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Aromatization of a Dihydro-3-ruthenaindolizine Complex

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Summary: Complex $RuHCl(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**1**) reacts with KTp (Tp = hydridotris(pyrazolyl)borate) to give the hydride-dihydrogen derivative $RuHTp(\eta^2\text{-}H_2)(P^iPr_3)$ (**2**), which has been characterized by X-ray diffraction analysis (d_{H-H} = 1.00(3) Å). Treatment of a toluene solution of **2** with 2-vinylpyridine leads to the 1,2-dihydro-3-ruthenaindolizine derivative $\overline{Ru(CH_2CH_2\text{-}C_5H_4N)}Tp(P^iPr_3)$ (**3**). Complex **3**

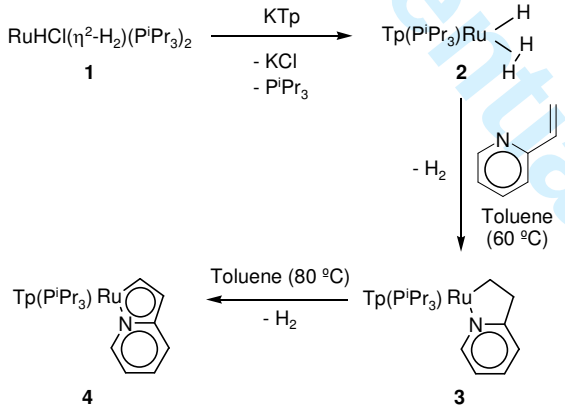
aromatizes in toluene at 80 ºC to afford the 3-ruthenaindolizine complex Ru(CHCH-C_5H_4N)Tp(P^iPr_3) (**4**) by loss of a hydrogen molecule in the absence of any hydrogen acceptor. The aromatic character of **4** is supported by X-ray diffraction analysis, NMR spectroscopy, and DFT calculations.

Aromatic metallacycles are transition metal containing ring systems that exhibit aromatic properties.[1] While much effort has been focused on metallacarbocycles,[2] important progress is also being made in synthesizing and studying the properties of heteroatom-containing species.[3]

Aromatization is a relevant reaction in classical organic chemistry that converts a substrate into an aromatic compound.[4] There are several methods to accomplish this transformation. The simplest and most important is the dehydrogenation, in which hydrogen is detached from a molecule. Although the reaction is strongly endothermic, the equilibrium is shifted to the right by adding a hydrogen acceptor. The presence of a transition metal catalyst facilitates the hydrogen transfer.[5]

We now show that the aromatization by dehydrogenation is a method, which can also be applied to the synthesis of aromatic heterometallacyclic compounds (Scheme 1). In this case, a hydrogen acceptor is not necessary even under mild conditions.

Scheme 1



The trihydride complex $OsH_3Cl(P^iPr_3)_2$ has shown to be a suitable precursor for the synthesis of $OsH_3Tp(P^iPr_3)$[6] and $[OsH_3(triamine)(P^iPr_3)]Cl$[7] compounds, which are allowing the development of new $Os(P^iPr_3)$ chemistry.[8] This compound is prepared by reaction of $OsH_2Cl_2(P^iPr_3)_2$ with molecular hydrogen, in toluene and in the presence of Et_3N.[10] Now we have observed that, under the same

conditions, $RuH_2Cl_2(P^iPr_3)_2$[11] affords the Ru- counterpart $RuHCl(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**1**).[12] Similarly to $OsH_3Cl(P^iPr_3)_2$, complex **1** is a useful starting compound to coordinate Tp to the $Ru(P^iPr_3)$ moiety. At room temperature, the treatment of a toluene solution of **1** with 1.2 equiv of KTp in tetrahydrofuran for 3 h leads to the hydride-dihydrogen $RuHTp(\eta^2\text{-}H_2)(P^iPr_3)$ (**2**), which is the Ru- counterpart of $OsH_3Tp(P^iPr_3)$. The difference in nature between the MH_3 units of these compounds is due to the poorer π-back bonder power of ruthenium with regard to osmium, which is revealed by the higher oxidizing character of ruthenium.[13] Complex **2** was isolated as a white solid in 67% yield.

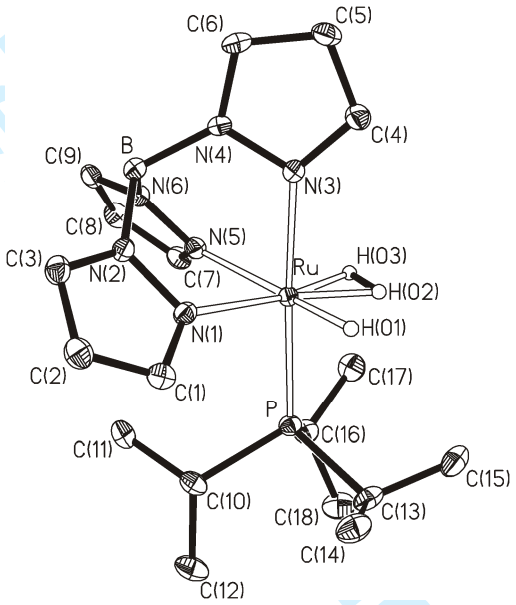


Figure 1. Molecular diagram of **2**. Selected bond lengths (Å) and angles (deg): Ru–N(1) 2.1365(18), Ru–N(3) 2.1315(17), Ru–N(5) 2.2111(18), Ru–P 2.2888(7), Ru–H(01) 1.58(2), Ru–H(02) 1.52(3), Ru–H(03) 1.62(2), H(02)–H(03) 1.00(3); H(01)–Ru–N(5) 171.0(8), N(3)–Ru–P 176.54(5), H(01)–Ru–H(02) 65.2(14), H(02)–Ru–H(03) 37.0(12).

Figure 1 shows the structure of **2** obtained by X-ray diffraction analysis. The geometry around the ruthenium atom can be described as a distorted octahedron with the coordinating nitrogen atoms of the terdentate ligand in *fac* sites. The metal coordination sphere is completed by the phosphine ligand trans disposed to N(3) (P–Ru–N(3) = 176.54(5)º), the hydride H(01) trans disposed to N(5) (H(01)–Ru–N(5) = 171.0(8)º), and the dihydrogen (H(02–H(03)) trans disposed to N(1). The hydrogen atoms bonded to

the metal center lie in the plane containing the atoms Ru, N(1), and N(5). The H(02)–H(03) separation of 1.00(3) Å supports the dihydrogen formulation.

In solution, the hydrogen atoms of the RuH_3 unit are involved in a thermally activated site exchange process. Thus, at room temperature, the high field region of the ^1H NMR spectrum in toluene-d_8 shows a single resonance at –10.66 ppm. It appears as a doublet with a H–P coupling constant of 18.0 Hz. This signal shows no sign of decoalescence down to 200 K. In agreement with the hydride-dihydrogen character of **2**, at 208 K, a $T_{1(min)}$ value of 26±1 ms was obtained for this resonance in the 300 MHz scale. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 80.9 ppm. These spectroscopic observations are similar to those reported for related $RuH(Tp^R)(\eta^2\text{-}H_2)(PR'_3)$ compounds.[14,15]

Complex **2** reacts with 2-vinylpyridine in toluene at 60 ºC to give the 1,2-dihydro-3-ruthenaindolizine derivative $Ru(CH_2CH_2\text{-}C_5H_4N)Tp(P^iPr_3)$ (**3**), which is isolated as an orange solid in 55% yield. The formation of this compound involves the dissociation of the dihydrogen ligand of **2** and the subsequent insertion of the vinyl substituent of the heterocycle into the Ru-H bond of the resulting $RuHTp(P^iPr_3)$ intermediate.

The presence of a five-membered ring in **3** is strongly supported by the $^{13}C\{^1H\}$ NMR spectrum of this compound in benzene-d_6, which shows at 45.4 ppm a singlet and at 13.8 ppm a doublet with a C–P coupling constant of 10 Hz that correspond to the py-CH_2 and Ru-CH_2 carbon atoms, respectively. The HSQC spectrum fits these signals with resonances at 3.51 and 2.46 ppm in the ^1H NMR spectrum.

Complex **3** undergoes aromatization in toluene at 80ºC, by quantitative dehydrogenation, to afford the 3-ruthenaindolizine compound $Ru(CHCH\text{-}C_5H_4N)Tp(P^iPr_3)$ (**4**). Treatment of **2** with 1.2 equiv of 2-vinylpyiridine in toluene under reflux affords **4** in a one-pot synthesis. This complex is isolated as an orange solid in 58% yield.

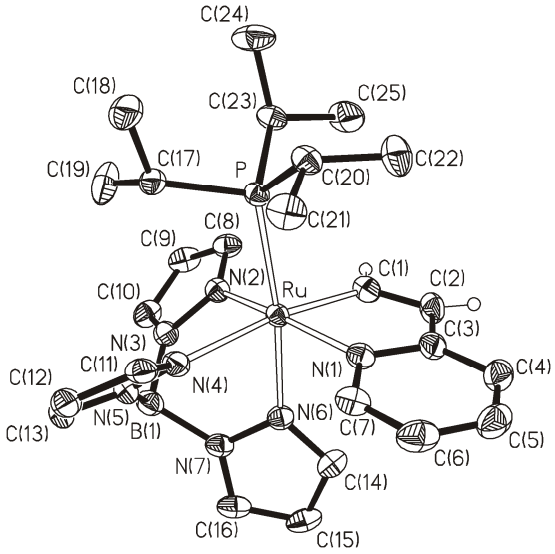
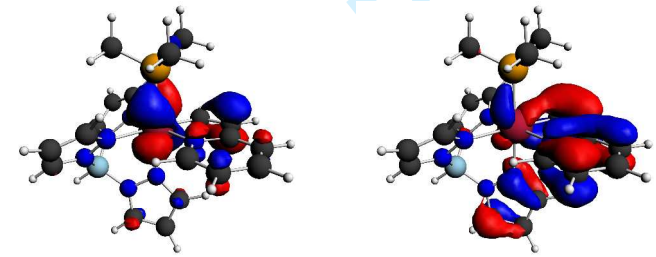


Figure 2. Molecular diagram of **4**. Selected bond lengths (Å) and angles (deg): Ru–C(1) 1.983(2), Ru–N(1) 2.0865(19), Ru–N(2) 2.0787(18), Ru–N(4) 2.2257(19), Ru–N(6) 2.1242(19), Ru–P 2.3641(6), C(1)–C(2) 1.352(3), C(2) –C(3) 1.428(3), N(1) –C(3) 1.381(3); C(1)–Ru–N(4) 171.13(9), C(1)–Ru–N(1) 78.59(9), N(1)–Ru–N(2) 165.61(7), N(6)–Ru–P 172.52(5).

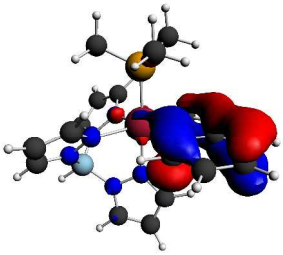
Figure 2 shows a view of the molecular geometry of **4**. The structure proves that this compound can be certainly regarded as a result of replacing the CH group at 3-position of the five-membered ring of a 10-π electrons indolizine derivative by the RuTp(P^iPr_3) metal fragment. The metallabicycle is almost planar (maximum deviation 0.0831(17) Å) for N(1). The significant electron delocalization through the bicyclic system translates in bond lengths between those expected for single and double bonds. The Ru-C(1) distance of 1.983(2) Å is significantly shorter than the Ru-C bond lengths in alkenylruthenium(II) derivatives (2.03–2.14 Å),[16] while it is longer than those found in the α,β-unsaturated carbene complex $[RuCl(=CHCH=CPh_2)(CO)(P^iPr_3)_2]BF_4$ (1.874(3) Å)[17] and in the alkoxycarbene compound $[RuTp\{C(OCH_3)CH_2CO_2CH_3\}(dippe)]BPh_4$ (1.86(2) Å)[18]. However, it is similar to those found in the complexes $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_3)CH_2Ph\}(CHIRAPHOS)]PF_6$ (1.93(2) Å),[19] $Ru\{C(C=CHPh)OC(O)CH_3\}(CO)\{\kappa^1\text{-}OC(CH_3)_2\}(P^iPr_3)_2]BF_4$ (1.967(8) Å),[20] $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2{\equiv}CH)CH=CPh_2\}(CO)(P^iPr_3)_2]BF_4$ (1.965(4) Å),[21] $Ru\{(E\text{-}CH=CHC(CH_3)=CH_2\}Cl(CO)(P^iPr_3)_2$ (1.989(3) Å),[22]

$[Ru(\eta^5\text{-}C_5H_5)\{CCH{=}C(OEt)OC{=}CPh_2\}(CO)(P^iPr_3)_2]BF_4$ (2.017(6) Å),[23] where a ruthenium-carbon bond between single and double has been also proposed. The C(1)–C(2) distance is longer than the carbon-carbon bond length reported for the double bond of single alkenyl ligands,[16a] whereas the C(2)–C(3) distance of 1.428(3) Å is the expected for an aromatic compound. The Ru–N(1) bond length of 2.0865(1) is shorter than the mean of the Ru-pyridine separations (2.133 Å).[24]

The presence of a Ru-C bond intermediate between single and double in **4** is also revealed by its $^{13}C\{^1H\}$ NMR spectrum, which shows the RuC resonance at 226.3 ppm as a doublet with a C-P coupling constant of 13 Hz. This chemical shift is similar to those reported for metallapyrroles,[3d] metallafuranes,[25] and benzylidene-osmium derivatives.[26] However, it appears at unusually low field when it is compared with the expected resonance for an alkenyl species. The resonance corresponding to the py-*C*H carbon atom is observed at 130.3 ppm as a singlet. In the ^1H NMR spectrum, the CH protons of the five-membered ring display doublets at 11.40 (RuCH) and 7.72 (py-C*H*) ppm, with a H-H coupling constant of 7.8 Hz. The $^{31}P\{^1H\}$ NMR shows a singlet at 46.4 ppm.


HOMO-1

HOMO-3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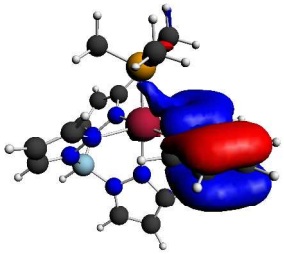
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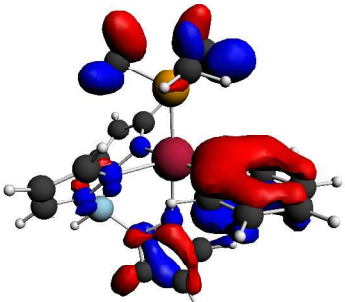
HOMO-31

Figure 3. Plot of the computed π-molecular orbitals (BP86/def2-SVP level) of model complex **4M**. The value of the outermost contour line is 0.035.

Figure 3 shows the computed π-molecular orbitals of the model compound Ru(CHCH-C_5H_4N)Tp(PMe_3) (**4M**).[27] A simple electron counting indicates that this compound possesses 10 π-electrons and, therefore, obeys the Hückel-aromaticity rule. The main characteristic of the orbital interactions in aromatic metallic molecules is the involvement in the π bonding of filled metal d orbitals instead p orbitals of main group elements.[28] Similarly to aromatic metallabenzenes, the ruthenium *d* orbitals clearly participate in the π-system of **4M**, incorporating formally 2 electrons to the total π-system. The d contribution is 70.4 % to the molecular orbital HOMO-1 and 13.7 % to the molecular orbital HOMO-3. The molecular orbitals HOMO-12, HOMO-14, and HOMO-31 are similar to molecular orbitals of the indolizine molecule. The contribution of the metal to them is negligible.

In conclusion, the aromatization by dehydrogenation, of great relevance in conventional organic chemistry, can enlarge its scope in organometallic chemistry since it proves to be useful to prepare aromatic metallacycles. The presence of a metal center appears to facilitate the dehydrogenation process. Thus, we show that the hydride-dihydrogen complex RuHTp(η^2-H_2)(P^iPr_3) inserts 2-vinylpyridine to give a 1,2-dihydro-3-ruthenaindolizine intermediate, which aromatizes in toluene at 80 ºC to afford the 3-ruthenaindolizine complex Ru(CHCH-C_5H_4N)Tp(P^iPr_3) by loss of a hydrogen molecule in the absence of any hydrogen acceptor.

Experimental Section

All reactions were carried out under Argon with rigorous exclusion of air using Schlenk-tube or glovebox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. KTp (Acros) and 2-vinylpyridine (Sigma-Aldrich) were used without further purification. The starting material RuHCl(η^2-H_2)(P^iPr_3)$_2$ (**1**)[12] was prepared *in situ* by reaction of $RuH_2Cl_2(P^iPr_3)_2$[11] with H_2 and

NEt_3. In the NMR spectra chemical shifts (expressed in ppm) are referenced to residual solvent peaks (^1H, ^{13}C) or external H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz. Infrared spectra were recorded on a Spectrum One spectrometer as neat solids. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of RuHTp(η^2-H_2)(P^iPr_3) (2). A solution of $RuH_2Cl_2(P^iPr_3)_2$ (1 g, 2.02 mmol) and NEt_3 (425 μL, 3.03 mmol) in 15 mL of toluene was introduced into a Schlenk flask equipped with a teflon stopcock and pressurized with H_2 (1 atm). The reaction mixture was stirred for 3 h at room temperature and then filtered. KTp (609 mg, 2.42 mmol) in 10 mL of THF was added to the resulting solution of toluene and the mixture was left to react for 3 h. After this time the solvent was removed in *vacuo* and the residue was extracted with diethyl ether (4 × 15 mL). The combined extracts were evaporated to dryness. The residue was washed with pentane (3× 5 mL) and methanol (5 mL) and vacuum dried. A white solid was obtained. Yield: 651 mg (67%). Anal. Calcd for $C_{18}H_{34}BN_6PRu$: C, 45.29; H, 7.18; N, 17.60. Found: C, 45.01; H, 7.59; N, 17.69. IR (ATR, cm^{-1}): ν(BH) 2464 (m), ν(RuH) 1974 (m), 1964 (m). ^1H NMR (300 MHz, toluene-d_8, 293 K): δ 7.81, 7.51, 5.95 (9H, 3:3:3 integration, all br, Tp), 1.93 (m, 3H, PCH), 1.03 (dd, $J_{H\text{-}P}$ = 12.4, $J_{H\text{-}H}$ = 7.1, 18H, PCHCH_3), −10.66 (d, $J_{H\text{-}P}$ = 18.0, 3H, RuH). ^1H NMR (300 MHz, toluene-d_8, 243 K): δ 7.84 (s, 2H, Tp), 7.59 (s, 2H, Tp), 7.52 (s, 1H, Tp), 7.39 (s, 1H, Tp), 6.00 (s, 2H, Tp), 5.74 (s, 1H, Tp), 1.78 (m, 3H, PCH), 0.98 (dd, $J_{H\text{-}P}$ = 10.6, $J_{H\text{-}H}$ = 6.5, 18H, PCHCH_3), −10.39 (3H, RuH). $T_{1(min)}$ (ms, CD_2Cl_2, 300 MHz, −11.10, 208 K): 26 (± 1). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, 293 K): δ 80.9 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, toluene-d_8, 293 K): δ 144.5, 133.9, 104.5 (all br, Tp), 23.2 (d, $J_{C\text{-}P}$ = 20, PCH), 19.7 (s, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, toluene-d_8, 243 K): δ 145.3 (s, 1C, Tp), 144.3 (s, 2C, Tp), 134.5 (s, 2C, Tp), 133.2 (s, 1C, Tp), 105.0 (s, 3C, Tp), 22.6 (d, $J_{C\text{-}P}$ = 20, PCH), 19.7 (s, PCHCH_3).

Preparation of Ru(CH_2CH_2-C_5H_4N)Tp(P^iPr_3) (3). A colorless solution of **2** (250 mg, 0.52 mmol) in 10 mL of toluene was treated with 1.2 equiv of 2-vinylpyridine (68 μL, 0.63 mmol) and heated at 333

K for 3 h in a Schlenk flask equipped with a teflon stopcock. The resulting orange solution was filtered through Celite and evaporated to dryness. The residue was washed with pentane (2 × 5 mL) at 195 K to afford an orange solid which was dried in *vacuo*. Yield: 168 mg (55 %). Anal. Calcd for $C_{25}H_{39}BN_7PRu$: C, 51.72; H, 6.77; N, 16.89. Found: C, 51.26; H, 6.98; N, 17.19. IR (ATR, cm^{-1}): ν(BH) 2467 (m). HRMS (electrospray, *m/z*): calcd for $C_{25}H_{39}BN_7PRu$ $[M]^+$ 581.2146, found 581.2123. ^1H NMR plus HMBC and HSQC (300 MHz, C_6D_6, 298 K): δ 8.64 (dd, J_{H-H} = 5.7, J_{H-H} = 1.1, 1H, H^6 py), 8.08 (m, 2H, Tp), 7.81 (d, 1H, Tp), 7.64 (d, 1H, Tp), 7.47 (d, 1H, Tp), 6.81 (d, J_{H-H} = 7.5, 1H, H^3 py), 6.65 (ddd, J_{H-H} = 7.5, J_{H-H} = 7.5, J_{H-H} = 1.1, 1H, H^4 py), 6.39 (s, br, 1H, Tp), 6.22 (t, 1H, Tp), 6.00 (dd, J_{H-H} = 7.5, J_{H-H} = 5.7, 1H, H^5 py), 5.96 (t, 1H, Tp), 5.81 (s, br, 1H, Tp), 3.51 (m, 2H, C*H*$_2$CH$_2$Ru), 2.46 (m, 5H, CH$_2$C*H*$_2$Ru + PCH), 1.10 (dd, J_{H-P} = 10.5, J_{H-H} = 7.2, 9H, PCHC*H*$_3$), 0.87 (dd, J_{H-P} = 11.7, J_{H-H} = 7.2, 9H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 51.2. $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4, MHz, C_6D_6, 298 K): δ 177.6 (s, C_{ipso} py), 154.1 (s, C^6 py), 147.3, 143.4, 137.5, 136.2, 135.9, 134.1 (all s, Tp), 131.6 (s, C^4 py), 120.4(s, C^5 py), 119.8 (s, C^3 py), 105.8, 105.7, 105.5 (all s, Tp), 45.4 (s, *C*H$_2$CH$_2$Ru), 27.3 (d, J_{C-P} = 14, PCH), 20.8, 20.6 (both s, PCH*C*H$_3$), 13.8 (d, J_{C-P} = 10, CH$_2$*C*H$_2$Ru).

Preparation of Ru(CHCH-C$_5$H$_4$N)Tp(P^{i}Pr$_3$) (4). Method a. An orange solution of **3** (20.0 mg, 0.03 mmol) in C_6D_6 in an NMR tube was heated at 353 K. After 3 h, the ^1H and $^{31}P\{^1H\}$ NMR spectra of the resulting solution revealed the formation of complex **4. Method b.** 2-Vinylpyridine (35 μL, 0.31 mmol) was added to a colorless solution of **2** (100 mg, 0.21 mmol) in 10 mL of toluene and heated under reflux for 3 h. The resulting red solution was filtered through Celite and evaporated to dryness. The residue was washed with pentane (2 × 5 mL) at 195 K to afford an orange solid which was dried *in vacuo*. Yield: 71 mg (58 %). Anal. Calcd for $C_{25}H_{37}BN_7PRu$: C, 51.93; H, 6.45; N, 16.95. Found: C, 51.75; H, 6.53; N, 16.87. IR (ATR, cm^{-1}): ν(BH) 2450 (m). HRMS (electrospray, *m/z*): calcd for $C_{25}H_{37}BN_7PRu$ $[M]^+$ 579.1990, found 579.1988. ^1H NMR plus HMBC and HSQC (300 MHz, C_6D_6, 298 K): δ 11.40 (d, J_{H-H} = 7.8, 1H, CH=C*H*Ru), 8.65 (d, J_{H-H} = 5.7, 1H, H^6 py), 8.27, 8.15, 7.79 (all s, Tp), 7.72 (d, J_{H-H} =

7.8, 1H, C*H*=CH-Ru), 7.68 (s, 1H, Tp), 7.28 (s, 1H, Tp), 7.17 (d, J_{H-H} = 8.1, 1H, -NC_5H_4), 6.93 (dd, J_{H-H} = J_{H-H} = 8.1, 1H, H^4 py), 6.53 (s, 1H, Tp), 6.23 (s, 1H, Tp), 6.14 (dd, J_{H-H} = 8.1, J_{H-H} = 5.7, 1H, H^5 py), 6.05 (s, br, 1H, Tp), 5.57 (s, br, 1H, Tp), 2.22 (m, 3H, PCH), 0.98 (dd, J_{H-P} = 11.3, J_{H-H} = 7.1, 9H, PCHCH_3), 0.93 (dd, J_{H-P} = 12.0, J_{H-H} = 7.2, 9H, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 46.4. $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4, MHz, C_6D_6, 298 K): δ 226.3 (d, J_{C-P} = 13, CH=*C*HRu), 173.0 (s, C_{ipso} py), 153.4 (s, C^6 py), 146.5, 143.8, 137.8, 136.3, 135.9, 134.0 (all s, Tp), 133.3 (s, C^4 py), 130.3 (s, *C*H=CHRu), 118.3 (s, C^3 py), 115.3 (s, C^5 py), 106.0, 105.9, 105.0 (all s, Tp), 25.6 (d, J_{C-P} = 17, PCH), 20.1, 19.8 (both s, PCH*C*H_3).

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Supporting Information Available: Crystal structure determination and CIF file giving crystal data for compounds **2** and **4** as well as computational details for **4M**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table of Contents

Aromatization of a Dihydro-3-ruthenaindolizine Complex

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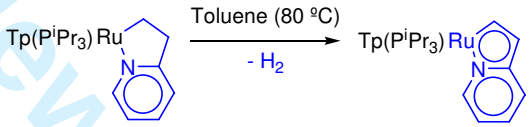

The hydride-dihydrogen complex RuHTp(η^2-H_2)(P^iPr_3) losses a hydrogen molecule and inserts 2-vinylpyridine to give a 1,2-dihydro-3-ruthenaindolizine intermediate, which easily aromatizes in toluene at 80 ºC to afford the 3-ruthenaindolizine complex Ru(CHCH-C_5H_4N)Tp(P^iPr_3) in the absence of any hydrogen acceptor.