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Synthesis and Reactivity of Ruthenium(BINAP)(PPh_3)

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Abstract: Ru(BINAP)(PPh_3)HCl cleanly reacts with $LiCH_2TMS$ to give Ru(BINAP)(PPh_3) (**1**) that has been fully characterized, including by X-ray diffraction (BINAP and TMS stand for (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl and trimethylsilyl respectively). In sharp contrast with other carbonyl-free phosphine complexes of Ru(0), **1** demonstrates a strikingly high thermal stability and no propensity for intramolecular C–H activation (cyclometalation). Yet **1** coordinates acetonitrile and readily exchanges its PPh_3 ligand with alkenes and dienes, thus behaving like a "masked" 16-e Ru(0) species. Electron-poor alkenes coordinate more readily than electron-rich ones, which testifies for the nucleophilic character of the Ru(0)-BINAP fragment. While being thermally stable, **1** is highly reactive and is capable of activating C–H and N–H bonds, and even of cleaving an inert N–Et bond. The combination of high reactivity and stability originates from the P,arene-chelation by the BINAP ligand, i.e., the coordinated π-arene stabilizes Ru(0) to prevent cyclometalation, yet it can slide upon substrate coordination, thereby enabling a variety of inert bond activation reactions to occur under mild conditions.

The development of effective strategies for stabilizing low-valent transition metal complexes is of fundamental importance for coordination chemistry and homogeneous catalysis.[1–2] Among various available strategies, stabilization by a tethered arene is particularly effective. For example, biaryl-based phosphines (Buchwald ligands) stabilizing Pd-(0)[3] have revolutionized the field of Pd cross-coupling reactions and led to numerous industrial applications.[4–7] Similar stabilizing strategies have been applied to various phosphine-based complexes of other metals in low oxidation states, including Ni(0),[8] Cu(I),[9] Rh(I),[10–11] Ir(I),[12–13] Pt-(0),[14] Au(I),[15–16] but not Ru(0).

Being by far the cheapest platinum-group metal, ruthenium has attracted significant attention for its applications in homogeneous catalysis. Ru(0) complexes are known to mediate many promising catalytic reactions, such as alkene (cross)-dimerizations[17] (Figure 1A) and C–H functionalizations with alkenes (Murai reaction, Figure 1B).[18–21] These catalytic transformations have several valuable features, including ***i)*** an ideal atom economy; ***ii)*** utilization of commodity alkenes; and ***iii)*** construction of valuable C–C bonds with the possibility of forging chiral centers.[22–23] However, the suboptimal catalyst performance and the need for high catalyst loadings currently preclude applications of these Ru(0)-catalyzed reactions outside academia.

One of the reasons for the rising interest in practical Ru(0) catalysis is the outstanding propensity of the coordinatively unsaturated Ru(0) center to activate C–H bonds (Figure 2A).[24] Such facile C–H activation is highly sought after for many catalytic transformations where it represents a key elementary step (Figure 1). In reality, however, performing the desired *intermolecular* C–H activation is extremely challenging due to the much faster *intramolecular* activation of the C–H bonds on the stabilizing ligands (cyclometalation; Figure 2B).[25–27] The excessive reactivity of Ru(0) toward C–H activation of the stabilizing phosphine ligands is currently mitigated by the use of either strong π-acceptor ligands (e.g., carbonyl, Figure 2C)[1,20,28] or polydentate phosphinebased ligands (Figure 2D).[29] Neither approach is ideal, as π-acceptor ligands diminish the electron density on the Ru(0) center that is key to efficient C–H activation, while polydentate ligands block vacant sites, thus limiting the reactivity. Consequently, the Ru(0) catalysis is currently performed by Ru(0)-carbonyl complexes with phosphine ligands (Figure 2C) or phosphine-free Ru(0)

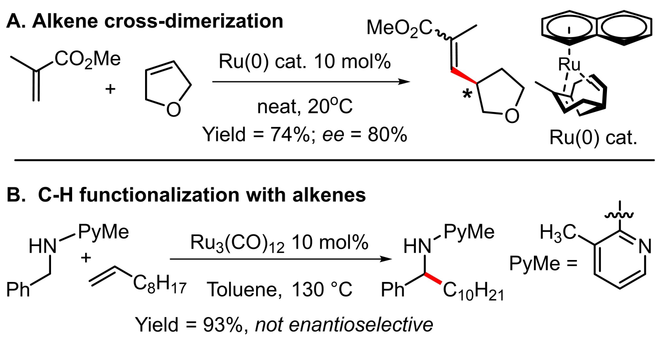

Figure 1. State-of-the-art for the Ru(0)-catalyzed alkene functionalizations.[17,19]

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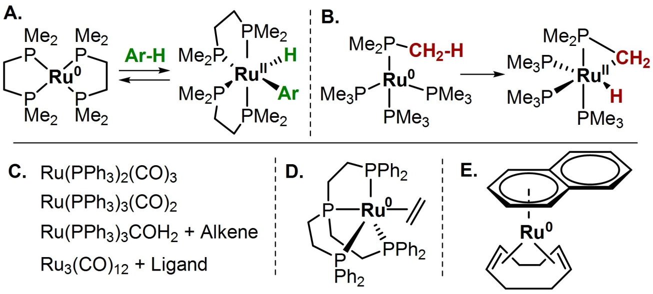

Figure 2. Top: C–H activations with Ru(0)-phosphine complex of arene substrates (A); and ligand (B). Bottom: common strategies for stabilizing Ru(0) center, involving π-acceptor carbonyl ligands (C); polydentate phosphines (D); and phosphine-free arene/diene complexes (E).

arene/diene systems (Figure 2E).[30] Herein, we report a new strategy for stabilizing Ru(0) that is based on the use of commercial BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) as a hemilabile tethered phosphine-arene ligand.

We found that dehydrohalogenation[31–33] of readily available Ru(BINAP)(PPh_3)HCl[34] with 1 equivalent of $LiCH_2TMS$ (TMS = trimethylsilyl) leads to the formation of dark-green Ru(BINAP)(PPh_3) (**1**, Figure 3). The reaction proceeds at ambient temperature in benzene or THF with >95 % NMR yield (^{1}H, ^{31}P{^{1}H} NMR). The selection of $LiCH_2TMS$ as a base was crucial for the reaction success. No reaction was observed with Cs_2CO_3 or KOAc even after heating at 80 °C in benzene. KO*t*-Bu was not selective, and the formation of multiple products besides **1** was observed. Reaction with *n*-BuLi (2.5 M in hexane) was difficult to control, resulting in either incomplete conversion of Ru(BINAP)(PPh_3)HCl or in the formation of ruthenium hydride products due to the subsequent reaction between the in situ generated **1** and *n*-BuLi. Isolation of **1** proved to be difficult because this complex does not precipitate from non-polar solvents like hexane and diethyl ether. Using a benzene-pentane solvent mixture for crystallization, we were able to isolate **1** as pure black-green crystals; in one preparation, 350 mg of **1** was obtained in a single batch (68 % yield).

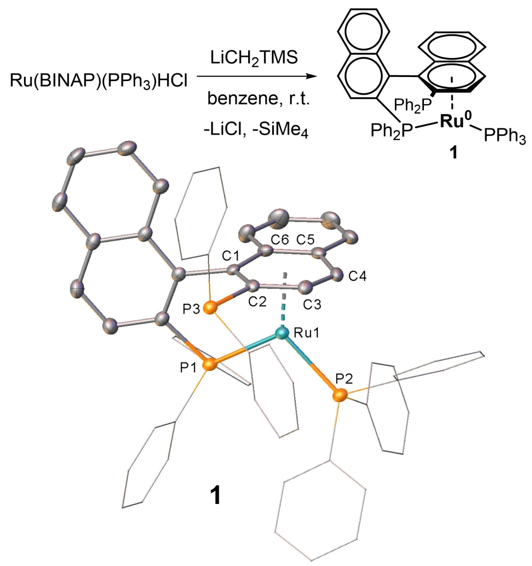

Figure 3. Synthesis of **1** and its crystal structure. Ellipsoids are represented at 50 % probability. Hydrogen atoms and solvent molecule have been omitted for clarity. The phenyl substituents are shown as wireframes, also for visual ease.

A single-crystal X-ray diffraction study of **1** revealed the P-arene chelation by the BINAP ligand (Figure 3).[35] The naphthalene moiety of BINAP demonstrates an η^6-coordination slightly distorted toward an η^4-mode. The virtually absent folding along the C1–C4 axis (ca. 3°) is in line with the η^6-coordination (c.f. 8° folding angle in η^6-coordinated Ru(COD)(naphthalene) vs. 41° in η^4-coordinated Ru(COD)(naphthalene)(PMe_3)).[36–37] At the same time, the significant difference between the Ru–C5/Ru–C6 distances (2.4247(19) and 2.3762(19) Å, respectively) and the average Ru–C1–4 distance (2.21 Å) points to some degree of η^4-distortion. The Ru–C_{ipso} (C2) distance of 2.1773(18) Å is also close to the average Ru–C1–4 distance, pointing to a π-arene over C_{ipso}-type coordination.[3] The geometry of **1** resembles that of [Ru(BINAP)(PPh_3)H]OTf, a cationic Ru(II) complex reported by Pregosin and co-workers.[38]

The simultaneous P and arene coordination by the BINAP ligand is also present in solutions of **1** in aromatic solvents and THF. This coordination mode is manifested by the presence of two high-frequency (δ 55.8 and 45.1 ppm) and one low-frequency (δ −17.5 ppm) resonances in the ^{31}P{^{1}H} NMR spectrum. While the high-frequency signals correspond to two P-atoms coordinated to the Ru(0) center (one from BINAP and one from PPh_3), the low-frequency resonance is characteristic of a phosphine that is not coordinated to metal. For Ru complexes, this is observed when the metal center binds to the aromatic ring of BINAP in an η^6-mode.[38–41] ^{31}P{^{1}H} NMR spectra of **1** at −80 °C to 60 °C showed no line broadening, suggesting a lack of fluxional behavior within NMR time scale in this temperature range. Notably, **1** demonstrated an outstanding stability for a Ru(0) phosphine complex (Figure 2B). Virtually no decomposition was observed after heating **1** in toluene-d_8 at 110 °C for 24 h, and only ca. 5 % of the complex decomposed after heating the same solution for one week (^{1}H and ^{31}P{^{1}H} NMR, Figures S19–21).

Complex **1** was found to be less stable in the presence of small coordinating molecules like acetone or pyridine. Upon addition of such molecules (500 equiv) to a solution of **1** in benzene-d_6, the complex slowly decomposed at room temperature with the release of PPh_3. With MeCN (500 equiv), **1** reacted within the time of mixing to produce a red-brown solution containing a 1:3 equilibrium mixture of **1** with a new species formulated as Ru(BINAP)(PPh_3)(CH_3CN) (**1-CH$_3$CN**, Figure 4). Similar to **1**, this new species displays three ^{31}P{^{1}H} NMR signals and no hydride peaks in the ^{1}H NMR spectrum. Furthermore, **1-CH$_3$CN** exhibits a ^{31}P{^{1}H} NMR signal at ca. 6.5 ppm (c.f. −17.5 ppm for **1**) and a significant increase in the P–P coupling constants from 2–3 Hz in **1** to 10–40 Hz. This NMR pattern is characteristic of the P,P,η^2-coordination of BINAP ligand as a 6-electron

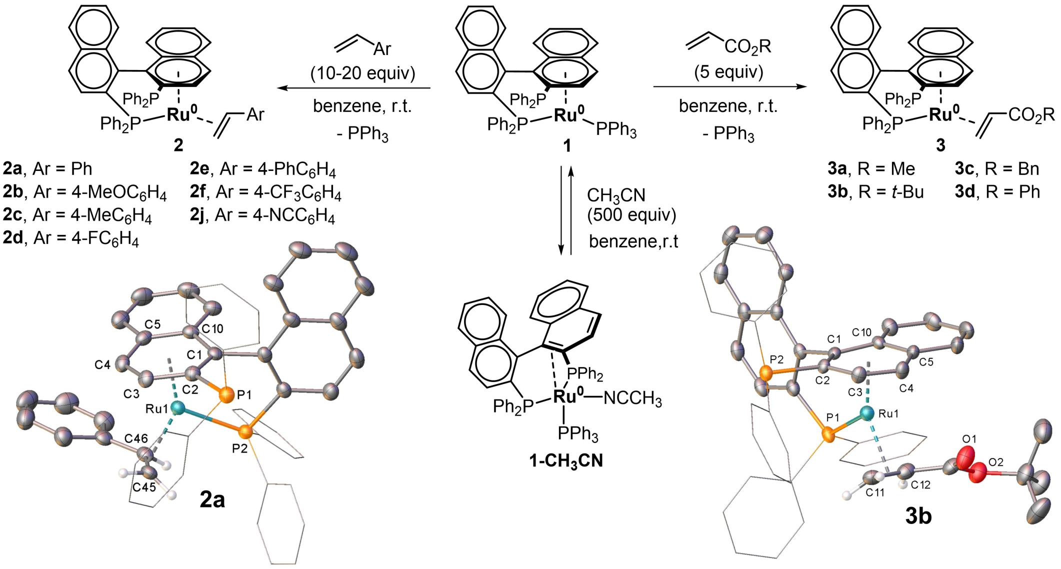

Figure 4. Reactions of 1 with styrenes, acrylates and acetonitrile. X-ray structures of **2a** and **3b**. Ellipsoids are represented at 50% probability. Hydrogen atoms, except the vinylic hydrogens, have been omitted for clarity. The phenyl substituents in phosphines are shown as wireframes, also for visual ease.

donor via two P-atoms and one double bond of the naphthalene due to η^6 to η^2 arene ligand slippage upon acetonitrile coordination.[42–44] A similar change in the naphthalene coordination mode was also observed for Ru–BINAP complexes with dienes and confirmed by an X-ray structure (see below).

We then studied the reactivity of **1** toward alkenes and dienes. Interestingly, the triphenylphosphine (PPh_3) ligand in **1** can be easily substituted with alkenes such as styrenes and acrylate esters, resulting in the clean formation of orange-red Ru(BINAP)(alkene) complexes (Figure 4). Two of these complexes, Ru(BINAP)(styrene) (**2a**) and Ru-(BINAP)(*t*-Bu-acrylate) (**3b**) were structurally characterized by single crystal X-ray diffraction which confirmed the coordination of BINAP via one P atom and η^6-arene (Figure 4). The solid-state structures were consistent with the $^{31}P\{^1H\}$ NMR spectra in solution, displaying two signals at around 61.0 ppm and −17.5 ppm for the coordinated and non-coordinated $-PPh_2$ groups of BINAP, respectively.

Reactions of **1** with alkenes demonstrated high functional group tolerance (Figure 4). The substitution of the PPh_3 ligand readily proceeded with styrenes bearing both electron-donating (**2b,c**) and electron-accepting (**2f,g**) functional groups, with the exception of very electron-poor 4-nitrostyrene that reacted with **1** to give a complex mixture of unidentified products. Notably, the displacement of PPh_3 in **1** was kinetically and thermodynamically more favorable for electron-deficient rather than electron-rich styrenes (Table S1).[45–47] For instance, the reaction of **1** with 4-cyanostyrene went to completion within 30 min to give **2j**, whereas the reaction with 4-methoxystyrene under the same conditions stopped at ca. 60% conversion after 24 h, reaching a thermodynamic equilibrium. These observations pointed to the dominant contribution of π-backdonation to the binding of the alkene to the Ru(0) center, highlighting the electron richness of this moiety.

In the reactions of **1** with acrylates, various ester groups, including *t*-Bu, benzyl, and phenyl, were easily tolerated (**3b–d**). However, for methyl methacrylate, the subsequent C–H activation process was significant even at room temperature (see below). Virtually no reaction was observed for electron-rich and/or bulkier alkenes such as vinyltrimethylsilane, vinyltrimethoxysilane, and both cis- and trans-stilbene. Notably, while styrene-based complexes **2** exist as a single species in solution, acrylate complexes **3** are present as a mixture of two isomers, presumably due to different orientations of the alkenes relative to the Ru–BINAP unit.

Reactions of **1** with dienes resulted in the substitution of the PPh_3 ligand and the clean formation of Ru(BINAP)-(diene) products **4** (Figure 5). In contrast with the reactions with alkenes, the substitution of PPh_3 with dienes is accompanied with a change in the BINAP coordination mode to P,P,η^2. This change in the coordination fashion, previously observed for the formation of **1-CH$_3$CN** (see above) is manifested by the $^{31}P\{^1H\}$ NMR signal at a higher frequency of ca. −3.5 ppm (c.f. −17.5 ppm for alkenes) and an increase in the P–P coupling from 2–3 Hz in **1** and **2** to 30–40 Hz in **4**.[42–44] This coordination mode change was further confirmed by the X-ray structure of the isoprene complex **4a** (Figure 5). Similar reactivity was observed for other dienes, including 1,3-dienes (**4a–c**) and norbornadiene (**4d**). Di-substituted dienes, such as Danishefsky's diene (**4e**) and 2,3-dimethylbutadiene (**4f**), were unreactive toward **1** under similar conditions (room temperature); even after 24 h at 70 °C, less than 5% conversion was observed.

While **1** coordinates a broad range of alkenes and dienes via PPh_3 substitution, for methyl methacrylate (MMA) and indene, a subsequent C–H activation process was readily noticeable at room temperature. Upon heating to 60 °C, the

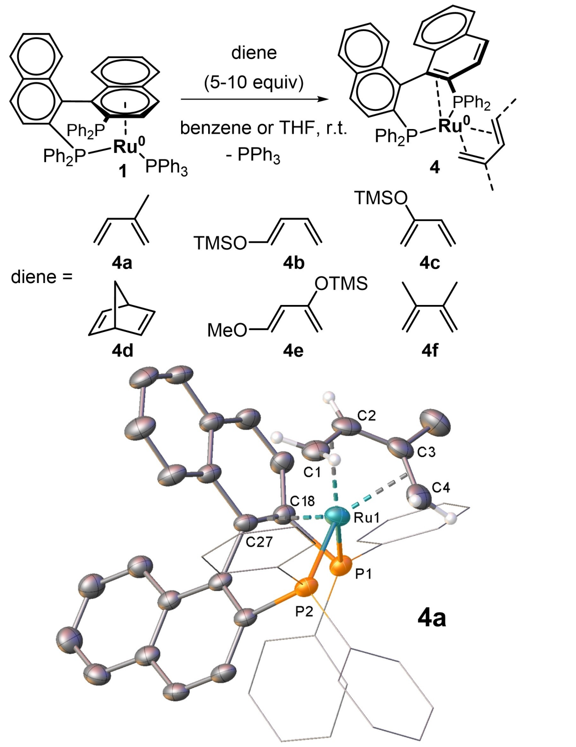

Figure 5. Reaction of **1** with dienes and X-ray structure of **4a**. Ellipsoids are represented at 50% probability. Only the major component of the disordered isoprene ligand in **4a** is shown. Hydrogen atoms, except those on diene, have been omitted for clarity. The phenyl substituents are shown as wireframes, also for visual ease.

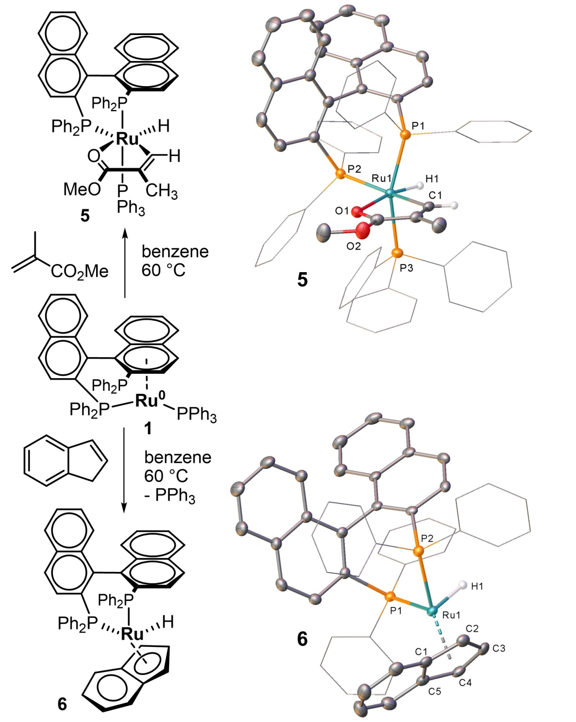

Figure 6. Reactions of **1** with methyl methacrylate and indene. X-ray structures of **5** and **6**. Ellipsoids are represented at 50% probability. Hydrogen atoms, except hydrides and those on alkene, have been omitted for clarity. The phenyl substituents are shown as wireframes, also for visual ease.

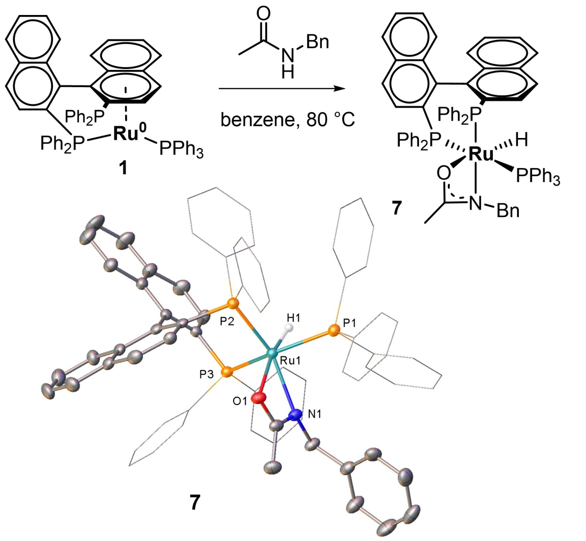

Figure 7. Reaction of **1** with N-benzylacetamide. X-ray structure of **7**. Ellipsoids are represented at 50% probability. Hydrogen atoms, except hydride, have been omitted for clarity. The phenyl substituents are shown as wireframes, also for visual ease.

organometallic Ru(II) hydrides, Ru(BINAP)(PPh_3)(MMA-yl)H (**5**) and Ru(BINAP)(indenyl)H (**6**), were formed as single major products ($^{31}P\{^1H\}$ and ^1H NMR), successfully isolated, and structurally characterized (Figure 6).

Complex **1** was also found to readily react with acids. The reaction with acetic acid produced previously reported Ru(BINAP)(PPh_3)(OAc)H.[48] A similar transformation was observed with *N*-benzylacetamide, giving rise to structurally similar Ru(BINAP)(PPh_3)($CH_3C(O)NBn$)H (**7**). All of the Ru insertions into the O–H, N–H, and C–H bonds proceeded with the change of the BINAP coordination mode from η^6-arene,P to conventional P,P-chelation (Figures 6, 7).

Next, we probed the ability of **1** to perform more challenging sp^3 C–H activation of saturated compounds in the presence of 2-amino pyridine and acetamide directing groups.[19–20,49–50] To our big surprise, the reaction of **1** with 2-(diethylamino)pyridine gave rise to Ru(BINAP)(PPh_3)(2-EtN–Py)H (**8**), obviously as a result of cleavage of the strong N–Et bond (Figure 8A). This unexpected transformation slowly occurred at as low as room temperature, and after 20 h at 60 °C, ca. 70% of **1** was converted to **8**. To confirm the structure of **8**, we also produced it by the reaction of **1** with 2-(ethylamino)pyridine, isolated, and fully characterized (Figure 8E). In solution, **8** exists as a mixture of two isomers in a ca. 3:4 ratio, apparently from two different orientations of the 2-EtN–Py group on the Ru center.

Not only aminopyridine, but the conventional amide group was also found to be capable to direct the N–Et bond

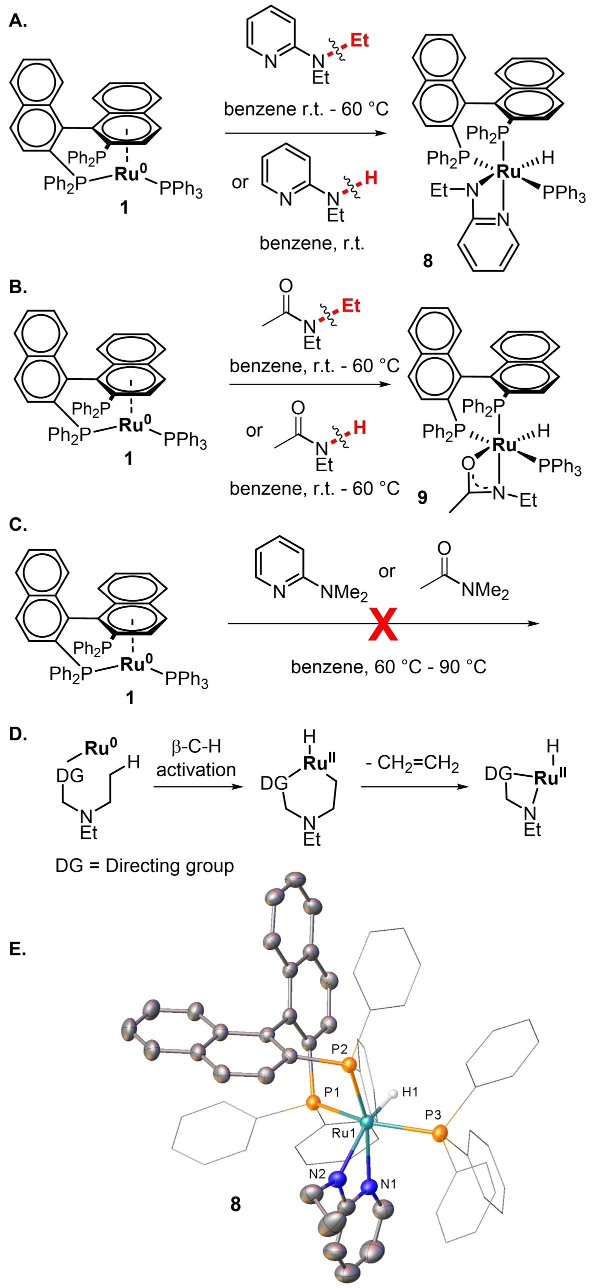

Figure 8. Reaction of **1** with 2-(diethylamino)pyridine and 2-(ethylamino)pyridine (A); reaction of **1** with *N,N*-diethylacetamide and *N*-ethylacetamide (B); lack of reactivity of 1 toward 2-(dimethylamino)pyridine and *N,N*-dimethylacetamide (C); proposed mechanism of N–Et bond cleavage (D); and X-ray structure of **8** (E). Ellipsoids are represented at 50 % probability. Solvent molecules and hydrogen atoms, except hydride, have been omitted for clarity. The phenyl substituents are shown as wireframes, also for visual ease.

cleavage. Complex **1** reacts with *N,N*-diethylacetamide under mild conditions (r.t. to 60 °C) with the formation of Ru(BINAP)(PPh_3)($CH_3C(O)NEt$)H (**9**) (Figure 8B). ^{1}H and ^{31}P{^{1}H} NMR signals from **9** strongly resemble those from structurally characterized **7**, and identical signals were obtained in an N–H activation of *N*-ethylacetamide with **1**. While **9** is the main product at low conversions of **1** at room temperature (ca. 10 % after 20 h), at higher temperature the reaction was less selective, resulting in the formation of several unidentified ruthenium hydride species (see Supporting Information for details, Figures S27–S29). In contrast, no reaction besides thermal decomposition was observed for NEt_3 (10 equiv, 110 °C, 24 h), highlighting the importance of the directing group for the N–Et bond cleavage process.

The cleavage of inert N–alkyl bonds is relatively rare. We are aware of only a single example of such reaction at a Ru center, where the N–*i*-Pr bond cleavage of an N-heterocyclic carbene ligand took place in a Ru-hydride complex.[51] It was proposed that this process occurs through β–C–H activation and subsequent extrusion of alkene.[52] We believe that a similar mechanism is operative in our case (Figure 8D). This mechanism is supported by the fact that no reaction was observed between **1** and 2-(dimethylamino)pyridine or *N,N*-dimethylacetamide, for which β–C–H activation is not feasible (Figure 8C). At the same time, the formation of ethylene in the reaction was not observed by ^{1}H NMR, leaving room for alternative mechanisms of N–Et bond cleavage.

In the course of this study we encountered several transformations catalyzed by **1**. For example, in the presence of **1** at ca. 1 % catalyst loading, the terminal double bond of 1-octene readily isomerizes into the internal double bond of 4-octene at 80 °C in benzene. 2-(Ethylamino)pyridine can be N-butylated by *n*-butanol at 140 °C with **1** as a catalyst (10 mol %, 46 h).

In summary, we have synthesized and characterized a novel Ru complex, Ru(BINAP)(PPh_3) (**1**). Being a phosphine Ru(0) complex, **1** demonstrates an unprecedentedly high stability to intramolecular C–H bond activation. Yet the Ru(0) center of **1** can add donors such as acetonitrile, and the PPh_3 ligand can be readily substituted with alkenes and dienes. **1** activates C–H and N–H bonds, and can even cleave the highly inert N–Et bond. The combination of stability and specific reactivity observed for **1** suggests that the P,arene chelation strategy is feasible for stabilizing reactive Ru(0)-species. **1** might be viewed as a "masked" 16-e Ru(0) complex. It is expected that in a catalytic reaction, the tethered arene ligand can effectively stabilize Ru(0) intermediates, yet slide upon interacting with incoming substrate molecules to provide a vacant coordination site needed for subsequent transformations at the highly reactive Ru(0) center. BINAP and similar ligands with a tethered phosphine-naphthalene unit provide a valuable entry into enantioselective Ru(0) catalysis, and studies toward this goal are currently underway in our group.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Ruthenium · Low-valent transition metal complexes · C–N activation · Tethered arene ligands · BINAP

[1] J. Chatt, *J. Inorg. Nuc. Chem.* **1958**, *8*, 515–531.
[2] R. H. Crabtree, *Chem. Rev.* **2015**, *115*, 127–150.
[3] R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461–1473.
[4] T. J. Colacot, *New trends in cross-coupling : theory and applications*, Royal Society of Chemistry, [Cambridge], **2015**.
[5] P. Ruiz-Castillo, S. L. Buchwald, *Chem. Rev.* **2016**, *116*, 12564–12649.
[6] A. C. Sather, S. L. Buchwald, *Acc. Chem. Res.* **2016**, *49*, 2146–2157.
[7] B. T. Ingoglia, C. C. Wagen, S. L. Buchwald, *Tetrahedron* **2019**, *75*, 4199–4211.
[8] S. H. Newman-Stonebraker, J. Y. Wang, P. D. Jeffrey, A. G. Doyle, *J. Am. Chem. Soc.* **2022**, *144*, 19635–19648.
[9] D. Wang, Q. Chen, X. Leng, L. Deng, *Inorg. Chem.* **2018**, *57*, 15600–15609.
[10] Z. Liu, H. Yamamichi, S. T. Madrahimov, J. F. Hartwig, *J. Am. Chem. Soc.* **2011**, *133*, 2772–2782.
[11] Y. Jin, J. Caner, S. Nishikawa, N. Toriumi, N. Iwasawa, *Nat. Commun.* **2022**, *13*, 7584.
[12] A. R. O'Connor, W. Kaminsky, B. C. Chan, D. M. Heinekey, K. I. Goldberg, *Organometallics* **2013**, *32*, 4016–4019.
[13] J. J. Moreno, M. F. Espada, E. Krüger, J. López-Serrano, J. Campos, E. Carmona, *Eur. J. Inorg. Chem.* **2018**, *2018*, 2309–2321.
[14] L. Ortega-Moreno, R. Peloso, C. Maya, A. Suárez, E. Carmona, *Chem. Commun.* **2015**, *51*, 17008–17011.
[15] C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179.
[16] G. Zuccarello, M. Zanini, A. M. Echavarren, *Isr. J. Chem.* **2020**, *60*, 360–372.
[17] Y. Hiroi, N. Komine, S. Komiya, M. Hirano, *Org. Lett.* **2013**, *15*, 2486–2489.
[18] S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, *366*, 529–531.
[19] C.-H. Jun, *Chem. Commun.* **1998**, 1405–1406.
[20] N. Chatani, T. Asaumi, S. Yorimitsu, T. Ikeda, F. Kakiuchi, S. Murai, *J. Am. Chem. Soc.* **2001**, *123*, 10935–10941.
[21] F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826–834.
[22] M. Holmes, L. A. Schwartz, M. J. Krische, *Chem. Rev.* **2018**, *118*, 6026–6052.
[23] R. S. Doerksen, T. Hodik, G. Hu, N. O. Huynh, W. G. Shuler, M. J. Krische, *Chem. Rev.* **2021**, *121*, 4045–4083.
[24] J. Chatt, J. M. Davidson, *J. Chem. Soc.* **1965**, 843–855.
[25] D. J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1979**, 1283–1289.
[26] H. Werner, R. Werner, *J. Organomet. Chem.* **1981**, *209*, C60–C64.
[27] F. Mohr, S. H. Privér, S. K. Bhargava, M. A. Bennett, *Coord. Chem. Rev.* **2006**, *250*, 1851–1888.
[28] B. E. Cavit, K. R. Grundy, W. R. Roper, *J. Chem. Soc. Chem. Commun.* **1972**, 60b–61.
[29] T. Ito, K. Takahashi, N. Iwasawa, *Organometallics* **2019**, *38*, 205–209.
[30] M. Hirano, S. Komiya, *Coord. Chem. Rev.* **2016**, *314*, 182–200.
[31] R. H. Heyn, K. G. Caulton, *J. Am. Chem. Soc.* **1993**, *115*, 3354–3355.
[32] V. V. Grushin, *Acc. Chem. Res.* **1993**, *26*, 279–286.
[33] R. H. Heyn, S. A. Macgregor, T. T. Nadasdi, M. Ogasawara, O. Eisenstein, K. G. Caulton, *Inorg. Chim. Acta* **1997**, *259*, 5–26.
[34] K. Abdur-Rashid, A. J. Lough, R. H. Morris, *Organometallics* **2001**, *20*, 1047–1049.
[35] Deposition Numbers 2311102 (for **1**), 2311103 (for **2a**), 2311104 (for **3b**), 2311105 (for **4a**), 2311106 (for **5**), 2311107 (for **6**), 2311108 (for **7**), and 2311109 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
[36] M. Crocker, M. Green, J. A. K. Howard, N. C. Norman, D. M. Thomas, *J. Chem. Soc. Dalton Trans.* **1990**, 2299–2301.
[37] M. A. Bennett, *Coord. Chem. Rev.* **1997**, *166*, 225–254.
[38] R. Hermatschweiler, P. S. Pregosin, A. Albinati, S. Rizzato, *Inorg. Chim. Acta* **2003**, *354*, 90–93.
[39] N. Feiken, P. S. Pregosin, G. Trabesinger, *Organometallics* **1997**, *16*, 3735–3736.
[40] T. J. Geldbach, P. S. Pregosin, *Eur. J. Inorg. Chem.* **2002**, 1907–1918.
[41] P. S. Pregosin, *Coord. Chem. Rev.* **2008**, *252*, 2156–2170.
[42] N. Feiken, P. S. Pregosin, G. Trabesinger, M. Scalone, *Organometallics* **1997**, *16*, 537–543.
[43] G. Trabesinger, A. Albinati, N. Feiken, R. W. Kunz, P. S. Pregosin, M. Tschoerner, *J. Am. Chem. Soc.* **1997**, *119*, 6315–6323.
[44] J. A. Wiles, C. J. A. Daley, R. J. Hamilton, C. G. Leong, S. H. Bergens, *Organometallics* **2004**, *23*, 4564–4568.
[45] R. Cramer, *J. Am. Chem. Soc.* **1967**, *89*, 4621–4626.
[46] S. S. Stahl, J. L. Thorman, N. de Silva, I. A. Guzei, R. W. Clark, *J. Am. Chem. Soc.* **2003**, *125*, 12–13.
[47] B. V. Popp, J. L. Thorman, C. M. Morales, C. R. Landis, S. S. Stahl, *J. Am. Chem. Soc.* **2004**, *126*, 14832–14842.
[48] M. Kitamura, M. Tsukamoto, Y. Bessho, M. Yoshimura, U. Kobs, M. Widhalm, R. Noyori, *J. Am. Chem. Soc.* **2002**, *124*, 6649–6667.
[49] S. Pan, K. Endo, T. Shibata, *Org. Lett.* **2011**, *13*, 4692–4695.
[50] L. Gonnard, A. Guérinot, J. Cossy, *Tetrahedron* **2019**, *75*, 145–163.
[51] S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 13702–13703.
[52] L. J. L. Häller, M. J. Page, S. Erhardt, S. A. Macgregor, M. F. Mahon, M. A. Naser, A. Vélez, M. K. Whittlesey, *J. Am. Chem. Soc.* **2010**, *132*, 18408–18416.

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Communications

Organometallic Chemistry

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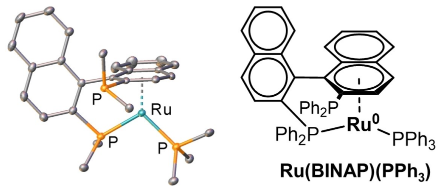
Synthesis and Reactivity of Ruthenium-(BINAP)(PPh$_3$)



- Masked 16-e Ru(0)
- High thermal stability
- No intramolecular C–H activation
- Coordination of alkenes/dienes
- C–H, N–H, N–Et bonds cleavage

The synthesis of a Ru(0)(BINAP)(PPh$_3$) complex (BINAP:2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) is reported. It behaves as a "masked" 16-electron Ru(0) complex: while being quite stable, it is capable to substitute PPh$_3$ with alkenes/dienes, and activate C–H, N–H or inert N–Et bonds. This compound gives novel insight into Ru(0) stabilization approaches while maintaining a high specific reactivity potentially useful for catalytic applications.