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Synthesis and Structure of a Triruthenium Complex Containing a Perpendicularly Coordinated μ_3-η^2:η^2(⊥)-Nitrile Ligand and Its Protonation To Yield a Perpendicularly Coordinated Iminoacyl Ligand

Toshiro Takao, Takashi Kawashima, Kouki Matsubara, and Hiroharu Suzuki*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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Summary: Treatment of the triruthenium pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ *(**1**;* $Cp^* = \eta^{5-C}{}_5Me_5$*) with RCN (R = Ph,* ^{t}*Bu) resulted in the exclusive formation of the* μ_3-η^2:η^2(⊥)*-nitrile complex* $(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}RCN)(\mu_3\text{-}H)(\mu\text{-}H)_2$ *(**3a**, R = Ph; **3b**, R =* ^{t}*Bu) with a coordination geometry of the nitrile ligand perpendicular to one of the Ru−Ru edges. Protonation of **3** quantitatively afforded the cationic* μ_3*-iminoacyl complex* $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}RCNH)(\mu\text{-}H)_2(\mu_3\text{-}H)](BF_4)$ *(**4a**, R = Ph; **4b**, R =* ^{t}*Bu), which clearly shows that the lone-pair electrons at the nitrogen atom do not participate in the bonding between the nitrile ligand of **3** and the metal centers.*

Recently, we have reported the synthesis of a series of perpendicularly coordinated alkyne complexes, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}RCCH)$ (**2a**, R = Ph; **2b**, R = ^{t}Bu; $Cp^* = \eta^5\text{-}C_5Me_5$), by the reaction of the triruthenium pentahydrido complex $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**) with terminal alkynes.[1a] Perpendicular coordination of alkyne to an M−M bond is characteristic of a cluster that adopts a coordinatively unsaturated 46e configuration.[2] Complex **2** was also observed during the reaction of **1** with alkanes as an intermediate;[3] thus, the (⊥)-alkyne complex **2** is an important compound to understand how the hydrocarbyls undergo skeletal rearrangement on the cluster. Various types of hydrocarbyl ligands have been so far introduced into the core of the cluster, mainly by the reaction of carbonyl clusters with alkynes in relation to metal surface chemistry.[4]

In contrast to the abundant chemistry of the alkyne cluster, little is known about the cluster containing an η^2-coordinated nitrile. Although several examples of an η^2-coordinated nitrile ligand have been known for monometallic complexes,[5] examples of bi-[6] and trimetallic complexes[7] having η^2-C≡N interaction have been quite limited. Nitrile is an important functional group for organic synthesis, because it can be readily converted into many organic materials such as amine and amide. It is, therefore, quite important to prove the reactivity of a nitrile ligand on the cluster in relation to elucidation of the mechanism of the reaction performed on a metal surface. We will report herein the synthesis of a triruthenium nitrile complex with an unusual coordination mode, $(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}RCN)(\mu_3\text{-}H)(\mu\text{-}H)_2$ (**3a**, R = Ph; **3b**, R = ^{t}Bu), and protonation resulting in the exclusive formation of an iminoacyl ligand, μ_3-η^2:η^2(⊥)-RCNH, which is also perpendicularly coordinated to one of the Ru−Ru bonds.

The reaction of a transition-metal complex having a hydrido ligand with nitrile often led to the formation of an alkylideneamide ligand as a result of insertion of nitrile into an M−H bond.[5] The reaction of the diruthenium tetrahydrido complex $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ with acetonitrile quantitatively afforded the bridging ethylideneamide complex $\{Cp^*Ru(MeCN)\}_2(\mu\text{-}N{=}CMeH)(\mu\text{-}H)$.[8] In contrast to the dinuclear system, reaction of **1** with RC≡N (R = Ph, ^{t}Bu) quantitatively yielded the perpendicularly coordinated nitrile complex **3** with liberation of dihydrogen (eq 1).[9] This reaction is very similar to that of **1** with alkyne, and this fact implies that a nitrile is coordinated to the ruthenium atoms through the C≡N triple bond as a four-electron donor rather than the lone pair at the nitrogen atom.

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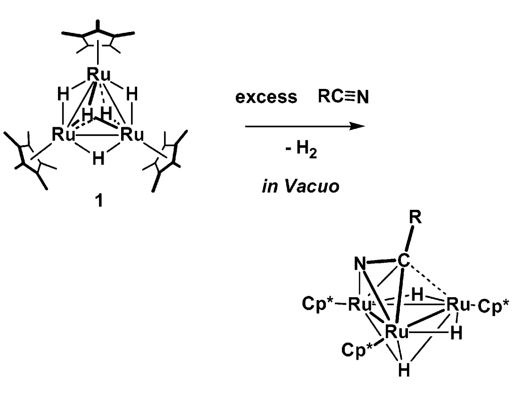

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(1)

3a; R = Ph
3b; R = ^{t}Bu

A notable feature of **3** is the η^2:η^2 coordination of the C≡N bond to the ruthenium atoms. The triiron complex $Fe_3(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-RCN})$ was the only example of a trimetallic complex having an η^2-coordinated nitrile ligand.[7a] The nitrile ligand of the triiron complex was located with the nitrogen atom directed inside the Fe_3 core and acted as a 6e donor with additional κN coordination, which makes the triiron cluster coordinatively saturated. In contrast, the nitrile ligand of **3** was located in the direction opposite to that found in the triiron complex, and the lone pair on the nitrogen atom did not participate in the coordination. This coordination mode of a nitrile ligand is unprecedented for a trimetallic complex. While the metal centers of the triiron complex are electron deficient due to carbonyl ligands, the triruthenium complex contains electron-rich metal centers because of the electron-releasing Cp* groups. Although **3** is coordinatively unsaturated (46e), κN coordination seemed not to be required, due to such electron-rich character. This causes a nitrile ligand to be a 4e donor and also to be in a perpendicular coordination.

The X-ray diffraction studies of **3a** were performed by using a red single crystal obtained from cold toluene solution, and the ORTEP diagram is given in Figure 1 with selected bond lengths and angles.[10] The C−N bond was disposed on the crystallographic mirror plane bisecting the Ru_3 triangle, and the nitrogen atom was oriented to the outside of the Ru_3 core. The phenyl ring was located inside the core with parallel orientation to the Ru(2)−Ru(2#) bond. This structure is very similar to that of the (⊥)-alkyne complex $\{Cp^*Ru(\mu\text{-H})\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-PhCCH})$ (**2a**),[1a] and the coordination mode of the nitrile is in marked contrast to that observed in $Fe_3(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-RCN})$.[7a] Orientation of the nitrile ligand in **3** is determined probably by the steric demand arising from the repulsion between the substituents R on the nitrile ligand and the Cp* groups as found in **2**.[11]

The bond distance between C(1) and N(1) is 1.358(6) Å, which represents the intermediate value between a C=N double bond (1.28 Å) and a C−N single bond (1.45 Å). Such elongation of the C−N bond implies strong back-donation from the electron-rich Ru_3 centers, which contain electron-releasing Cp* groups, to the nitrile ligand. This is in striking contrast to the C−N bond length found in $Fe_3(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-PhCN})$ (1.290(5) Å),[7] which has electron-withdrawing carbonyl ligands. Such bond elongation by the ⊥ coordination was also found in the (⊥)-alkyne complex **2a**; the C−C bond length of the phenylacetylene moiety (1.392(7) Å) lies between a C=C double bond (1.34 Å) and a C−C single bond (1.54 Å). The bond lengths between the ruthenium atoms and the nitrile carbon (Ru(1)−C(1), 2.124(5) Å; Ru(2)−C(1), 2.273(3) Å) indicate bonding interactions between C(1) and all ruthenium atoms.

In the ^{1}H NMR spectrum of **3a** measured at −10 °C, two sharp signals assignable to the Cp* groups were observed at δ 2.14 and 1.55 with an intensity ratio of 2:1. The two doubly bridging hydrido ligands resonated at δ −3.96, and the triply bridging hydride was observed at δ −24.36. Although both Cp* and hydrido signals were observed as sharp signals at −10 °C, they became broad as the temperature was increased (Figure 2). However, coalescence of these signals was not observed because of the thermal instability of **3** above room temperature. The temperature dependence of the ^{1}H NMR signals for the Cp* and the hydrido ligands strongly implied *switchback motion* of the μ_3-(⊥)-nitrile ligand. Such a dynamic process has also been observed for the μ_3-(⊥)-alkyne complex.[1b] The motion of the nitrile ligand in **3** makes the magnetic environment of the Cp* and hydrido ligands equivalent. Spin saturation transfer was observed at 40 °C between the two hydrido signals at δ −3.96 and −24.36 (see Figure S-1 in the Supporting Information).

The ^{13}C signal for the nitrile carbon of **3a** was observed in a considerably higher magnetic field region, δ 97.8. A similar upfield shift of the ^{13}C signals for the triply bridging carbon was observed in the μ_3-(⊥)-alkyne

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(9) A 50 mL Schlenk tube was charged with tetrahydrofuran (15 mL) and **1** (299 mg, 0.42 mmol). Benzonitrile (0.85 mL, 8.3 mmol) was added with vigorous stirring. Then, the pressure in the flask was reduced, using the vacuum line to remove the dihydrogen produced in the reaction. The reaction mixture was stirred at 25 °C for 6 h. Dihydrogen was periodically removed from the reaction flask every 30 min during the reaction. The color of the solution turned from reddish brown to brownish yellow. The solvent and the remaining benzonitrile were removed under reduced pressure. The residual solid was purified by the use of column chromatography on alumina (Merck, Art. No. 1097) with tetrahydrofuran. The third reddish brown band including **3a** was collected, and the solvent was removed under reduced pressure. Complex **3a** was obtained as a brownish yellow solid in 60% yield (204 mg). Complex **3b** was synthesized by the reaction of **1** with a large excess amount of pivalonitrile at 90 °C. Since the side reaction of **3b** with dihydrogen was slow, a periodic purge of the liberated dihydrogen was not needed. Complex **3b** was isolated in a manner similar to that for **3a** as a reddish brown solid in 60% yield. NMR data for **3a**: ^{1}H NMR (400 MHz, toluene-d_8, −10 °C, TMS) δ −24.36 (s, 1H, Ru−*H*), −3.96 (s, 2H, Ru−*H*), 1.55 (s, 15H, C_5Me_5), 2.14 (s, 30H, C_5Me_5), 6.03 (d, J_{H-H} = 7.1 Hz, 2H, *o-Ph*), 6.92 (t, J_{H-H} = 7.1 Hz, 2H, *m-Ph*), 7.34 (t, J_{H-H} = 7.1 Hz, 1H, *p-Ph*); ^{13}C NMR (100 MHz, THF-d_8, −40 °C, TMS) δ 11.9 (q, J_{C-H} = 126.4 Hz, C_5Me_5), 12.7 (q, J_{C-H} = 126.4 Hz, C_5Me_5), 84.3 (s, C_5Me_5), 91.2 (s, C_5Me_5), 97.8 (s, *C*N), 123.2 (d, J_{C-H} = 160.6 Hz, *p-Ph*), 126.3 (d, J_{C-H} = 157.7 Hz, *Ph*), 126.8 (d, J_{C-H} = 157.7 Hz, *Ph*), 143.3 (s, *ipso-Ph*). **3b**: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C, TMS) δ −24.89 (s, 2H, Ru−*H*), −0.38 (s, 1H, Ru−*H*), 0.51 (s, 9H, $C(CH_3)_3$), 1.92 (s, 15H, C_5Me_5), 2.01 (s, 30H, C_5Me_5); ^{13}C NMR (100 MHz, benzene-d_6, 25 °C, TMS) δ 12.4 (q, J_{C-H} = 126 Hz, C_5Me_5), 13.1 (q, J_{C-H} = 126 Hz, C_5Me_5), 32.1 (s, $C(CH_3)_3$), 32.9 (q, J_{C-H} = 125 Hz, $C(CH_3)_3$), 82.0 (s, C_5Me_5), 89.4 (s, C_5Me_5), 96.8 (s, *C*N).

(10) Crystal data for **3a**: empirical formula $C_{37}H_{53}NRu_3$, T = 153 K, λ = 0.710 69 Å, space group *C*2/*m* (No. 12), a = 17.354(2) Å, b = 18.293(3) Å, c = 11.311(2) Å, β = 106.663(7)°, V = 3439.7(10) Å^3, Z = 4, D_c = 1.574 g/cm^3. The final structure for **3a** was refined to R1 = 0.0381 and wR2 = 0.0990 for 4836 observed reflections ($I > 2\sigma$) and 153 parameters. The structure of **3b**, which contains the ^{t}Bu group inside of the Ru_3 core, was also confirmed by the X-ray studies, but precise discussion about the structural parameters was prevented due to the disordered structures around the coordinated nitrile group. The results of the diffraction studies of **3b** are given in the Supporting Information.

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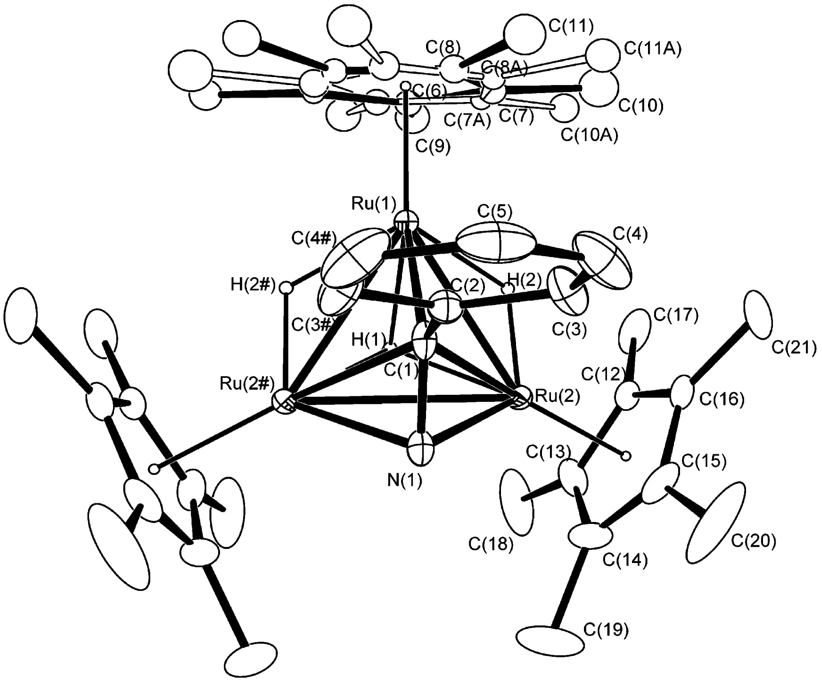

Figure 1. Molecular structure and labeling scheme of **3a** with thermal ellipsoids at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)–Ru(2), 2.7670(4); Ru(2)–Ru(2#), 2.9363(7); Ru(1)–C(1), 2.124(5); Ru(2)–C(1), 2.273(3), Ru(2)–N(1), 2.026(3); C(1)–N(1), 1.358(6); C(1)–C(2), 1.483(6); Ru(2)–Ru(1)–Ru(2#), 65.350(13); Ru(2)–Ru(1)–C(1), 53.44(9); Ru(1)–Ru(2)–Ru(2#), 57.955(8); C(1)–Ru(2)–N(1), 36.25(16); Ru(1)–C(1)–Ru(2), 78.76(18); Ru(2)–C(1)–Ru(2#), 80.47(14); Ru(1)–C(1)–N(1), 126.0(3); Ru(1)–C(1)–C(2), 117.7(3); C(2)–C(1)–N(1), 116.3(4); Ru(2)–N(1)–Ru(2#), 92.89(15).

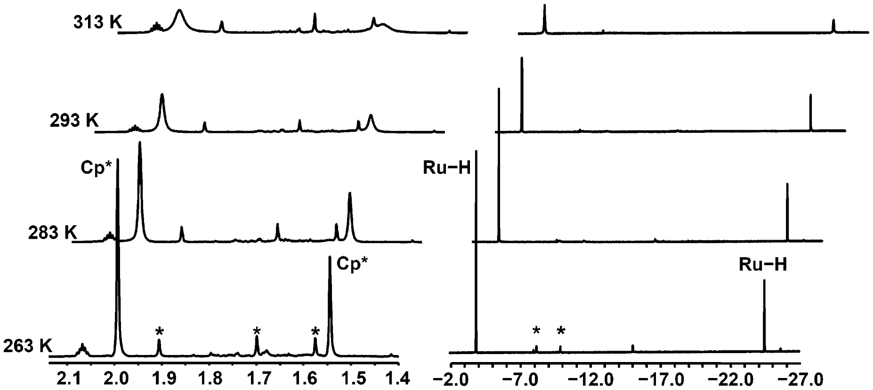

Figure 2. Variable-temperature ^{1}H NMR spectra of **3a** showing the Cp* region (left) and the hydride region (right) (400 MHz, toluene-d_8). Signals marked with asterisks are derived from a product by the thermal decomposition of **3a**.

complexes **2**, which appeared around 70 ppm.[1a] It is most likely due to hypervalency of the "inner" carbon atom, which connected with three metal centers and two carbon atoms. In addition, the ring current shield effect caused by the three Cp* groups also causes the upfield shift, which was clearly seen in the chemical shift of the ortho proton signal of the phenyl group observed at δ 6.03.

As mentioned above, the μ_3-($\perp$)-nitrile complex **3** showed marked resemblance to the μ_3-($\perp$)-alkyne complex both structurally and spectroscopically. As demonstrated by the X-ray diffraction study, the nitrile ligand acts as a 4e donor similar to the μ_3-η^2:η^2($\perp$)-alkyne ligand of **2**; thus, the lone-pair electron on the nitrogen atom should not take part in the coordination to the metal centers. Since a nitrile is commonly coordinated to a metal center with its lone pair in a κN fashion, an electrophile could not approach the lone pair directly.[12] In contrast, a lone-pair electron of the η^2-coordinated nitrile was not involved in bonding to the metal; thus, it is expected to exhibit a nucleophilic character and would provide an alternative method of nitrile functionalization. Parkin and co-workers have demonstrated direct alkylation of an η^2-coordinated nitrile to the corresponding η^2-iminoacyl complex.[13]

Addition of an equimolar amount of $HBF_4{\cdot}Et_2O$ to the diethyl ether solution of **3a** resulted in quick color change from brownish-yellow to deep purple, and formed a precipitate of a monocationic μ_3-($\perp$)-iminoacyl complex $[(Cp^*Ru)_3(\mu\text{-}\eta^2{:}\eta^2\text{-}PhCNH)(\mu_3\text{-}H)(\mu\text{-}H)_2](BF_4)$ (**4a**) in 91% yield (eq 2).[14] Treatment of **4** with a base, such as NaOMe, resulted in deprotonation of the iminoacyl group and afforded **3**. While several trimetallic μ_3-iminoacyl complexes containing an RNCR′ ligand coor-

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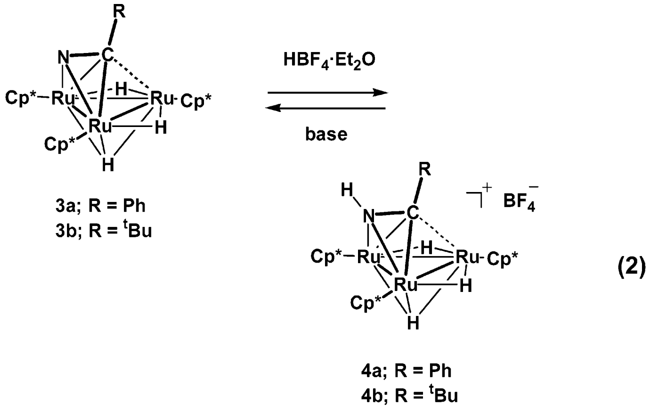

3a; R = Ph
3b; R = ^{t}Bu

4a; R = Ph
4b; R = ^{t}Bu

dinated parallel to one of the M−M bonds have been known,[15] to the best of our knowledge, this is the first example of an iminoacyl ligand coordinated to trimetallic centers in a perpendicular fashion.

Perpendicular coordination of the iminoacyl ligand was confirmed by the X-ray diffraction studies of **4a**.[16] Since there are two independent molecules in the unit cell, only one of the molecules is shown in Figure 3. The bond distance between N(1) and C(1) was 1.351(5) Å, which was nearly equal to that of **3a**. Other structural parameters of **4a** are also quite similar to those of **3a**.

In the ^{1}H NMR spectra of **4a**, a broad signal assignable to N*H* was observed at δ 12.90, which was diminished by the addition of D_2O. A downfield shift of the ^{13}C signal of the triply bridging carbon from δ 97.8 to 139.3 was observed upon protonation, which suggests that the interaction among the μ_3-carbon atom and the Ru_3 center is considerably different from that of **3a**. The stretching vibration of the N−H bond of **4a** appeared at 3233 cm^{-1} in the IR spectra.

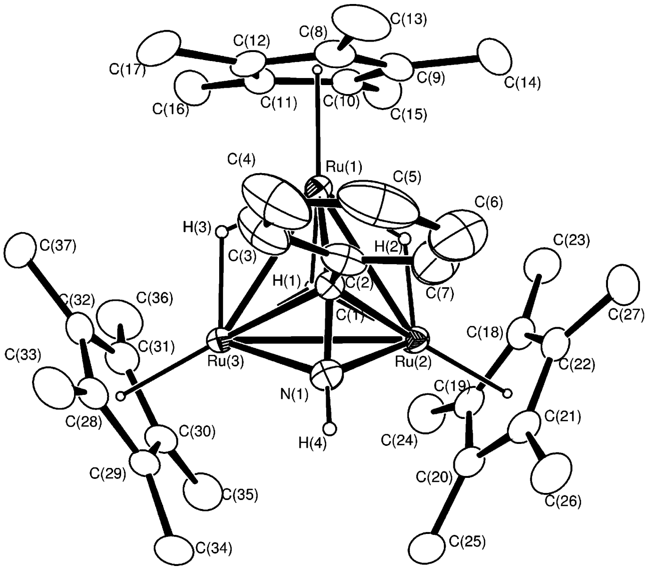

Figure 3. Molecular structure and labeling scheme of the cationic part of **4a** with thermal ellipsoids at the 40% probability level. One of the two independent molecules is shown, and the counteranion is omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2), 2.7510(5); Ru(1)−Ru(3), 2.7519(5); Ru(2)−Ru(3), 2.9830(5); Ru(1)−C(1), 2.098(4); Ru(2)−C(1), 2.310(4), Ru(2)−N(1), 2.027(4); Ru(3)−C(1), 2.354(4); Ru(3)−N(1), 2.049(3); C(1)−N(1), 1.351(5); Ru(2)−Ru(1)−Ru(3), 65.350(13); Ru(1)−Ru(2)−Ru(3), 57.190(12); Ru(1)−Ru(3)−Ru(2), 57.160(12); Ru(1)−C(1)−Ru(2), 121.6(3); Ru(2)−C(1)−Ru(3), 79.52(18); C(2)−C(1)−N(1), 115.9(4); Ru(2)−N(1)−Ru(3), 94.07(15).

When the reaction was carried out with $DBF_4{\cdot}Et_2O$, incorporation of deuterium was only observed at the N−H position. Incorporation of deuterium into the hydrido position has never been observed. This strongly indicates that protonation of **3** directly occurred at the nitrogen atom and also shows the existence of the lone pair at the nitrogen atom.

In conclusion, we have prepared triruthenium complexes containing perpendicularly coordinated nitrile and iminoacyl ligands. Such a coordination mode of the nitrile ligand as a 4e donor to a trimetallic complex is a first. Highly electron-rich ruthenium centers possessing electron-releasing Cp* groups would enable such coordination of a nitrile ligand. We are currently investigating skeletal rearrangement of the μ_3-($\perp$)-nitrile ligand on the Ru_3 plane and reactivities of the nitrile ligand, especially hydrogenation and hydration on the trimetallic cluster.

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Supporting Information Available: Text, tables, and figures giving synthetic details for compounds **3a**,**b** and **4a**,**b** and X-ray crystallographic data for **3a**,**b** and **4a**; these X-ray data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) A 50 mL Schlenk tube was charged with diethyl ether (5 mL) and **3a** (44.8 mg, 0.055 mmol). Tetrafluoroboric acid−diethyl ether complex (7.5 μL, 0.055 mmol) was added with vigorous stirring. The solution immediately turned from brownish yellow to purple, and a deep purple precipitate was formed. After 20 min of stirring, the deep purple precipitate was separated by removing the supernatant and washed five times with 5 mL of diethyl ether. The residual solid was dried in vacuo, and a 45.1 mg amount of complex **4a** was obtained as a deep purple solid (91%). Complex **4b** was obtained by a method similar to that adopted in the preparation of **4a**. NMR data for **4a**: ^{1}H NMR (400 MHz, acetone-d_6, −30 °C, TMS) δ −22.70 (s, 1H, Ru−*H*), −2.62 (s, 2H, Ru−*H*), 1.77 (s, 15H, C_5Me_5), 2.02 (s, 30H, C_5Me_5), 5.80 (d, J_{H-H} = 6.8 Hz, 2H, *o-Ph*), 6.99 (t, J_{H-H} = 7.4 Hz, 1H, *p-Ph*), 7.11 (t, J_{H-H} = 7.6 Hz, 2H, *m-Ph*), 12.90 (br s, $w_{1/2}$ = 10.3 Hz, 1H, N−*H*); ^{13}C NMR (100 MHz, acetone-d_6, −40 °C, TMS) 11.2 (q, J_{C-H} = 126.6 Hz, C_5Me_5), 11.9 (q, J_{C-H} = 126.8 Hz, C_5Me_5), 90.7 (s, C_5Me_5), 94.6 (s, C_5Me_5), 124.6 (d, J_{CH} = 158.2 Hz, *Ph*), 126.1 (d, J_{C-H} = 158.2 Hz, *p-Ph*), 128.0 (d, J_{C-H} = 159.8 Hz, *Ph*), 139.3 (s, *C*N), 142.9 (s, *ipso-Ph*). **4b**: ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, TMS) δ −24.27 (s, 1H, Ru−*H*), −2.31 (s, 2H, Ru−*H*), 0.45 (s, 9H, $C(CH_3)_3$), 1.94 (s, 30H, C_5Me_5), 2.15 (s, 15H, C_5Me_5), 12.09 (br s, $w_{1/2}$ = 22.9 Hz, 1H, N−*H*); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, TMS) 12.0 (q, J_{C-H} = 127.0 Hz, C_5Me_5), 12.7 (q, J_{C-H} = 126.6 Hz, C_5Me_5), 31.3 (q, J_{C-H} = 129.9 Hz, $C(CH_3)_3$), 39.9 (s, $C(CH_3)_3$), 89.7 (s, C_5Me_5), 95.2 (s, C_5Me_5), 153.2 (s, *C*N).

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(16) Crystal data for **4a**: empirical formula $C_{37}H_{53}BF_4NRu_3$, T = 153 K, λ = 0.710 69 Å, space group $P\bar{1}$ (No. 2), a = 10.8217(10) Å, b = 19.8704(16) Å, c = 20.0472(18) Å, α = 116.505(4)°, β = 102.326(4)°, γ = 89.202(4), V = 3752.4(6) Å^3, Z = 4, D_c = 1.598 g/cm^3. The final structure for **4a** was refined to R1 = 0.0452 and wR2 = 0.0923 for 15 265 observed reflections ($I > 2\sigma$) and 889 parameters.