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A Sandwich Zwitterionic Ruthenium Complex Bearing a Cyanamido Group

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S Supporting Information

ABSTRACT: A sandwich zwitterionic ruthenium complex (4) was prepared by an intramolecular 1,3-dipolar cycloaddition of the ruthenium azido isocyanide $[CpMe_5Ru(CNAr)_2N_3]$ (2). The reaction involved a formal 1,3-migration mechanism along a highly conjugated system linking to a cyanamido group.



T he design and construction of reactive charge-neutral zwitterionic platinum-group-metal complexes have attracted considerable interest over the past few years because some such complexes have a high potential as catalysts in varied organic transformations.¹⁻⁴ For instance, while zwitterionic rhodium(I) complexes have shown divergent reactivity, such as in the hydrosilylation of ketones,^{2a} diboration of vinylarenes,^{2b} hydroformylation of olefins,^{2c,d} and tandem cyclohydrocarbonylation/CO insertion of α -imino alkynes,^{2g} several zwitterionic ruthenium(II) complexes³ have been recently applied to the activation in the atom transfer radical addition of CCl₄,^{4a} the geminal Si–H bond of an organosilane,^{4b} the ring-opening metathesis polymerization of cyclooctene,^{4c} reversible H₂ splitting,^{4d} and so on.^{4d}

On the other hand, 1.3-dipolar cycloaddition of metal azido and isocyanides is one of the routes to the preparation of transition-metal cyanamido complexes with terminal nitrogen coordination as well as C-bonded tetrazolato compounds,⁵ where cyanamido complexes are regarded as the thermolysis products of the C-bonded tetrazolato compounds.^{5a,f-h} Recently, it has been postulated that π -bonded cyanamido allyl metal intermediates might isomerize in solution and might play a key role in the metal-catalyzed (especially palladiumcatalyzed) preparation of organic cyanamides.⁶ Due to the importance of cyanamides for heterocyclic compounds in the fields of organic and inorganic chemistry,⁷ the inferred mechanism of the isomerized π -bonded cyanamido allyl metal intermediates is significant in understanding the formation of cyanamides⁶ as well as cyanamido complexes.⁵ However, such species have not been evidenced experimentally to date. Herein, we report a half-sandwich cyanamido ruthenium compound (3) and one sandwich arene ruthenium complex with a cyanamido anion group (4), both of which likely derive from isomerized π bonded cyanamido allyl ruthenium intermediates. Probably owing to their high reactivity, the formal 1,3-isomerized

products of π -bonded cyanamido allyl metal intermediates such as 4 have not been isolated and characterized structurally before the present work.

As shown in Scheme 1, the complex $[Cp*RuL_2Cl]$ (1; L = CNAr, Ar = 2,6-dimethylphenyl) was easily obtained by the

Scheme 1. Preparation of Complexes 1-4



reaction of $[Cp^*RuCl]_4^8$ and 2 equiv of 2,6-dimethylphenyl isocyanide (L) in CH_2Cl_2 in 94.4% yield as dark orange crystals (Scheme 1).⁹ The ruthenium azido complex $[Cp^*RuL_2N_3]$ (2) was further synthesized by the salt elimination reaction of 1 and NaN₃ in dry ethanol as a orange solid in 90.1% yield.¹⁰ The intramolecular [3 + 2] cycloaddition occurred when 2 was refluxed in *o*-xylene for 4 days in the presence of additional 0.6 equiv of 2,6-dimethylphenyl isocyanide (L) (Scheme 1). The reaction led to the formation of 3 and 4 as a mixture ([3]/[4] = 4/1), which was further isolated in good to fair yield (63.0% for 3, 24.8% for 4), respectively.¹¹ Alternatively, the reaction may be performed within 5 h at 200 °C in a sealed evacuated Carius tube by using 1,2,4,5-tetramethylbenzene as solvent. Complexes

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3 and 4 are readily soluble in THF and chlorinated solvents but only somewhat soluble in ether.

The elemental analysis results are in complete agreement with the formulas of compounds 1-4.¹² The ¹H NMR (CD₃Cl, 23 °C) spectrum of complex 3 shows signals at δ 1.91 (s), 2.31 (s), 2.40 (s), 6.55-6.81 (m), and 7.06 (s) ppm that are assigned to CpMe₅, NCNAr, and CNAr groups, respectively. Two resonances at δ 117.98 and 170.60 ppm in the ¹³C{¹H} NMR spectrum evidenced the NCN and Ru-CN groups. The N=C=N stretching vibrations in the IR spectrum appear at 1598 (m) and 2164 (m) cm⁻¹, while the band at 2363(w) cm⁻¹ is attributed to CN of the coordinated acetonitrile.¹³ The ¹H NMR spectrum (CD₂Cl₂, 23 °C) of compound 4 is, however, quite different from that of 3 and shows one set of signals at δ 1.82 (s, 15 H), 2.14 (s, 6 H), and 4.95 (m, 3 H) ppm. The upfield resonance at δ 4.95 (m) is assigned to the protons on the η^6 -coordinated phenyl ring, suggesting the formation of a metal arene complex. The ¹³C{¹H} NMR spectrum shows the upfield signals of the carbon atoms on the phenyl ring at about δ 90 ppm. The broad resonance at δ 131.54 ppm is assigned to the NCN group. The -N=C=N stretching vibration of 4 in the IR spectrum appears at 2096 (m) cm⁻¹ but bands without stretching appear at about 2360 and 1600 cm⁻¹.

An X-ray crystal structure determination of 1–4 was carried out.^{12,13} In the structures of complexes 1–3, the Ru center is coordinated by two CNAr units, one chloro for 1 (azido for 2 or NCNAr for 3), and one η^5 -CpMe₅ group. The overall geometry about ruthenium exclusively featured a typical "piano stool" conformation (Figure 1).¹³ The bond distances (Ru(1)–



Figure 1. ORTEP drawing of complex **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)-C(30) = 2.237(5), Ru(1)-C(1) = 1.931(3), Ru(1)-N(3) = 2.080(3), N(3)-C(19) = 1.152(5), C(19)-N(4) = 1.269(1), N(4)-C(20) = 1.391(2); C(10)-Ru(1)-C(1) = 90.85(5), C(10)-Ru(1)-N(3) = 90.84(1), Ru(1)-C(1)-N(1) = 178.15(9), Ru(1)-N(3)-C(19) = 170.16(5), N(3)-C(19)-N(4) = 170.16(5), C(19)-N(4) -C(20) = 128.28(4).

N(3) = 2.080(3) Å and Ru(1)-C(1) = 1.931(3) Å) and bond angles $(C(10)-Ru(1)-C(1) = 90.85(5)^{\circ}$ and $C(10)-Ru(1)-N(3) = 90.84(1)^{\circ})$ at ruthenium in 3 are comparable to those found in 1 and 2.^{12,13}

In contrast to the piano-stool structures of 1–3, the X-ray analysis clearly revealed that 4 is a sandwich molecule with $[\eta^{5}-(CpMe_{5})]^{-}$ and $[\eta^{6}-(arene)NCN]^{-}$ moieties (Figure 2).^{12,13} The carbon atom (C(6)) deviation from the least-squares plane of phenyl ring is only 0.0331° (0.0105 Å), and the angle between two best planes of the ligand rings is 0.41°, so that the sandwich is almost perfectly stacked parallel. The longer C(1)–



Figure 2. ORTEP drawing of complex **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)-C(1) = 2.194(2), Ru(1)-C(6) = 2.235(5), Ru(1)-C(1) = 2.360(1), C(1)-N(1) = 1.360(9), N(1)-C(9) = 1.297(7), C(9)-N(2) = 1.149(8); C(1)-N(1)-C(9) = 127.48(9), N(2)-C(9)-N(1) = 169.97(2).

N(1) bond length (1.360(9) Å, vs N(1)-C(9) = 1.297(7) Å) and C(9)-N(2) (1.149(8) Å) and the smaller bond angle at $N(1) (C(1)-N(1)-C(9) = 127.48(9)^{\circ}, vs N(2)-C(9)-N(1)$ = $169.97(2)^{\circ}$) are indicative of C(1)-N(1) single-bond character. The difference between Ru(1)-C(1) (2.360(1) Å) and the average Ru(1)-C bond length in the phenyl ring (2.235(5) Å) is 0.12(2) Å. The packing structure of 4 showed that the cyanamido group was neither affected by any packing force from the group and atoms nor oriented to the metal center of a neighboring molecule. The amino nitrogen atom (N(1)) of the cyanamido group has therefore one lone pair of electrons that seems to conjugate with both cyano and arene groups. Since the C(1) atom is almost coplanar, the phenyl ring must remain aromatic to comply with the 4n + 2 rule; complex 4 is thus a zwitterionic species with an anionic NCN⁻ functional group. Ruthenium arene complexes with an anionic functional group on the phenyl ring are rare, and only a few structurally characterized examples such as $[CpRu(\eta^6 C_6H_5BPh_3$], $[(\eta^6-C_6H_5BPh_2H)Ru(PMe_3)_2(SiMe_3)]$, $[(\eta^6-C_6H_5BPh_2H)Ru(PMe_3)]$, $[(\eta^6-C_6H_5BPh_2H$ $C_6H_5BPh_3$ (depe)], and $[(\eta^6-C_6H_5BPh_3)Ru((1-3,5,6-\eta) C_8H_{11}$ as well as [CpMe₅Ru(η^6 -PhCOO)], [(η^5 - C_8H_{11})Ru- $(\eta^6$ -PhSO₃)], and $[(\eta^5$ -C₅H₄OH)Ru $(\eta^6$ -p-MeC₆H₄SO₃)] are known.^{14,15} However, it is notable that the significantly longer Ru(1)-C(1) bond length may indicate another resonance form of 4: namely, a η^5 species containing a C=N-C=N group, similar to that found in $[CpMe_5Ru(\eta^5-C_5F_5C=O)]$.^{14n- \tilde{F}_F}

The mechanism for the formation of 3 and 4 seems to be an alternative three-step mechanism involving intermediates A-C at high temperatures (Scheme 2). The C-bonded tetrazolato ruthenium complex (A) forms and then decomposes at high temperatures to give a π -bonded cyanamido allyl metal intermediate (B). It seems reasonable that a formal 1,3migration of the [Ru]L₂ unit would occur along the allyl group in B to give complexes 3 and 4.^{16a} It seems that 3 is a kinetic product and 4 is a thermodynamic species.^{16b} However, we could not observe the proton resonances of these intermediates in the ¹H NMR spectra at varying temperatures (100–145 °C), indicating that they are all unstable at high temperatures.¹⁶ We also investigated the possible equilibrium between complexes 3 and 4. Compound 3 only converted to compound 4 (only about 5% yield) slightly when an *o*-xylene- d_{10} solution of **3** was heated at 145 °C in a sealed combustion tube for 100 h. In contrast, compound 4 is quite stable and could not convert to compound 3 even after 150 h under similar conditions.¹⁶

Scheme 2. Suggested Mechanism for the Formation of Complexes 3 and 4



In summary, an intramolecular 1,3-dipolar cycloaddition of the azido metal isocyanide 2 occurred to afford the two isomeric cyanamido ruthenium complexes 3 and 4, the latter of which is a zwitterionic ruthenium complex with a noncoordinating cyanamido group that has potential in organic transformations.⁴ The formation of isomers 3 and 4 suggested that a metal 1,3-migration to ²N or even to ⁵N occurred probably via the π -allyl ruthenium cyanamido intermediate B after the breakdown of the tetrazolato ring. The migration to ²N may be regarded as a formal Curtius rearrangement,¹⁷ while the migration to ⁵N, however, was never observed due to a bulky substituent on the nitrogen atom. In addition, the structure of 4 rendered a unique example that may give insight into the bonding capability of the phenylcyanamido ligand with transition metals, which usually presents a terminal or side-on cyanamido coordination with metals.^{18a} The successful preparation and structural characterization of 4 may thus open a path to the preparation of novel sandwich zwitterionic phenylcyanamide complexes with specific electronic and magnetic communication properties.¹

ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving crystal data, structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for 1-4, experimental details, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(9) Preparation of 1: to a mixture of $[(\eta^{5}\text{-}CpMe_{5})\text{RuCl}]_{4}$ (0.89 g, 0.82 mmol) and CNAr (1.41 g, 10.70 mmol) was added CH₂Cl₂ (25 mL) via a syringe. After the solution was stirred for 24 h, the volatile components were removed under reduced pressure. The resulting residue was washed with *n*-hexane (5 × 10 mL) to give 1 as a pure orange solid (1.65 g, 94.4%). Mp: 162 °C. ¹H NMR (CD₃Cl, 23 °C): δ 1.89 (s, 15 H, CpCH₃), 2.43 (s, 12 H, ArCH₃), 7.05 (s, 6 H, Ar H) ppm. ¹³C{¹H} NMR (CD₃Cl, 23 °C): δ 10.32 (s, CpCH₃), 19.17 (s, PhCH₃), 94.49 (s, CpCCH₃), 126.65, 127.60, 134.26, 171.69 (5s, C on the phenyl rings) ppm. Anal. Calcd for C₂₈H₃₃ClN₂Ru: C, 62.20; H, 6.15; N, 12.95. Found: C, 61.80; H, 6.19; N, 12.56. Single crystals suitable for X-ray diffraction analysis were obtained from a mixture of CH₂Cl₂ and *n*-hexane (1/3) at -25 °C.

(10) Preparation of 2: to a mixture of 1 (0.36 g, 0.73 mmol) and NaN₃ (0.19g, 2.92mmol) was added dry ethanol (30 mL) via a syringe. After it was refluxed for 6 h, the solution was cooled to room temperature. The volatile components were removed under reduced pressure, and the resulting residue was extracted with CH₂Cl₂. The solution was filtered, and the filtrate was concentrated to ca. 5 mL to afford a bright red crystalline solid in the presence of *n*-hexane (5 mL) (0.31 g, 90.1%). Mp: 148 °C. ¹H NMR (CD₃Cl, 23 °C): δ 1.90 (s, 15 H, CpCH₃), 2.47 (s, 12 H, ArCH₃), 7.10 (s, 6 H, Ar H) ppm. ¹³C{¹H} NMR (CD₃Cl, 23 °C): δ 10.29 (s, CpCH₃), 19.11 (s, ArCH₃), 94.69 (s, CpCMe), 126.83, 127.60, 129.47, 134.36, 170.57 (5s, C on the phenyl rings) ppm. IR (KBr, cm⁻¹): 3171 (m), 2104 (s), 2019 (s), 1589 (w), 1261 (m), 1025 (m), 773 (m), 723 (m), 672 (m), 512 (m); Anal. Calcd for C28H33N5Ru: C, 62.20; H, 6.15; N, 12.95. Found: C, 61.80; H, 6.19; N, 12.56. Single crystals suitable for X-ray diffraction analysis were obtained from a mixture of THF and Et₂O (1/2) at -5°C.

(11) Preparation of 3 and 4: a suspension of 2 (2.16 g, 4.0 mmol) in o-xylene (80 mL) was refluxed for 4 days under an argon atmosphere. The volatile components were removed under reduced pressure. The resulting residue was extracted with cold THF (0 $^{\circ}$ C, 3 \times 10 mL), and the solvent was then removed under high vaccum. The resulting yellow solid was washed with Et₂O to afford 3 as a spectrally pure solid. Single crystals suitable for X-ray diffraction analysis were obtained from a mixture of THF and $Et_2O(1/2)$ at room temperature (1.62 g, 63%). Mp: 191 °C. ¹H NMR (CD₃Cl, 23 °C): δ 1.91 (s, 15H, CpCH₃), 2.31 (s, 6 H, ArCH₃), 2.40 (s, 12 H, ArCH₃), 6.54–6.56 (m, 1 H, NCCAr H), 6.80 (d, 2 H, NCNAr H), 7.06 (s, 6 H, CNAr H) ppm. ¹³C{¹H} NMR (CD₃Cl, 23 °C): δ 10.46 (s, CpCH₃), 19.04 (s, ArCH₃), 19.66 (s, ArCH₃), 95.98 (s, CpCMe), 117.76 (s, CRu), 126.85, 127.64, 127.71, 129.70, 130.46, 134.52, 147.10 (overlapped, Ar), 170.60 (s, NCN). IR (KBr, cm⁻¹): 2362 (w), 2164 (s), 2043 (s), 1589 (m), 1262 (m), 1189 (m), 1082 (m), 1029 (m), 768 (s), 753 (s), 669 (s), 522 (m), 504 (s). Anal. Calcd for C37H42N4Ru: C, 69.02; H, 6.58; N, 8.70. Found: C, 69.20; H, 6.54; N, 8.69. Single crystals suitable for X-ray diffraction analysis were obtained from a mixture of CH_2Cl_2 and Et_2O (1/3) at -5 °C. The resulting residue after extraction with cold THF was dissolved in CH_2Cl_2 and THF (4/6) to give 4 as colorless crystals at -30 °C (0.62 g, 24.8%). Mp: 351 °C dec. ^TH NMR (CD₃Cl, 23 °C): δ 1.82 (s, 15 H, CpCH₃), 2.17 (s, 6 H, ArCH₃), 4.93 (t, 1 H, NCCAr H), 5.08 (d, 2 H, NCNAr H). ¹³C{¹H} NMR (CD₃Cl, 23 °C): δ 10.10 (s, CpCH₃), 17.56 (s, ArCH₃), 88.37 (s, CpCMe), 80.48, 90.48, 92.09 (3s, overlapped, Ph), 131.54 (br, NCN). IR (KBr, cm⁻¹): 3158 (s), 2096 (m), 2044 (s), 1303 (s), 1259 (s), 1152 (s), 1019 (s), 798 (m), 722 (s), 669 (m), 588 (m). Anal. Calcd for C19H24N2Ru: C, 59.51; H, 6.83; N, 7.30. Found: C, 59.32;

H, 6.72; N, 7.21. Single crystals suitable for X-ray diffraction analysis were obtained from a mixture of CH_2Cl_2 and THF (4/6) at ambient temperature.

(12) See the Supporting Information for the plots of compounds 1 and 2.

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