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Beyond Click-Chemistry: Transformation of Azides with Cyclopentadienyl Ruthenium Complexes

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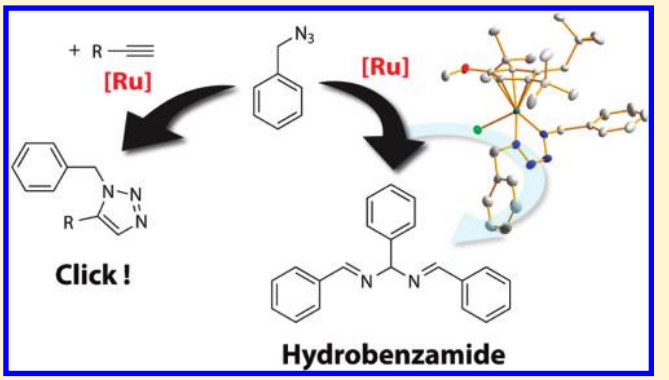
Supporting Information

ABSTRACT: The cyclopentadienyl Ru complexes Cp*RuCl(cod) (cod = 1,5-cyclooctadiene), Cp*RuCl$(PPh_3)_2$, and $[Cp^{\wedge}RuCl_2]_2$ ($Cp^{\wedge}$ = η^5-1-methoxy-2,4-di-*tert*-butyl-3-neopentylcyclopentadienyl) are able to catalyze the decomposition of benzyl azides to give 1,3,5-triphenyl-2,4-diazapenta-1,4-diene ("hydrobenzamide"), benzyl-benzylideneamine, and benzonitrile. Reactions with the catalyst precursor $[Cp^{\wedge}RuCl_2]_2$ are particularly fast and give hydrobenzamide with high selectivity. A similar coupling reaction is observed for other benzylic azides but not for (2-azidoethyl)benzene and ethyl-4-azidobutanoate. If the reactions are performed in the presence of water, benzylic azides are converted into aldehydes. Mononuclear tetrazene complexes are formed in stoichiometric reactions of $[Cp^{\wedge}RuCl_2]_2$ with benzyl azide and (2-azidoethyl)benzene.



INTRODUCTION

Ruthenium-catalyzed azide−alkyne cycloaddition (RuAAC) reactions were reported in 2005 by Jia and Fokin.[1] This catalytic process allows the synthesis of 1,5-disubstituted triazoles from azides and alkynes. Due to its unique regioselectivity, RuAAC complements the very popular copper-catalyzed azide−alkyne cycloaddition (CuAAC), which gives rise to 1,4-disubstituted triazoles.[2] Meanwhile, the scope and limitations of RuAAC reactions have been investigated in some detail,[3] variants have been developed,[4] and numerous applications have been reported.[5] The most popular catalyst precursors for RuAAC are Cp*RuCl(cod) (Cp* = pentamethylcyclopentadienyl; cod = 1,5-cyclooctadiene) and Cp*RuCl$(PPh_3)_2$. These complexes are a source of the [Cp*RuCl] fragment, which is believed to be the catalytically active species.[3b]

It has been reported that Cp*RuCl(cod) reacts with two equivalents of (2-azidoethyl)benzene to give a highly stable and catalytically inactive tetraazadiene complex.[3b] This finding led to the recommendation that the "azide should not be added to the catalyst before the alkyne".[3b] We observed that cyclopentadienyl Ru complexes are also able to convert azides in a *catalytic* fashion. Details about this new catalytic transformation are reported below.

RESULTS AND DISCUSSION

During investigations in the context of RuAAC we observed that Cp*RuCl(cod) led to a conversion of benzyl azide, even if no alkyne was present. The process was clearly catalytic with turnover numbers (TONs) of more than 50 after 12 h for reactions performed in benzene at 50 °C. Intrigued by this process, we analyzed the reaction products by NMR and GC-MS. It was found that a mixture of three products was formed: 1,3,5-triphenyl-2,4-diazapenta-1,4-diene ("hydrobenzamide", **A**), benzyl-benzylideneamine (**B**), and benzonitrile (**C**) (Scheme 1).

Next, we examined whether other Ru complexes are able to catalyze this transformation as well. The Ru^{II} complex Cp*RuCl$(PPh_3)_2$ gave similar results to those observed for Cp*RuCl(cod): after 14 h, the majority of benzyl azide had reacted to give a mixture of **A**, **B**, and **C** with no special selectivity (Table 1, entries 1 and 2). The Ru^{III} complex $[Cp^*RuCl_2]_2$, on the other hand, gave only a low conversion (entry 3). We then investigated the catalytic activity of $[Cp^{\wedge}RuCl_2]_2$ ($Cp^{\wedge}$ = η^5-1-methoxy-2,4-di-*tert*-butyl-3-neopentylcyclopentadienyl). This complex is easily accessible by reaction of $RuCl_3(solv)_n$ with *tert*-butyl acetylene.[6] Its $Cp^{\wedge}$ ("Cp-roof") ligand is sterically more demanding than the classic Cp* ligand, which imparts a unique reactivity to $Cp^{\wedge}$Ru complexes.[7] When subjected to the standard reaction conditions (2 mol % Ru, benzene, 50 °C), we observed a dramatically enhanced activity and selectivity: complete conversion of benzyl azide was observed after only 2 h, with the main product being 1,3,5-triphenyl-2,4-diazapenta-1,4-diene (**A**) (entry 4). Commonly used Ru complexes without a cyclopentadienyl ligand or the Cu^{I} complex CuBr(IMes) (active in CuAAC)[8] gave no measurable conversion of benzyl azide (entries 5−9).

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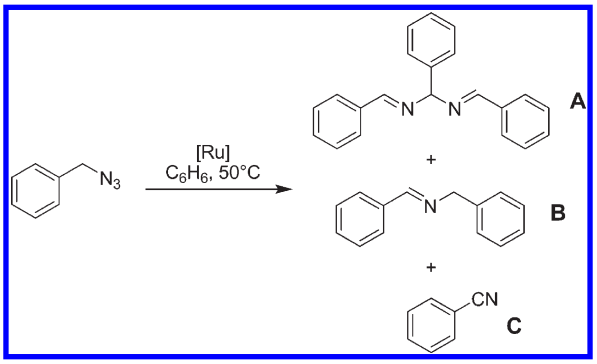
A transition metal-catalyzed conversion of benzyl azide into 1,3,5-triphenyl-2,4-diazapenta-1,4-diene (**A**) is—to the best of our knowledge—unprecedented. A noncatalytic version of this reaction is known, but the conditions are very harsh (flash vacuum pyrolysis at >400 °C).[9] 1,3,5-Triaryl-2,4-diazapenta-1,4-dienes are interesting synthetic intermediates because they can be converted into 1,3-diazabuta-1,3-dienes,[10] α-aminophosphonates,[11] dibenzylamines,[12] or amarines.[13] The latter are valuable precursors for the synthesis of 1,2-diamino-1,2-diarylethanes[13,14] and imidazoles.[9] Traditionally, 1,3,5-triphenyl-2,4-diazapenta-1,4-diene (**A**) is prepared by reaction of benzaldehyde with liquid ammonia.[10b,15] Our Ru-catalyzed method starting from benzyl azide thus represents an interesting alternative.

Scheme 1. Ru-Catalyzed Conversion of Benzyl Azide



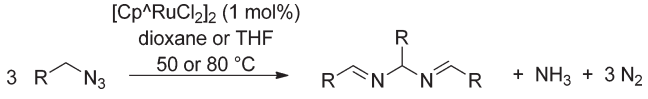
The scope and the limitations of the new reaction were examined in a series of experiments. The $[Cp^{\wedge}RuCl_2]_2$-catalyzed conversion of benzyl azide into hydrobenzamide **A** proceeds well in aprotic organic solvents such as tetrahydrofuran, dioxane, diethyl ether, acetonitrile, hexane, benzene, and toluene. Likely side products are dinitrogen and ammonia.[9] The latter was detected indirectly with a pH paper. In methanol, the reaction was less selective and a significant amount of benzyl-benzylideneamine (**B**) was observed by NMR spectroscopy. It is worth noting that benzyl-benzylideneamine can be synthesized in good yields from benzyl azide with the catalyst tetrathiomolybdenate.[16]

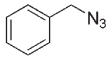
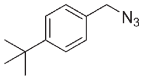
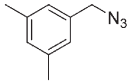
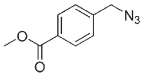
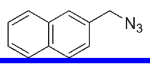
Table 1. Catalytic Activity of Different Ru and Cu Complexes for the Conversion of Benzyl Azide[a]

entry	catalyst	time [h]	conv [%]	yield **A** [%]	yield **B** [%]	yield **C** [%]
1	Cp*RuCl(cod)	14	78	30	32	10
2	$Cp^*RuCl(PPh_3)_2$	14	86	24	39	11
3	$[Cp^*RuCl_2]_2$	14	16	3	7	4
4	$[Cp^{\wedge}RuCl_2]_2$	2	100	89	3	3
5	$RuHCl(PPh_3)_3(CO)$	12	0	–	–	–
6	$(p\text{-cymene})RuCl_2(PPh_3)$	12	0	–	–	–
7	$[(p\text{-cymene})RuCl_2]_2$	12	0	–	–	–
8	$RuCl_2(PPh_3)_3$	12	0	–	–	–
9	CuBr(IMes)	12	0	–	–	–

[a] Reaction conditions: $[BnN_3]$ = 200 mM, [Ru] or [Cu] = 4.0 mM (2 mol %), C_6H_6, 50 °C. Mesitylene was used as internal standard. Yields of **A** and **B** were calculated from the NMR spectra. Yields of **C** were determined by GC-MS.

Table 2. Ru-Catalyzed Synthesis of 1,3,5-Triaryl-2,4-diazapenta-1,4-dienes[a]



entry	substrate	solvent	T [°C]	time[h]	yields (isol.) [%]	yields (NMR) [%]
1		THF	50	1	70	85
2		Dioxane	80	2	61	79
3		Dioxane	80	3	62	77
4		THF	50	4	62	80
5		Dioxane	80	2	66	77

[a] Reaction conditions: [substrate] = 200 mM; [Ru] = 4.0 mM (2 mol %). NMR yields were determined using mesitylene as internal standard.

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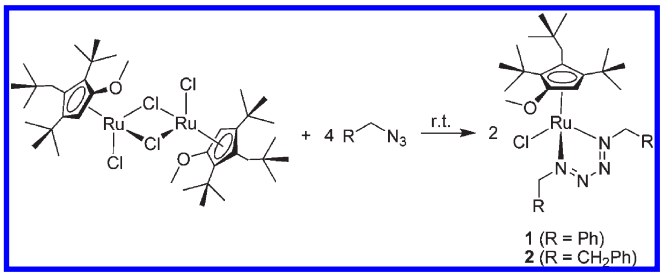
Scheme 2. Synthesis of the Tetrazene Complexes 1 and 2



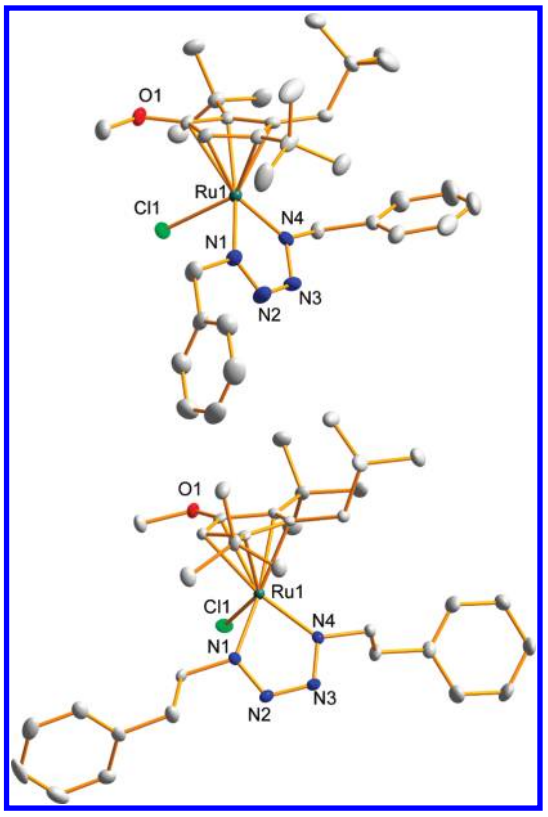


Figure 1. Graphical representation of the molecular structure of complexes **1** (top) and **2** (bottom) in the crystal. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are not shown for clarity.

The substrate scope was investigated using different azides. Preliminary tests had shown that the reactions are slightly faster in ethers. Therefore, THF and dioxane were used as solvents. All benzylic azides that we have tested were converted with good selectivity into the corresponding 1,3,5-triaryl-2,4-diazapenta-1,4-dienes using 1 mol % of complex $[Cp^{\wedge}RuCl_2]_2$ (2 mol % Ru) as catalyst precursor (Table 2). The crude yields range between 77% and 85%; the isolated yields are somewhat lower due to loss of product during purification (selective precipitation). The reactions were performed at slightly elevated temperature (50 or 80 °C), but they also proceed at room temperature. Benzyl azide, for example, was completely converted within 6 h at room temperature in THF (2 mol % Ru). We have also examined the catalytic activity of $Cp^{\wedge}RuCl(nbd)$ (nbd = norbornadiene),[6a] which can be regarded as a "Cp-roof" analogue of the commonly used Cp*RuCl(cod).

Table 3. Selected Bond Distances (Å) for Complexes 1 and 2

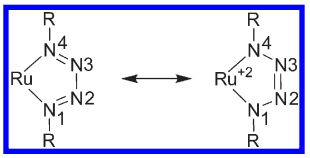
	1	2
Ru1−N1	1.998(4)	1.993(3)
Ru1−N4	1.953(4)	1.947(3)
Ru1−Cl1	2.3852(12)	2.3892(9)
N1−N2	1.304(6)	1.313(4)
N2−N3	1.314(6)	1.325(4)
N3−N4	1.328(5)	1.338(4)

1,3,5-Triphenyl-2,4-diazapenta-1,4-diene was formed from benzyl azide in a crude yield of 97% after 9 h using 2 mol % $Cp^{\wedge}RuCl(nbd)$ (THF, 50 °C). The yield was significantly lower when the reaction was carried out in dioxane at 80 °C. These results point to a possible advantage of the Ru^{II} complex $Cp^{\wedge}RuCl(nbd)$ compared to the Ru^{III} complex $[Cp^{\wedge}RuCl_2]_2$. However, it has to be taken into account that the synthesis of the catalyst precursor $Cp^{\wedge}RuCl(nbd)$ is more complicated. Therefore, reactions with $[Cp^{\wedge}RuCl_2]_2$ seem more appealing from a synthetic point of view.

We have also attempted reactions with (2-azidoethyl)benzene and ethyl-4-azidobutanoate as substrates. Very low conversions (<5%) were observed after 24 h, indicating that the catalytic conversion is limited to benzyl azides.

In order to obtain information about possible intermediates, stoichiometric reactions between $[Cp^{\wedge}RuCl_2]_2$ and benzyl azide or (2-azidoethyl)benzene were carried out (Scheme 2). In both cases, mononuclear Ru^{II} complexes with tetrazene chelate ligands were obtained (**1** and **2**). Plausible reducing agents for these transformations are the azides. Both complexes are green, air-stable compounds. Their structures were evidenced by NMR spectroscopy, elemental analyses, and single-crystal X-ray analyses (Figure 1).

Overall, the structures of **1** and **2** are similar. Both compounds are mononuclear half-sandwich complexes with a $Cp^{\wedge}$ ligand, a chloro ligand, and a tetrazene ligand. The bond lengths of the tetrazene ligand are of special interest. When coordinated to Ru, tetrazene ligands can exist as neutral tetraazadienes or as dianionic ligands.[17] An example of the former is found for the complex $RuCl_2(PMe_3)_2[(mes)NNNN(mes)]$ (mes = mesityl), which features short N1−N2 and N3−N4 bonds (1.307(4) and 1.313(4) Å) and a longer N2−N3 bond (1.338(4) Å).[18] The tetrazene ligand in (*p*-cymene)Ru[(2,4,6-*t*-$Bu_3C_6H_2$)NNNN(mes)], on the other hand, should be described as a dianionic ligand with longer N1−N2 and N3−N4 bonds (1.365(4) and 1.358(3) Å) and a short N2−N3 bond (1.288(4) Å).[19]



For complexes **1** and **2**, the situation is different: one can observe an increase in the bond lengths from N1−N2 (1.304(6) and 1.313(4) Å) to N2−N3 (1.314(6) and 1.325(4) Å) and finally N3−N4 (1.328(5) and 1.338(4) Å) (Table 3). It is conceivable that this distortion is induced by the likewise highly asymmetric $Cp^{\wedge}$ ligand.

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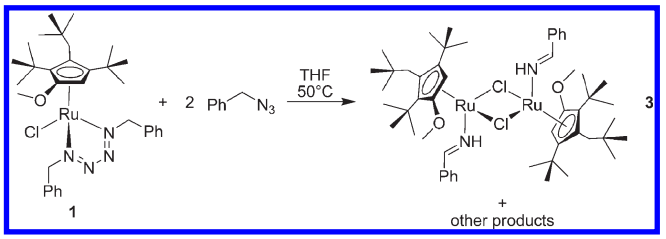
Scheme 3. Reaction of 1 with Benzyl Azide



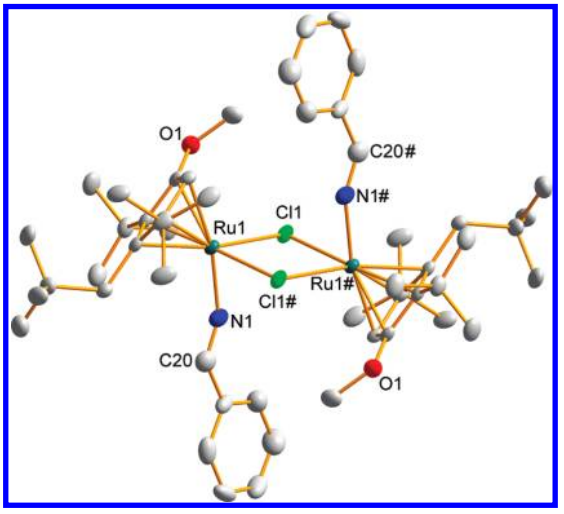


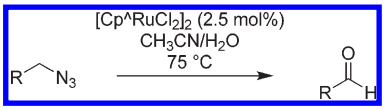
Figure 2. Graphical representation of the molecular structure of complex **3** in the crystal. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru1−N1 2.106(3), N1−C20 1.242(4); C20−N1−Ru1 144.5(3), N1−Ru1−Cl1 79.78(8), N1−Ru1−Cl1# 82.04(7).

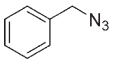
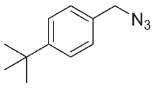
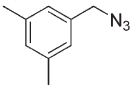
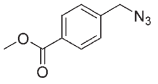
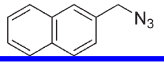
Tetrazene complexes are likely intermediates during the transformation of the catalyst precursor $[Cp^{\wedge}RuCl_2]_2$ into the catalytically active species. This assumption is supported by the fact that the color of the reaction mixture changes from brown to green after addition of the azide. However, the green color does not persist and quickly changes to red. We have therefore examined the reaction of complex **1** with additional benzyl azide (Scheme 3).

As observed for the catalytic reaction, the color of the reaction mixture changed from green to red. An NMR spectroscopic investigation of the mixture indicated the formation of several complexes. Attempts to separate one of these products on a preparative scale failed. However, we were able to isolate small amounts of crystals from the mixture.[20] A crystallographic analysis revealed the formation of the dinuclear imine complex **3** (Figure 2). It is interesting to note that addition of (2-azidoethyl)benzene to a solution of complex **2** did not result in a reaction (dioxane, 80 °C). This finding is in line with the inability of $[Cp^{\wedge}RuCl_2]_2$ to catalyze the conversion of nonbenzylic azides.

The metal-induced transformation of benzyl azide into a metal-imine complex has already been observed in a few cases.[21] It is assumed that these complexes are formed via benzyl azide complexes, which liberate dinitrogen to give nitrene complexes. The latter tautomerize to give the imine complexes.[21a] A similar reaction pathway may be operational in our case, but a direct involvement of the tetrazene ligand cannot be excluded.

Table 4. Ru-Catalyzed Conversion of Benzylic Azides into Aldehydes[a]



entry	substrate	time [h]	yields (GC-MS) [%]
1		8	79
2		7	86
3		5	75
4		5	73
5		7	74

[a] Reaction conditions: [azide] = 100 mM; [Ru] = 5.0 mM (5 mol %), $[H_2O]$ = 4.0 M. The yields were determined by GC-MS using mesitylene as internal standard.

The isolation of complex **3** is evidence that the $Cp^{\wedge}Ru$ fragment is able to mediate the transformation of benzyl azide into phenylmethanimine. Phenylmethanimine is a direct precursor for hydrobenzamide **A**, a reaction that takes place even without catalyst.[10b] A key role of the catalyst therefore seems to be the azide to imine conversion. However, further studies would be needed for a more detailed proposal about the catalytic cycle.

The proposition of arylmethanimines as key intermediates suggested that it might be possible to convert benzyl azides into benzaldehydes if the reaction is performed in the presence of water. This turned out to be the case. Best results were obtained when the catalyst precursor $[Cp^{\wedge}RuCl_2]_2$ was first dissolved in a mixture of water and acetonitrile (1:1) under heating. A yellow catalyst stock solution was obtained, which was used for subsequent reactions. Using 2.5 mol % $[Cp^{\wedge}RuCl_2]_2$ (5 mol % Ru) we were able to convert different benzylic azides into the corresponding aldehydes with yields between 73% and 86% (Table 4). A similar reaction has been described for the Mo^{IV} complex $MoO_2(Et_2NCS_2)_2$, but more forcing conditions are required.[22] The hydrolytic decomposition of benzyl azide was also tested with $[Cp^*RuCl_2]_2$ as catalyst precursor, but only a low conversion of the substrate was observed after 24 h. This finding corroborates the importance of the sterically very demanding $Cp^{\wedge}$ ligand for these transformations.

The formation of aldehydes can be explained by hydrolysis of the intermediate imines. Alternatively, one could imagine hydrolysis of 1,3,5-triaryl-2,4-diazapenta-1,4-dienes, which are formed in a Ru-catalyzed process. Indeed, the hydrolysis of hydrobenzamide derivatives has been known for a long time.[23] To test whether hydrolysis of hydrobenzamide is occurring under our reaction conditions, a solution of hydrobenzamide was stirred in a mixture of water and acetonitrile (1:20) at 75 °C. After 4 h, 80%

of the initial compound was hydrolyzed. These experiments suggest that imine and hydrobenzamide hydrolysis are both plausible reaction pathways.

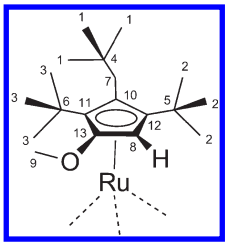
CONCLUSION

We have shown that cyclopentadienyl Ru complexes are able to catalyze the decomposition of benzylic azides. The reaction is particularly fast and selective if $[Cp^{\wedge}RuCl_2]_2$, a Ru complex with a sterically very demanding cyclopentadienyl ligand, is used as catalyst precursor. The decomposition of benzylic azides should be considered as a potential side reaction in RuAAC, in particular if alkynes with a low intrinsic reactivity are employed. From a synthetic point of view it is interesting that reactions with $[Cp^{\wedge}RuCl_2]_2$ provide 1,3,5-triaryl-2,4-diazapenta-1,4-dienes with high selectivity. To the best of our knowledge, this is the first report of a transition metal-catalyzed reaction of this kind. The process may be of interest for synthetic organic chemistry, because it offers an alternative, base-free route to an important class of compounds.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed inside a glovebox under an atmosphere of dinitrogen. Thoroughly dried and deoxygenated solvents were used. The complexes $[Cp^{\wedge}RuCl_2]_2$,[6] CuBr(IMes),[8] $RuHCl(PPh_3)_3CO$,[24] $Cp^*RuCl(PPh_3)_2$,[3b] $[Cp^*RuCl_2]_2$,[25] Cp*RuCl(cod),[26] $[(p\text{-cymene})RuCl_2]_2$,[27] $(p\text{-cymene})RuCl_2(PPh_3)$,[27] and $RuCl_2(PPh_3)_3$[28] were prepared according to literature procedures. Benzyl azide was purchased from Alfa Aesar. The other azides were synthesized in analogy to a reported procedure from the corresponding benzylic bromides.[29] 2-(Bromomethyl)naphthalene, methyl 4-(bromomethyl)benzoate, and 4-(*tert*-butyl)benzyl bromide were purchased from Aldrich, and 3,5-dimethylbenzyl bromide was from Acros. ^1H and ^{13}C spectra were recorded on a Bruker Advance DPX 400 spectrometer using the residual protonated solvents (^1H, ^{13}C) as internal standards. All spectra were recorded at room temperature. Column chromatography was performed using silica gel 60 (230−400 mesh, 0.04−0.063 nm) from Fluka. The GC measurements were performed with a GC/MS using a Varian 3800 spectrometer coupled to a Varian 2200 mass spectrometer. Elemental analyses were performed with an EA 1110 CHN instrument.

Synthesis and Characterization of Complexes 1 and 2.



Cp^RuCl(PhCH$_2$NNNNCH$_2$Ph) (**1**). Benzyl azide (54 mg, 0.38 mmol) was added to a solution of $[Cp^{\wedge}RuCl_2]_2$ (86 mg, 0.19 mmol) in toluene (3 mL). The solution was stirred at room temperature for 6 h. After removal of the solvent, the residue was purified by flash chromatography on silica gel, using CH_2Cl_2 as eluant. The product was isolated as a green powder (65 mg, 52%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 3H, *t*-Bu), 1.13 (s, 3H, *t*-Bu), 1.45 (s, 3H, *t*-Bu), 1.95 (d, br, $^2J_{HH}$ = 15 Hz, 1H, $CH_2-Cp^{\wedge}$), 3.11 (d, $^2J_{HH}$ = 16 Hz, 1H, $CH_2-Cp^{\wedge}$), 3.81 (s, 3H, OCH_3), 4.81 (s, 1H, CH), 5.51 (d, $^2J_{HH}$ = 16 Hz, 1H, N−CH_2), 5.74 (d, $^2J_{HH}$ = 9 Hz, 1H, N−CH_2), 5.78 (d, $^2J_{HH}$ = 10 Hz, 1H, N−CH_2), 6.09 (d, $^2J_{HH}$ = 14 Hz, 1H, N−CH_2), 7.25−7.36 (m, 8H, Ar), 7.52−7.54 (m, 2H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$): δ 32.04, 32.21, 32.21 (C1, C2, C3), 33.90, 34.73 (C4, C5), 37.60 (C7), 57.77 (C9), 62.84 (C8), 71.78 (N−CH_2), 94.27, 102.79, 107.37 (C10, C11, C12), 127.27, 127.49, 128.15, 128.23, 128.34, 130.06, 136.30, 137.29 (C−Ar), C6 and C13 not observed. Anal. Calcd (%) for $RuClN_4OC_{33}H_{47}$: C, 60.76; H, 7.26; N, 8.58. Found: C, 60.74; H, 7.36; N, 8.54. Single crystals were obtained from a solution of cold toluene/pentane.

Cp^RuCl(PhCH$_2$CH$_2$NNNNCH$_2$CH$_2$Ph) (**2**). (2-Azidoethyl)benzene (60 mg, 0.40 mmol) was added to a solution of $[Cp^{\wedge}RuCl_2]_2$ (80 mg, 0.17 mmol) in THF (3 mL). The solution was stirred at room temperature for 6 h. After removal of the solvent, the residue was purified by flash chromatography on silica gel, using CH_2Cl_2 as eluant. The product was isolated as a green powder (87 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 3H, *t*-Bu), 1.16 (s, 3H, *t*-Bu), 1.50 (s, 3H, *t*-Bu), 1.88 (m, 1H, $CH_2-Cp^{\wedge}$), 3.11 (d, $^2J_{HH}$ = 15 Hz, 1H, $CH_2-Cp^{\wedge}$), 3.39−3.52 (m, 2H, Ph−CH_2), 3.57−3.64 (m, 1H, Ph−CH_2), 3.73 (s, 3H, OCH_3), 3.77−3.88 (m, 1H, Ph−CH_2), 4.62−4.69 (m, 2H, N−CH_2, H−$Cp^{\wedge}$), 4.76−4.86 (m, 2H, N−CH_2), 5.05 (m, br, 1H, N−CH_2), 7.25−7.29 (m, 2H, Ar), 7.33−7−39 (m, 8H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$): δ 31.87, 32.28, 32.35 (C1, C2, C3), 34.00, 34.79 (C4, C5), 35.63 (Ph−CH_2), 36.86 (Ph−CH_2) 37.01 (C7), 57.70 (C9), 63.08 (C8) 69.95 (N−CH_2), 70.78 (N−CH_2), 93.70, 102.09, 106.29 (C10, C11, C12), 126.37, 126.41, 128.61, 129.06, 129.13, 139.06, 139.77 (C−Ar), C6 and C13 not observed. Anal. Calcd (%) for $RuClN_4OC_{35}H_{51}$: C, 61.78; H, 7.55; N 8.23. Found: C, 62.03; H, 7.44; N, 8.01. Single crystals were obtained from a MeOH/CH_2Cl_2 solution by slow evaporation.

Crystallographic Analyses. The data collections for the three crystal structures (**1**, **2**, and **3**) were measured at low temperature using Mo Kα radiation. An Oxford Diffraction Sapphire/KM4 CCD was employed for **1**, while the remaining samples were measured on a Bruker APEX II CCD. Both diffractometers have a kappa geometry goniometer. Data reduction were carried out by Crysalis PRO[30] (**1**) and EvalCCD[31] (**2**, **3**) and then corrected for absorption.[32] The solutions and refinements were performed by SHELX.[33] The structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. Twinning problems were discovered in the case of **1**. The twinning by reticular merohedry was analyzed by the TWINROTMAT routine of PLATON.[34] A HKLF5 file was then generated and used in the refinement of the structure, obtaining final BASF parameters of 0.0032(7), 0.029(7), 0.097(10), and 0.0034(8).

General Procedure for the Synthesis of 1,3,5-Triaryl-2,4-diazapenta-1,4-dienes. The catalyst precursor $[Cp^{\wedge}RuCl_2]_2$ ($[Ru]_{final}$ = 2 mol %) was added to a solution of the respective benzylic azide in dioxane or THF ($[azide]_{final}$ = 200 mM). The mixture was stirred at the given temperature (Table 2). After the given time (Table 2), the solvent was removed. The product was isolated as described below.

1,3,5-Triphenyl-2,4-diazapenta-1,4-diene. The reaction was performed with 193 mg (1.36 mmol) of benzyl azide in THF. After removal of the solvent, the residue was dissolved in EtOH (6 mL), and the resulting solution was dropped into water (20 mL). After a few minutes of stirring, a white suspension formed. The product was isolated by filtration, washed with water (10 mL), and dried *in vacuo* to give a white solid (95 mg, 70%). The spectroscopic data for the product correspond to those previously described.[9] ^1H NMR (400 MHz, $CDCl_3$): δ 6.01 (s, 1H, CH), 7.29−7.33 (m, 1H, Ar), 7.37−7.47 (m, 8H, Ar), 7.53−7.55 (m, 2H, Ar), 7.87−7.90 (m, 4H, Ar), 8.61 (s, 2H, NCH). ^{13}C NMR (400 MHz, $CDCl_3$): δ 92.69 (CH), 127.28, 127.86, 128.57, 131.07, 136.03, 141.76 (C−Ar), 160.72 (NCH). Anal. Calcd (%) for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.87; H, 5.97; N, 9.36.

1,3,5-Tri(4-tert-butylphenyl)-2,4-diazapenta-1,4-diene. The reaction was performed with 145 mg (766 μmol) of 4-*tert*-butylbenzyl azide in dioxane. After removal of the solvent, the residue was dissolved in EtOH (9 mL). Brine (2 mL) was then added dropwise to precipitate the product followed by H_2O (1 mL). The product was isolated by filtration, washed with water (12 mL), and dried *in vacuo* to give an off-white solid (72 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9 H, *t*-Bu), 1.35 (s, 18H, *t*-Bu), 5.97 (s, 1H, CH), 7.37−7.39 (m, 2H, Ar), 7.43−7.47 (m, 6H, Ar), 7.80−7.82 (m, 4H, Ar), 8.57 (s, 2H, NCH). ^{13}C NMR (400 MHz, $CDCl_3$): δ 31.22, 31.35, 34.49, 34.93 (*t*-Bu), 92.61 (CH), 125.39, 125.49, 126.81, 128.49, 133.50, 139.10, 150.48, 154.37 (C−Ar), 160.20 (NCH). Anal. Calcd (%) for $C_{33}H_{42}N_2$: C 84.93, H 9.07, N 6.00. Found: C 84.64, H 9.37, N 5.96.

1,3,5-Tri(3,5-dimethylphenyl)-2,4-diazapenta-1,4-diene. The reaction was performed with 188 mg (980 μmol) of 3,5-dimethylbenzyl azide in dioxane. After removal of the solvent, the residue was suspended in EtOH (9 mL). Brine (3 mL) was then added dropwise to precipitate the product followed by H_2O (4 mL). The product was isolated by filtration, washed with water (12 mL) and *i*-PrOH (6 mL), and dried *in vacuo* to give a white solid (77 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 6H, CH_3), 2.37 (s, 12H, CH_3), 5.88 (s, 1H, CH), 6.95 (s, 1H, Ar), 7.10 (s, 2H, Ar), 7.13 (s, 2H, Ar), 7.51 (s, 4H, Ar), 8.52 (s, 2H, NCH). ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.15, 21.41 (CH_3), 93.17 (CH), 125.03, 126.56, 129.47, 132.69, 136.06, 138.03, 138.11, 141.70 (C−Ar), 160.82 (NCH). Anal. Calcd (%) for $C_{27}H_{30}N_2$: C, 84.77; H, 7.90; N, 7.32. Found: C, 84.64; H, 7.94; N, 7.42.

1,3,5-Tri(4-methylbenzoate)-2,4-diazapenta-1,4-diene. The reaction was performed with 177 mg (922 μmol) of methyl(4-azidomethyl)benzoate in THF. After removal of the solvent, the residue was dissolved in EtOH (9 mL). Brine (5 mL) was then added dropwise to precipitate the product followed by H_2O (15 mL). The product was isolated by filtration, washed with water (9 mL) and *i*-PrOH (4 mL), and dried *in vacuo* to give an off-white solid (90 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H, CH_3), 3.95 (s, 6H, CH_3), 6.09 (s, 1H, CH), 7.61 (d, 2H, *J* = 8.28 Hz, Ar), 7.94 (d, 4H, *J* = 8.40 Hz, Ar), 8.08 (d, 2H, *J* = 8.36 Hz, Ar), 8.12 (d, 4H, *J* = 8.32 Hz, Ar), 8.64 (s, 2H, NCH). ^{13}C NMR (400 MHz, $CDCl_3$): δ 52.15, 52.33 (CH_3), 91.84 (CH), 127.31, 128.62, 129.90, 130.04, 132.44, 139.47, 145.85 (C−Ar), 160.51 (NCH), 166.53, 166.80 (CO). Anal. Calcd (%) for $C_{27}H_{24}N_2O_6$: C, 68.63; H, 5.12; N, 5.93. Found: C, 68.88; H, 5.28; N, 5.99.

1,3,5-Trinaphthyl-2,4-diazapenta-1,4-diene. The reaction was performed with 152 mg (830 μmol) of 2-azidoethylnaphthalene in dioxane. After removal of the solvent, the residue was suspended in EtOH (12 mL). Water (10 mL) was then added dropwise to precipitate the product. The product was isolated by filtration, washed with water (10 mL) and EtOH (6 mL), and dried *in vacuo* to give a light brown solid (82 mg, 66%). The product has already been prepared, but no characterization was reported in the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (s, 1H, CH), 7.48−7.58 (m, 6H, Ar), 7.74−7.76 (m, 1H, Ar), 7.84−7.94 (m, 9H, Ar), 8.07 (s, 1H, Ar), 8.20−8.23 (m, 4H, Ar), 8.86 (s, 2H, NCH). ^{13}C NMR (400 MHz, $CDCl_3$): δ 92.85 (CH), 124.26, 125.50, 126.00, 126.07, 126.15, 126.49, 127.34, 127.69, 127.90, 128.22, 128.44, 128.46, 128.73, 130.87, 133.08, 133.18, 133.46, 133.74, 134.95, 139.27 (C−Ar), 161.09 (NCH). Anal. Calcd (%) for $C_{33}H_{24}N_2$: C, 88.36; H, 5.39; N, 6.25. Found: C, 88.06; H, 5.42; N, 6.49.

General Procedure for the Catalytic Conversion of Azides into Aldehydes. A stock solution of the catalyst was prepared by dissolving $[Cp^{\wedge}RuCl_2]_2$ (20 mg, 45 μmol) in a mixture of acetonitrile (500 μL) and water (500 μL) at 75 °C for 3 h ([Ru] = 45 mM). An aliquot of the catalyst stock solution (100 μL) was added to a solution of the respective benzylic azide in a mixture of acetonitrile and water (0.8 mL, 50:1) (final conc: [azide] = 100 mM; [Ru] = 5 mmol, [H_2O] = 4.0 M). The reaction was stirred at 75 °C. After 5−8 h (Table 4), the yield of the aldehyde was determined by GC-MS using mesitylene as internal standard.

■ ASSOCIATED CONTENT

Supporting Information. X-ray analysis data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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