz), 135.6 (d, $J_{CP} = 10$ Hz), 137.8 (d, $J_{CP} = 39$ Hz, C^{IV}−P), 138.9 (s, C_1), 139.2 (dd, $J_{CP} = 36$ Hz, $J_{CP} = 3$ Hz, C^{IV}−P), 150.5 (br s, C_6).

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(10) 2-Propanol (5 mL) was added to a mixture of complex **4** (100 mg, 0.11 mmol) and *t*BuOK (25 mg, 0.22 mmol) under argon in the Schlenk. The cloudy brown solution was heated at 80 °C for 5 min. The solution turned to red immediately, and a red precipitate formed. The latter was isolated by filtration and washed with 2-propanol and then hexanes to obtain **5** as a very air-sensitive red solid. Yield: 60% (57 mg). ^{31}P{^{1}H} NMR (THF-d_8): 29.7 (d, $^2J_{PP} = 0$ Hz, $^3J_{PP} = 26$ Hz, P═N), 57.9 (dd, $^2J_{PP} = {}^3J_{PP} = 26$ Hz, PPh_3), 74.5 (apparent d, $^2J_{PP} = 36$ Hz, PPh_2). ^{1}H NMR (THF-d_8): 22.91 (dd, $^2J_{HP} = 41.5$ Hz, $^2J_{HP} = 31.2$ Hz, 1H, Ru−H hydrido), 3.87 (m, ABXY, 1H, $^2J_{HH} = 14.3$ Hz, PCH_2P), 4.19 (m, ABXY, 1H, $^2J_{HH} = 14.3$ Hz, PCH_2P), 5.56 (br s, 1H, NH), 5.71−5.82 (m, 1H, CH_5), 6.14 (vd, $J_{HH} = 7.7$ Hz, $C(H_2)$ or $C(H_3)$), 6.24−6.33 (m, 1H, $C(H_2)$ or $C(H_3)$), 6.37−6.45 (m, 1H, $C(H_4)$), 6.75−7.56 (m, 35H). ^{13}C{^{1}H} NMR (THF-d_8): 48.4 (b, AXY, PCH_2P), 111.3 (s, C_5), 115.2 (s, C_4), 117.6 (d, $J_{CP} = 9$ Hz, C_2 or C_3), 118.9 (s, C_2 or C_3), 126.0, 127.6, 128.0, 128.5, 128.7, 129.4 (d, $J_{CP} = 12$ Hz), 129.6 (d, $J_{CP} = 12$ Hz), 132.8, 132.9, 133.1 (d, $J_{CP} = 10$ Hz), 133.5 (d, $J_{CP} = 10$ Hz), 134.6 (d, $J_{CP} = 13$ Hz), 134.9 (d, $J_{CP} = 11$ Hz), 139.0 (b, C_6), 141.3 (d, $J_{CP} = 37$ Hz, C^{IV}−P), 148.8 (b, C^{IV}−P), 161.0 (s, C_1).

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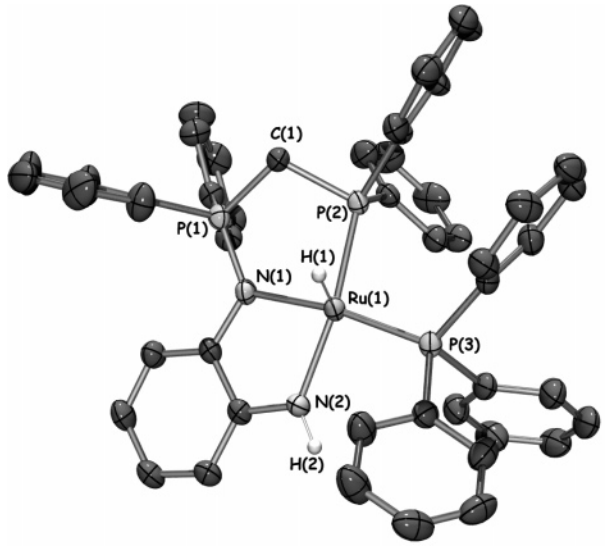

Figure 2. Molecular structure of hydrido amido complex **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ru(1)−P(2), 2.2125(5); Ru(1)−P(3), 2.2298(5); Ru(1)−N(1), 2.148(2); Ru(1)−N(2), 2.031(2); Ru(1)−H(1), 1.53(2); C(1)−P(1), 1.794(2); C(1)−P(2), 1.865(2); N(2)−H(2), 0.93(2); P(1)−N(1), 1.612(2); N(1)−Ru(1)−N(2), 77.09(6); N(1)−Ru(1)−P(2), 85.66(4); P(3)−Ru(1)−N(2), 94.59(5); N(1)−Ru(1)−P(3), 170.54(4); N(2)−Ru(1)−P(2), 157.91(5); N(1)−Ru(1)−H(1), 100.2(2); N(2)−Ru(1)−H(1), 113.8(8); P(2)−Ru(1)−H(1), 82.5(7); P(3)−Ru(1)−H(1), 87.3(8).

on both the nitrogen atom and the Ru center, H(2) and H(1), respectively. The sp^2 character of nitrogen is corroborated by the planarity at the nitrogen atom N(2), as shown by the sum of the angles, 358.7°. Moreover, the amido nitrogen−ruthenium bond length Ru(1)−N(2) of 2.031(2) Å is shorter than the amine nitrogen−ruthenium distance in complex **4** (2.181(4) Å). These data are consistent with a dative π donation from the amido nitrogen to the ruthenium center.[13] A deviation of phosphorus P(2) from the mean plane (defined by the plane containing P(3), Ru(1), N(1), and N(2)) could be related to the significant deshielding ($\Delta\delta \cong 30$ ppm vs **4**) observed in the ^{31}P NMR spectrum for this phosphine, while other phosphorus centers are less affected by the transformation to the hydrido complex.[14] As expected, the strongest σ-donor ligand hydride is located in the apical position trans to the vacant site and the Ru−H(1) distance (1.53(2) Å) is typical of a ruthenium−hydride bond.[12]

In this complex, as in **4**, the Ru(1)−P(2) and Ru(1)−P(3) bond distances of 2.2125(5) and 2.2298(5) Å respectively reflect a slightly higher trans effect of the iminophosphorane moiety compared to the amido moiety. In terms of thermal and kinetic stabilities, solutions of complex **5** proved to be very stable under argon or nitrogen for extended periods or after heating at 100 °C for 1 week. As postulated, this remarkable stability can be traced back to the lack of an H atom on the carbon atom α to the amino group. The usual decomposition pathway involving β-hydride elimination from a CH group, which can lead to the corresponding imine moiety,[15,16] is simply not possible.

Preliminary reactivity tests in the transfer hydrogenation of ketones under the "standard conditions" (80 °C in 2-propanol with excess of base vs ruthenium catalyst: acetophenone/Ru/Base = 200/1/20) with either complex **4** or complex **5** (without added base) showed a very moderate activity (35% and 30%, respectively after 4 h). The fast formation (and precipitation) of complex **5** from complex **4** under the reaction conditions explains their similar activities. The low activity of our complexes **4** or **5** can then be ascribed to the high stability of complex **5** and its reluctance to give a dihydride species, which are the postulated hydrogen-transferring species.[1]

In conclusion, we have devised a straightforward and high-yielding access to a new heterotridentate (P,N,N′) phosphine−iminophosphorane−amine ligand from the commercially available bis-phosphine dppm and studied its coordination toward the $[RuCl_2(PPh_3)]$ fragment. Taking advantage of the amine substructure of the ligand, we isolated and fully characterized a rare ruthenium hydrido amido complex. Such complexes are postulated to act as intermediates in the "outer sphere" mechanism of the ruthenium-catalyzed transfer hydrogenation of ketones. The reactivity of this key intermediate toward dihydrogen and DFT calculations aimed at rationalizing its stability are currently under investigation, and these results will be presented in due course.

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Supporting Information Available: Text giving experimental details and CIF files and tables giving crystallographic data for **2**, **4**, and **5**, including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference numbers 279051−279053 also contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, U.K.; fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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