Template Synthesis of Ruthenium Complexes with Saturated and Benzannulated NH,NH-Stabilized N-Heterocyclic Carbene Ligands

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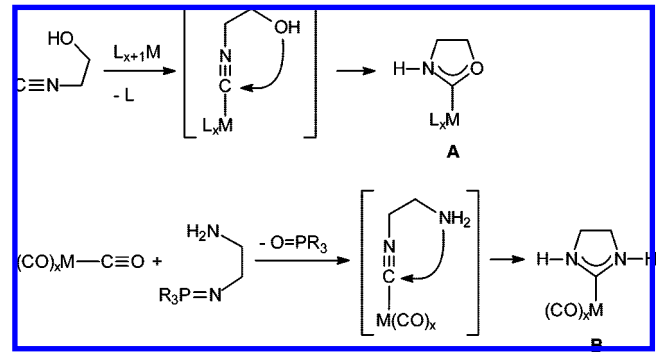
Reaction of $[RuCl_2(p\text{-cymene})]_2$ with 2-azidoethyl isocyanide (**1a**) or 2-azidophenyl isocyanide (**1b**) leads to the isocyanide complexes $[RuCl_2(p\text{-cymene})(\mathbf{1a})]$ [**2a**] and $[RuCl_2(p\text{-cymene})(\mathbf{1b})]$ [**2b**], respectively. Complex [**2a**] reacts with triphenylphosphine to yield the complex with a phosphinimine-substituted isocyanide ligand [**3**]. The attempted hydrolysis of the phosphinimine group in [**3**] with $HCl \cdot Et_2O$ produced the complex with a protonated phosphinimine ligand [**4**]Cl instead of the expected complex with a 2-aminoethyl isocyanide ligand. An alternative method for the reduction of the azido group in [**2a**] and [**2b**] using $FeCl_3$/NaI has been applied leading to complexes with the 2-amino-substituted isocyanide ligands, which undergo intramolecular ring closure to yield the complexes of type $[RuI_2(p\text{-cymene})(NHC)]$, [**5a**] and [**5b**].

Introduction

The majority of N-heterocyclic carbenes and their metal complexes are obtained from cyclic azolium salts.[1] However, the nucleophilic attack at the carbon atom of a coordinated isocyanide[2] constitutes an alternative method to generate metal carbene complexes. Protic nucleophiles HX such as alcohols and primary or secondary amines have been particularly useful in this reaction. This carbene complex synthesis was unintentionally first applied in 1925 when Tschugajeff and Skanawy-Grigorjewa reacted tetrakis(methyl isocyanide) platinum(II) with hydrazine.[3] Only 50 years later were the reaction products recognized as carbene complexes.[4] Some interesting modifications of this reaction have been reported recently.[5]

While the addition of HX to coordinated isocyanides usually leads to the formation of complexes with acyclic carbene ligands, the use of functional isocyanides, which contain both the isocyanide group and the nucleophile in the same molecule, gives access to complexes with heterocyclic carbene ligands through an intramolecular 1,2-addition across the C≡N triple bond. Fehlhammer et al. have introduced readily available and stable 2-hydroxyalkyl isocyanides such as $C{\equiv}NCH_2CH_2OH$, in which the nucleophile and the isocyanide group are already linked before coordination of the ligand to a metal center. If suitably activated by coordination to transition metals in higher oxidation states these ligands spontaneously cyclize to form oxazolidin-2-ylidene complexes **A** (Scheme 1)[6] allowing even the isolation of homoleptic tetra-[7a] and hexacarbene complexes.[7b] An interesting alternative to this cyclization reaction has been proposed by Liu et al. who reacted an amine phosphinimine with a metal carbonyl complex. The phosphinimine reacts with a carbonyl group to give an isocyanide and $R_3P{=}O$. The amine-functionalized isocyanide subsequently cyclizes to yield the complex with an NH,NH-stabilized heterocarbene ligand **B** (Scheme 1).[8] In addition, the metal template controlled coupling of propargyl amine with phenyl

Scheme 1. Template Syntheses of Cyclic Heteroatom-Stabilized NHC Ligands



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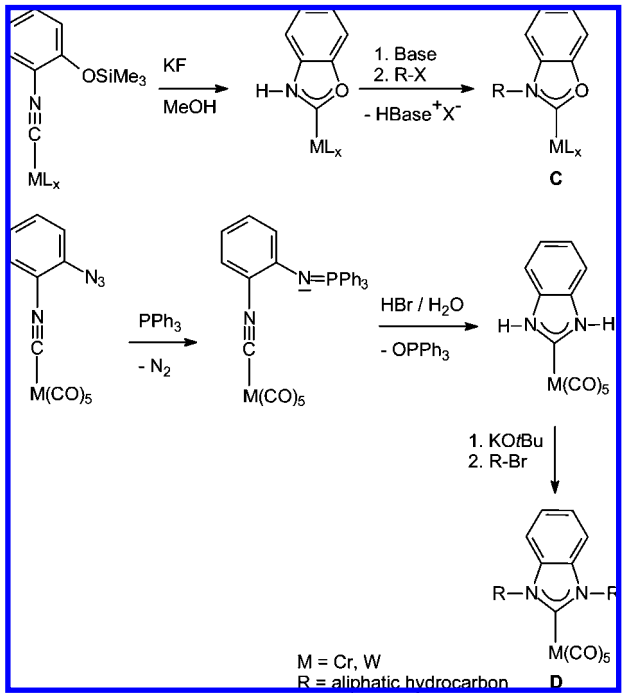
Scheme 2. Template Syntheses of Complexes with Benzannulated NHC Ligands



isocyanide to yield an NH,NPh-stabilized NHC ligand has also been reported.[9]

We have used β-functionalized aryl isocyanides where the electrophilic isocyanide and the nucleophilic substituent are not only linked together but also suitably oriented in one plane for an intramolecular cycloaddition reaction. Contrary to aliphatic 2-hydroxyethyl isocyanide,[6,7] free 2-hydroxyphenyl isocyanide is not stable and cyclizes to give benzoxazole.[10] However, lithiation of benzoxazole and subsequent reaction with Me_3SiCl yields 2-(trimethylsiloxy)phenyl isocyanide,[11] a synthon for 2-hydroxyphenyl isocyanide. Coordination of 2-(trimethylsiloxy)phenyl isocyanide to a transition metal and subsequent hydrolysis of the Me_3Si-O bond has yielded a number of NHC complexes **C** with the benzoxazolin-2-ylidene ligand, which is easily alkylated at the ring nitrogen atom (Scheme 2).[12] The cyclization of 2-functionalized phenyl isocyanides can also be employed for the generation of complexes bearing benzannulated cyclic diaminocarbenes.[13] In this case 2-azidophenyl isocyanide[14] (Scheme 2) or 2-nitrophenyl isocyanide[15] was used as synthon for the unstable 2-aminophenyl isocyanide. Again the ring nitrogen atom can be alkylated leading to complexes of type **D**, which in one case allowed the preparation of a cyclic tetracarbene ligand at a platinum(II) center.[14b] The metal template controlled cyclization of 2-aminophenyl isocyanides followed by *N*,*N*′-alkylation provides an alternative route to complexes with benzannulated N-heterocyclic carbenes, which is particularly useful for the preparation of complexes with NHC ligands, which are difficult to stabilize in the free state.[16]

Ruthenium(II) complexes of type $[RuCl_2(PCy_3)(NHC)(CHPh)]$ (type II Grubbs catalysts) bearing saturated NHC ligands are important catalysts for olefin metathesis. These complexes are normally generated from ruthenium(II) precursors like $[RuCl_2(PR_3)_2(CHPh)]$ (type I Grubbs catalysts) and an NHC ligand.[17] We searched for alternative methods for the synthesis of ruthenium(II) olefin metathesis catalysts employing the cyclization of 2-functionalized isocyanides for the generation of an NHC ligand at the ruthenium center instead of the substitution of a ligand at ruthenium(II) for a stable NHC. Here we describe the addition and intramolecular cyclization of 2-azidoethyl isocyanide **1a** and 2-azidophenyl isocyanide **1b** at Ru^{II} templates.

Results and Discussion

We have previously described the cyclization of 2-azidophenyl isocyanide **1b** at different template metals (Scheme 2).[14] Recently we succeeded in the preparation of 2-azidoethyl isocyanide **1a**, which after coordination to tungsten(0)[18] or rhenium(I)[19] can be intramolecularly cyclized to yield complexes with an NH,NH-stabilized saturated NHC ligand. The preparation of **1a**, for example, by formylation of 2-azidoethyl amine and subsequent dehydration with diphosgene[18] proceeds with low yield (2 steps, 16%), and the workup is tedious. Alternatively, both **1a** and **1b** can be prepared in high yields (47% and 57%) from 2-azidoethylamine or 2-azidoaniline, respectively, using $CHCl_3$/NaOH under standard phase transfer catalysis (PTC) conditions.

Reaction of the dinuclear complex $[RuCl_2(p\text{-cymene})]_2$ with a slight excess of **1a** gives the monomeric isocyanide complex $[RuCl_2(p\text{-cymene})(\mathbf{1a})]$ [**2a**] (complexes are written in brackets throughout the manuscript) in nearly quantitative yield (Scheme 3). The resonance for the isocyanide carbon atom was observed in the $^{13}C\{^1H\}$ NMR spectrum at $\delta = 142.4$ ppm. This resonance lacks the typical $^1J_{C,N}$ coupling found for the free ligand **1a** and related aliphatic isocyanides.[2a,20] In contrast to

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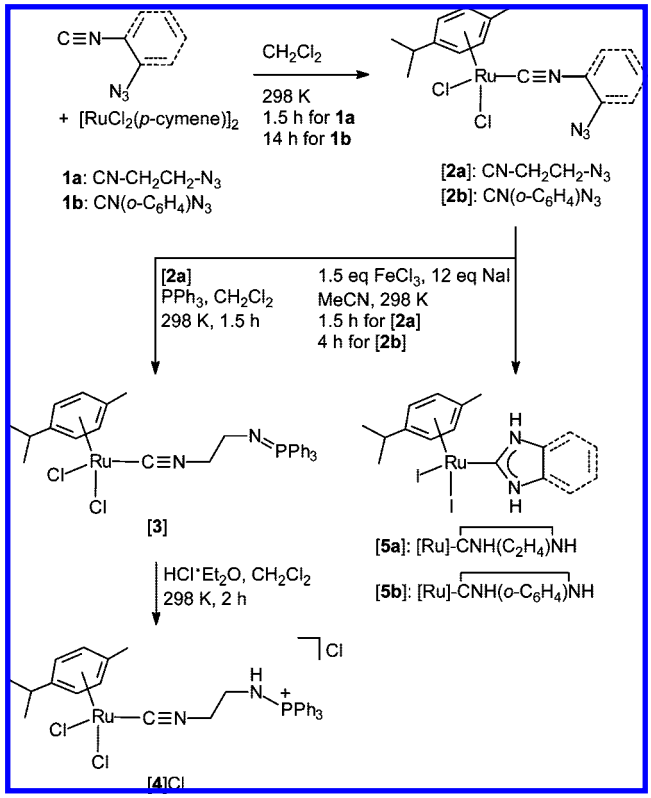
Scheme 3. Reactions of 1a and 1b with $[RuCl_2(p\text{-cymene})]_2$ Followed by Intramolecular Cyclization of the Isocyanide Ligands



the free ligand **1a**, the ^{1}H NMR spectrum of [**2a**] exhibits two well-resolved triplets for the isocyanide methylene groups at δ = 4.04 and 3.69 ppm (**1a**, broad singlet at δ = 3.60 ppm).[18]

Notably, the IR spectrum of [**2a**] exhibits two vibrations at $\tilde{\nu}$ = 2138 and 2106 cm^{-1} for the azido functionality. The existence of two vibrational modes for an azido substituent has been reported for only a few other compounds.[21] The isocyanide stretching vibration was observed at $\tilde{\nu}$ = 2199 cm^{-1} and thus shifted by 53 cm^{-1} to higher wavenumbers compared with the free ligand **1a** ($\tilde{\nu}$ = 2152 cm^{-1}) implying a desirable activation of the isocyanide carbon toward nucleophilic attack.[12d]

Single crystals of [**2a**] suitable for an X-ray diffraction analysis were grown by cooling of a saturated ethanol solution of the complex. The structure analysis reveals essentially linear isocyanide and azido functionalities (Figure 1). Bond parameters within the isocyanide ligand of [**2a**] do not differ significantly from equivalent parameters reported for complex $[W(CO)_5$-(**1b**)].[14a]

We have demonstrated that coordinated azido functionalized isocyanides react in a Staudinger-type reaction[22] with tertiary phosphines to yield phosphinimines,[14,18] which upon hydrolysis liberate an amine function (Scheme 2). This reaction was carried out with ruthenium complex [**2a**], which reacts with triphenylphosphine under liberation of dinitrogen and formation of complex [**3**] with a phosphinimine-substituted isocyanide (Scheme 3). The reaction can be monitored by IR spectroscopy. In the course of the reaction, the intensity of the absorptions for the azido function diminish. The isocyanide absorption is only marginally shifted to higher wavenumbers (from $\tilde{\nu}$ = 2199 cm^{-1} for [**2a**] to $\tilde{\nu}$ = 2204 cm^{-1} for [**3**]). The ^{31}P{^{1}H} NMR spectrum

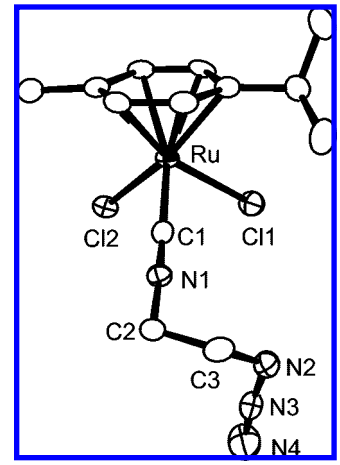


Figure 1. Molecular structure of complex [**2a**] (50% displacement ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (deg): Ru−C1 1.969(5), Ru−Cl1 2.3979(13), Ru−Cl2 2.4060(13), N1−C1 1.148(6), N1−C2 1.441(6), N2−C3 1.482(7), N2−N3 1.213(6), N3−N4 1.135(6); Ru−C1−N1 176.7(4), C1−N1−C2 175.7(5), N2−N3−N4 171.6(5).

reveals a broad signal at δ = 15.1 ppm typical for the phosphinimine group.[14a] Formation of the phosphinimine is also corroborated by two resonances for the methylene groups of the isocyanide in the ^{1}H NMR spectrum at δ = 3.86 ppm (t) and δ = 3.43 ppm (dt), the latter one being split by $^3J_{H,H}$ (6.6 Hz) and $^3J_{H,P}$ (15.2 Hz) coupling.

In the next step, it was intended to cleave the phosphinimine in [**3**] hydrolytically using water and a catalytic amount of acid to produce the amine functionalized isocyanide, which was supposed to cyclize to the NH,NH-stabilized NHC ligand. Following published procedures,[14,18] we treated complex [**3**] with H_2O/HBr in methanol. The NMR spectra indicated the formation of a product mixture and were inconsistent with the formation of a carbene complex. Treatment of [**3**] with an equimolar amount of HCl·Et_2O yielded a uniform reaction product. Again no carbene complex was detected by NMR spectroscopy. The ^{13}C{^{1}H} NMR spectrum exhibits the resonance for an isocyanide carbon atom at δ = 142.6 ppm essentially unchanged from the isocyanide carbon resonance in [**2a**] and [**3**]. Surprisingly, the ^{31}P{^{1}H} NMR spectrum exhibited a signal at δ = 38.8 ppm. This value is typical for quasi-phosphonium compounds (−NH$^+$−PPh$_3$) with a phosphorus−nitrogen bond.[23] From the spectroscopic data, it was concluded that the P═N bond in [**3**] was not cleaved but instead [**4**]Cl (Scheme 3) containing a protonated phosphinimine group had been obtained.

This assumption was confirmed by an X-ray diffraction study with crystals of [**4**]Cl·0.5EtOH (Figure 2) obtained by slow evaporation of the solvents from an ethanol/acetone solution of [**4**]Cl. The cation [**4**]$^+$ contains an isocyanide ligand substituted with a protonated phosphinimine. The geometric parameters of the isocyanide group are identical within experimental error to those found for [**2a**]. Protonation of the phosphinimine is detectable by the expansion of the P−N2 bond length to 1.633(5) Å relative to the values reported for related phosphinimines (1.564(4) Å), which therefore are reasonably described with a P═N double bond as depicted for [**3**] in Scheme 3.[14a] The P−N2 bond length in [**4**]$^+$ compares well to

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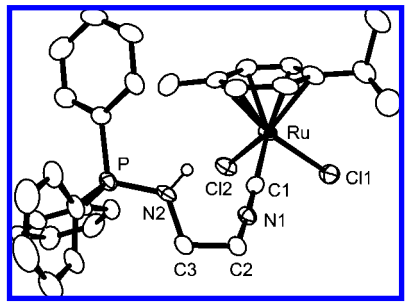

Figure 2. Molecular structure of $[\mathbf{4}]^+$ in $[\mathbf{4}]Cl \cdot 0.5EtOH$ (50% displacement ellipsoids;, hydrogen atoms are omitted with the exception of the hydrogen atom bound to N2). Selected bond lengths (Å) and angles (deg): Ru−C1 1.980(6), Ru−Cl1 2.419(2), Ru−Cl2 2.417(2), P−N2 1.633(5), N1−C1 1.145(7), N2−C3 1.479(7); Ru−C1−N1 176.2(5), P−N2−C3 120.4(4).

the P−N bond lengths reported for some quasi-phosphonium salts (1.621(3)−1.646(3) Å).[23] Nitrogen atom N2 is sp^2-hybridized (angle P−N2−C3 120.4(4)°), while the phosphorus atom is surrounded in a tetrahedral fashion. Significant (p→d)π backbonding has been proposed for nitrogen-substituted quasi-phosphonium salts.[23]

Hydrolysis of the phosphinimine group in [**3**] at ambient temperature appears impossible. A prolonged reaction time or a higher reaction temperature led to decomposition of the complex. We therefore searched for an alternative method to convert the azido group in complexes of type [**2**] into a primary amine group. A literature search revealed that $BH_3 \cdot THF$, $BHCl_2 \cdot Me_2S$,[24] and Me_3SiI[25] have been used for the reduction of organic azides to yield amines, but these methods proved ineffective for our purposes. The reduction of organic azides to amines with $FeCl_3$/NaI mixtures followed by an aqueous workup has been reported recently.[26] We have adopted this method for the reduction of the azido groups in organometallic compounds of type [**2**] (Scheme 3). Both [**2a**] and [**2b**] react with a mixture of $FeCl_3$/NaI under reduction of the azido group to yield a primary amine, which then intramolecularly attacks the isocyanide carbon atom with formation of the NH,NH-stabilized carbene ligand. The required large excess of NaI leads to an exchange of the halogenato ligands at the ruthenium atom resulting in the diiodo complexes of type [**5**] (Scheme 3).

The $^{13}C\{^1H\}$ NMR spectrum of [**5a**] shows the characteristic resonance for the carbene carbon atom at $\delta = 205.6$ ppm. The NH protons were observed in the ^1H NMR spectrum at $\delta = 6.80$ ppm. Interestingly, the IR spectrum (in KBr) showed two NH vibrations at $\tilde{\nu} = 3432$ cm^{-1} and $\tilde{\nu} = 3348$ cm^{-1}. In the solid state, this behavior is due to an intermolecular hydrogen bond between an NH proton and a iodo ligand from an adjacent molecule.

Crystals of [**5a**] suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a dichloromethane solution of [**5a**]. The structure analysis confirms both the formation of a diiodo NHC Ru^{II} complex and the existence of an intermolecular NH···I hydrogen bond (NH···I distance 3.016 Å). Similar NHC-NH···X interactions have previously been described.[19,27]

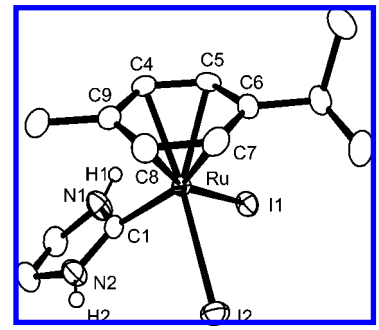

Figure 3. Molecular structure of [**5a**] (50% displacement ellipsoids; hydrogen atoms have been omitted with the exception of the N−H hydrogen atoms). Selected bond lengths (Å) and angles (deg): Ru−I1 2.7255(5), Ru−I2 2.7161(5), Ru−C1 2.031(4), Ru−C4 2.177(4), Ru−C5 2.176(4), Ru−C6 2.279(4), Ru−C7 2.219(4), Ru−C8 2.172(4), Ru−C9 2.198(4); N1−C1−N2 107.0(3).

The Ru−C1 bond length (2.031(4) Å, Figure 3) compares well to previously reported values for $Ru-C_{NHC}$ bond lengths in $[Ru^{II}(arene)(NHC)X_2]$[28] and other Ru^{II}NHC complexes.[29] The *trans* effect of the carbene ligand manifests itself in different $Ru-C_{cymene}$ bond lengths. The $Ru-C_{cymene}$ bond lengths *trans* to the NHC ligand are significantly longer (Ru−C6 2.279(4) Å, Ru−C7 2.219(4) Å) than those *trans* to the iodo ligands (range 2.172(4)−2.198(4) Å).

Once a suitable protocol for the reduction of the azido group in [$RuCl_2$(*p*-cymene)(**1a**)] with $FeCl_3$/NaI had been developed, we extended this method to the analogous complex [$RuCl_2$(*p*-cymene)(**1b**)] [**2b**], bearing the aromatic azido-substituted isocyanide ligand **1b** (Scheme 3). The reduction of the azido group in [**2b**] with $FeCl_3$/NaI requires a slightly prolonged reaction time compared with that for [**2a**] but gives the complex with the benzannulated NH,NH-stabilized carbene ligand in high yield (81%).

Complex [**2b**] exhibits the spectroscopic features expected for the presence of an aromatic isocyanide. The isocyanide C≡N stretching mode was observed at $\tilde{\nu} = 2147$ cm^{-1} in the IR spectrum. The $^{13}C\{^1H\}$ NMR resonance for the isocyanide carbon atom in [**2b**] ($\delta = 154.4$ ppm) vanishes upon reduction of the azido group and the resonance for the newly formed carbene carbon atom of [**5b**] was observed at $\delta = 180.6$ ppm.

Conclusion

Despite the dominance of azolium salts as precursors for N-heterocyclic carbenes and their metal complexes,[1] alternative synthetic strategies for the generation of NHC complexes are still needed. This is particularly true when the NHC ligand itself is not stable or when complexes with reactive NHCs that can be modified at the ring nitrogen atoms are required. The template-controlled cyclization of 2-azido-substituted isocyanides provides access to NH,NH-stabilized cyclic diaminocarbene ligands, which subsequently can be substituted with alkyl groups at the ring nitrogen atoms. The standard procedure for the cyclization of 2-azido-functionalized isocyanides (Staudinger reaction followed by hydrolysis) does not work for 2-azidoethyl isocyanide coordinated to the {Ru(*p*-cymene)X_2} complex fragment, which yields upon hydrolysis a Ru^{II} complex with a

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protonated phosphinimine ligand. We have introduced the reduction of coordinated 2-azido-substituted isocyanides with $FeCl_3$/NaI, which works for both aliphatic and aromatic isocyanides yielding NH,NH-stabilized saturated imidazolidin-2-ylidenes and unsaturated benzimidazolin-2-ylidenes. Further work is directed toward the functionalization of the NH,NH-stabilized NHC ligands at the Ru^{II} center with alkyl groups and the linkage of the NH,NH-stabilized carbene ligands to other donors coordinated to the metal center.[14b,19]

Experimental Procedures

General Comments. *Caution! Aliphatic azides are high energy density materials. Vigorous heating of 2-azidoethylamine did cause an explosive decomposition. Organic azides should not be heated to temperatures higher than 100 °C.* All preparations were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. The preparation of 2-azidoethyl isocyanide **1a**[18] and of 2-azidophenyl isocyanide **1b**[14a] by formylation of the corresponding primary amines followed by dehydration has been reported. Here we used a new synthetic approach to these isocyanides leading to materials with spectroscopic properties identical to those previously reported. $[RuCl_2(p\text{-cymene})]_2$ was prepared according to a literature procedure.[30] Triphenylphosphine was recrystallized from hot hexane prior to use. All other chemicals were used as received. NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer. IR spectra were measured with a Bruker Vector 22 spectrometer. MALDI mass spectra were obtained with a Varian MAT 212 spectrometer.

2-Azidoethyl Isocyanide, 1a. A mixture of 2-azidoethylamine (27.0 g, 0.31 mol), chloroform (31 mL, 0.39 mmol), dichloromethane (100 mL), aqueous sodium hydroxide (90 g of a 50% solution, 1.13 mol), and tetrabutylammonium bromide (1.4 g, 4.34 mmol) was stirred vigorously at ambient temperature for 4 days. Ice cold water was then added to dissolve the formed colorless solid. The organic phase was separated and dried over sodium carbonate. At ambient temperature, the organic solvents and unreacted starting material were removed under high vacuum. The resulting brown oil was heated to 60 °C and condensed into a flask cooled with liquid nitrogen under high vacuum. Yield: 14.0 g (0.15 mol, 47%) of a colorless liquid. The analytical data for **1a** obtained this way are identical to those previously reported.[18]

2-Azidophenyl Isocyanide, 1b. A suspension made up from 2-azidoaniline (9.3 g, 69.3 mmol), chloroform (7.2 mL, 90.2 mmol), dichloromethane (200 mL), aqueous sodium hydroxide (20 g of a 50% solution, 250 mmol), and benzyltriethylammonium chloride (220 mg, 0.1 mmol) was heated under reflux in the dark for 16 h. After the mixture cooled to room temperature, ice cold water (20 mL) was added. The organic phase was separated and dried over magnesium sulfate. The crude reaction product was purified by column chromatography (SiO_2, diethyl ether/petrol ether 1:15, v/v). Yield: 5.7 g (39.5 mmol, 57%) of a pale brown solid. The analytical data for **1b** obtained this way are identical to those previously reported.[14a]

Complex [2a]. A solution of $[RuCl_2(p\text{-cymene})]_2$ (305 mg, 0.50 mmol) and 2-azidoethyl isocyanide **1a** (110 mg, 1.15 mmol) in dichloromethane (15 mL) was stirred for 90 min at ambient temperature. The solvent was removed in vacuo, and the remaining solid residue was washed with diethyl ether (3 × 10 mL) and dried in vacuo. Yield: 380 mg (0.95 mmol, 95%) of a red crystalline solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 5.65 (d, 2H, ^3J = 6.1 Hz, Ar_{cymene}−H), 5.46 (d, 2H, ^3J = 6.1 Hz, Ar_{cymene}−H), 4.04 (t, 2H, ^3J = 5.5 Hz, CH_2NC), 3.69 (t, 2H, ^3J = 5.4 Hz, CH_2N_3), 2.87 (sept, 1H, ^3J = 6.9 Hz, C*H*$(CH_3)_2$), 2.28 (s, 3H, Ar−CH_3), 1.30 (d, 6H, ^3J = 6.9 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 142.4 (CN), 107.9 (Ar−C−*i*Pr), 107.4 (Ar−C−Me), 88.1, 87.9 (Ar−CH), 49.9 (CH_2N_3), 44.9 (CH_2NC), 31.2 (*C*H$(CH_3)_2$), 22.4 (CH(*C*H$_3)_2$), 18.8 (Ar−CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2199 (vs, CN), 2138 (s, N_3), 2106 (s, N_3). MS (MALDI) *m*/*z*: 402 $[M]^+$, 367 $[M - Cl]^+$.

Complex [2b]. The complex was prepared as described for [**2a**] from 200 mg (0.33 mmol) of $[RuCl_2(p\text{-cymene})]_2$ and 99 mg (0.68 mmol) of **1b** by using a reaction time of 14 h. Yield: 270 mg (0.60 mmol, 91%) of a red crystalline solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.42 (m, 2H, Ar_{benzyl}−H), 7.24 (m, 1H, Ar_{benzyl}−H), 7.14 (m, 1H, Ar_{benzyl}−H), 5.75 (d, 2H, ^3J = 6.0 Hz, Ar_{cymene}−H), 5.56 (d, 2H, ^3J = 6.0 Hz, Ar_{cymene}−H), 2.97 (sept, 1H, ^3J = 6.9 Hz, C*H*$(CH_3)_2$), 2.34 (s, 3H, Ar−CH_3), 1.33 (d, 6H, ^3J = 6.9 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 154.4 (CN), 137.1, 130.7, 128.5, 125.4, 118.9 (Ar_{benzyl}−C), 108.9 (Ar_{cymene}−C−*i*Pr), 108.8 (Ar_{cymene}−C−Me), 89.2, 88.9 (Ar_{cymene}−CH), 31.2 (*C*H$(CH_3)_2$), 22.4 (CH(*C*H$_3)_2$), 18.9 (Ar−CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2147 (vs, CN), 2120 (s, N_3). Elemental analyses of complexes [**2a**] and [**2b**] with azido-functionalized isocyanide ligands could not be obtained due to their propensity for explosive decomposition.

Complex [3]. A solution of [**2a**] (330 mg, 0.82 mmol) and triphenylphosphine (250 mg, 0.95 mmol) in dichloromethane (10 mL) was stirred for 3 h at ambient temperature. The solvent was removed in vacuo, and the residue was washed with diethyl ether (3 × 10 mL). Yield: 509 mg (0.80 mmol, 98%) of a red solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.58 (m, 6H, $Ar_{phosphine}$−H), 7.46 (m, 9H, $Ar_{phosphine}$−H), 5.46 (d, 2H, ^3J = 6.0 Hz; Ar_{cymene}−H), 5.27 (d, 2H, ^3J = 6.0 Hz, Ar_{cymene}−H), 3.86 (t, 2H, ^3J = 6.6 Hz, CH_2NC), 3.43 (dt, 2H, ^3J = 6.6 Hz, $^3J_{H,P}$ = 15.2 Hz, CH_2N=PPh_3), 2.78 (sept, 1H, ^3J = 6.9 Hz, C*H*$(CH_3)_2$), 2.15 (s, 3H, Ar−CH_3), 1.15 (d, 6H, ^3J = 6.9 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 137.9 (CN), 132.3 (d, $J_{C,P}$ = 9.2 Hz, *o*-$C_{phosphine}$), 131.9 (d, $J_{C,P}$ = 2.3 Hz, *p*-$C_{phosphine}$), 128.8 (d, $J_{C,P}$ = 11.6 Hz; *m*-$C_{phosphine}$), 107.0, 106.6 (Ar_{cymene}−C−*i*Pr and Ar_{cymene}−C−Me), 87.4, 87.2 (Ar_{cymene}−CH), 49.0 (d, $^2J_{C,P}$ = 23.0 Hz, CH_2N=PPh_3), 45.1 (d, $^3J_{C,P}$ = 2.3 Hz, CH_2CH_2N=PPh_3), 31.0 (*C*H$(CH_3)_2$), 22.4 (CH(*C*H$_3)_2$), 18.7 (Ar−CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 15.1 (br). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2204 (s, CN). MS (MALDI) *m*/*z*: 637 $[M + H]^+$.

Complex [4]Cl. A solution of [**3**] (75 mg, 0.118 mmol) in dichloromethane (5 mL) was treated with HCl·Et_2O (2 M solution, 0.06 mL, 0.12 mmol) at ambient temperature. After the addition, the solution was stirred for 2 h. The solvents were removed, and the remaining solid residue was washed with diethyl ether (2 × 10 mL). Yield: 78 mg (116 mmol, 99%) of a red solid. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 142.6 (CN), 135.1 (s, *p*-$C_{phosphine}$), 134.2 (d, $J_{C,P}$ = 7.9 Hz, $C_{phosphine}$), 130.6 (d, $J_{C,P}$ = 11.3 Hz, $C_{phosphine}$), 120.3 (d, $^1J_{C,P}$ = 102.3 Hz, *ipso*-$C_{phosphine}$), 107.9 (Ar_{cymene}−C−*i*Pr), 105.3 (Ar_{cymene}−C−Me), 89.1, 88.8 (Ar_{cymene}−CH), 48.6 (m, CH_2), 43.8 (m, CH_2), 31.0 (*C*H$(CH_3)_2$), 22.7 (CH(*C*H$_3)_2$), 19.3 (Ar−CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 38.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ 1993 (s, CN). MS (MALDI) *m*/*z*: 637 $[M - Cl]^+$.

Complex [5a]. To a solution of $FeCl_3$ (200 mg, 1.24 mmol) and NaI (1.50 g, 10.0 mmol) in acetonitrile (10 mL) was added solid [**2a**] (332 mg, 0.83 mmol). After the solution was stirred for 90 min at ambient temperature, the solvent was removed in vacuo. The residue was dissolved in dichloromethane (30 mL) and treated with aqueous $Na_2S_2O_3$ (5 mL of a 20% solution) and aqueous Na_2CO_3 (5 mL of a 20% solution). The organic phase was separated and dried over Na_2CO_3. The solvent was then removed in vacuo. Yield: 395 mg (0.71 mmol, 86%) of a dark red solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 6.80 (s, br, 2H, NH), 5.45 (d, 2H, ^3J = 6.0 Hz, Ar_{cymene}−H), 5.24 (d, 2H, ^3J = 6.0 Hz, Ar_{cymene}−H), 3.75 (s, 4H, NCH_2CH_2N), 3.00 (sept, 1H, ^3J = 6.9 Hz, C*H*$(CH_3)_2$), 2.34

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(s, 3H, Ar−CH_3), 1.27 (d, 6H, ^3J = 6.9 Hz, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 205.6 (NCN), 108.6 (Ar_{cymene}−C−*i*Pr), 101.2 (Ar_{cymene}−C−Me), 86.4, 85.0 (Ar_{cymene}−CH), 46.3 (NCH_2CH_2N), 31.5 (*C*H(CH_3)$_2$), 22.9 (CH(*C*H_3)$_2$), 19.8 (Ar−CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3432 (s, NH), 3348 (s, NH). MS (MALDI) *m*/*z*: 433 $[M - I]^+$. Anal. Calcd: C, 27.92; H, 3.61; N, 5.01. Found: C, 28.15; H, 3.66; N, 5.33.

Complex [5b]. Complex [**5b**] was prepard as described for [**5a**] from [**2b**] (300 mg, 0.67 mmol) applying a 4 h reaction time. Yield: 328 mg (0.54 mmol, 81%) of a dark red solid. ^1H NMR (400.1 MHz, $CDCl_3$): δ 10.77 (s, br, 2H, NH), 7.09 (m, 2H, Ar_{benzyl}−H), 6.85 (m, 2H, Ar_{benzyl}−H), 5.67 (d, 2H, ^3J = 6.0 Hz, Ar_{cymene}−H), 5.54 (d, 2H, ^3J = 6.0 Hz, Ar_{cymene}−H), 2.89 (sept, 1H, ^3J = 6.7 Hz, C*H*(CH_3)$_2$), 2.30 (s, 3H, Ar-CH_3), 1.21 (d, 6H, ^3J = 7.0 Hz, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 180.6 (NCN), 133.3 (Ar_{benzyl}−*ipso*-C), 122.9 (Ar_{benzyl}−*ortho*-C), 110.2 (Ar_{benzyl}−*meta*-C), 108.8 (Ar_{cymene}−C−*i*Pr), 102.4 (Ar_{cymene}−C−Me), 86.5, 85.4 (Ar_{cymene}−CH), 31.6 (*C*H(CH_3)$_2$), 22.9 (CH(*C*H_3)$_2$), 20.0 (Ar-CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3312 (m, br, NH). MS (MALDI) *m*/*z*: 522 $[M - I + MeCN]^+$, 481 $([M - I]^+)$. Anal. Calcd: C, 33.62; H, 3.32; N, 4.61. Found: C, 33.86; H, 3.38; N, 4.87.

X-ray Diffraction Studies. X-ray diffraction data for [**2a**], [**4**]Cl·0.5EtOH, and [**5a**] were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K ([**2a**] and [**5a**]) or 298(2) K ([**4**]Cl·0.5EtOH) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[31] program package. For further crystal and data collection details, see Table 1. Structure solutions were found with the SHELXS-97[32] package using the heavy-atom method and were refined with SHELXL-97[33] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. Complex [**4**]Cl·0.5EtOH crystallizes together with one disordered molecule of ethanol in the unit cell.

Table 1. Crystallographic Data for the Complexes [2a], [4]Cl·0.5EtOH, and [5b]

parameter	[**2a**]	[**4**]Cl·0.5EtOH	[**5a**]
formula	$C_{13}H_{18}N_4C_{12}Ru$	$C_{32}H_{37}N_2C_{13}O_{0.5}PRu$	$C_{13}H_{20}N_2I_2Ru$
cryst size [mm^3]	0.15 × 0.02 × 0.02	0.08 × 0.06 × 0.02	0.20 × 0.10 × 0.03
M_r	402.28	696.03	559.18
a [Å]	5.8684(12)	12.202(3)	8.0779(12)
b [Å]	15.528(3)	12.792(3)	25.339(4)
c [Å]	17.330(4)	12.965(3)	8.4881(12)
α [deg]	90	68.867(4)	90.0
β [deg]	94.179(4)	62.535(3)	110.130(3)
γ [deg]	90	72.561(4)	90.0
V [$Å^3$]	1575.0(6)	1652.9(6)	1631.3(4)
Z	4	2	4
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
ρ_{calcd} [g cm^{-3}]	1.697	1.399	2.277
μ [mm^{-1}]	1.330	0.790	4.733
2θ range [deg]	3.5−50.0	3.5−55.2	3.2−60.1
data collected	12377	16025	18491
no. unique data, R_{int}	2761, 0.0742	7602, 0.0788	4749, 0.0446
no. obsd data [$I \geq 2\sigma(I)$]	2091	4492	4180
R	0.0397	0.0705	0.0357
wR	0.702	0.1326	0.0717
no. of variables	184	357	166

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Supporting Information Available: X-ray crystallographic files for complexes [**2a**], [**4**]Cl·0.5EtOH, and [**5a**] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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