*Cleavage Reactions*

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# Cleavage of the C≡N Bond on a Triruthenium Cluster: Synthesis and Structure of a Triruthenium Complex Containing a $\mu_3$-Nitrido Ligand**

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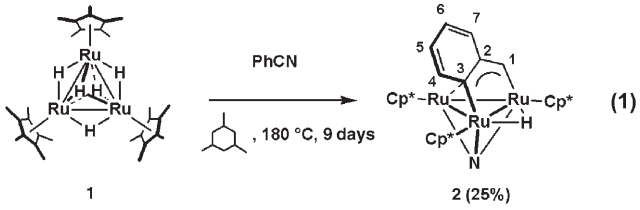
Since a nitrile group contains an sp hybridized nitrogen atom as well as dinitrogen, cleavage of the C≡N bond of nitrile is regarded as an analogue of N≡N bond activation of dinitrogen. The nitrogenase enzyme was shown to catalyze reductive cleavage of the C≡N bond of nitrile.[1] Carbon–nitrogen bond cleavage of nitrile by using the dimolybdenum sulfido complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$ ($Cp = \eta^5\text{-}C_5H_5$) under a dihydrogen atmosphere was demonstrated by Rakowski DuBois and co-workers.[2] Heterolytic cleavage of dihydrogen by the sulfido complex was proposed as a prerequisite for further C–N bond cleavage. In general, the electronic property of the hydrido ligand continuously changes from "protonic" to "hydridic" depending upon whether it is combined with a metal center, thus the polyhydrido cluster effectively cleaves the C≡N bond of nitrile. We report herein cleavage of the C≡N bond of nitrile in the reaction of a triruthenium hydrido complex.

Transformation of a nitrile ligand on a triiron framework has been elucidated in the pioneering studies performed by Kaesz and co-workers.[3] They showed step-wise reduction of a $\mu_3$-nitrile ligand to give a $\mu_3$-imido ligand through formation of a $\mu_3$-alkylideneamido complex upon treatment with dihydrogen. In spite of several studies with trimetallic carbonyl clusters of iron,[3,4] ruthenium,[5] and osmium,[6] C≡N bond cleavage has never been observed.

A $\mu_3$-nitrido-$\mu_3$-allyl complex, $[(Cp^*Ru)_3(\mu_3\text{-}N)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHC_6H_4)(\mu\text{-}H)]$ (**2**; $Cp^* = \eta^5\text{-}C_5Me_5$), was isolated from the reaction of **1** with equimolar benzonitrile at 180 °C in 25 % yield [Eq. (1)].[7] The $\mu_3$-nitrido ligand of **2** was formed




1 2 (25%) (1)

as a result of C≡N bond cleavage of benzonitrile. While there have been numerous examples of the C≡N bond cleavage of nitrile by way of hydration,[8] C≡N bond scission to form a metal nitride is rare.[9] To the best of our knowledge, this is the first example of C≡N bond cleavage performed on a trimetallic complex to form a $\mu_3$-nitrido ligand.

The molecular structure of **2** was determined by an X-ray diffraction study (Figure 1).[10] Although distinction between a $\mu_3$-nitrido and a $\mu_3$-imido ligand only on the basis of the X-ray diffraction study is difficult, the diamagnetic property of **2** rules out the presence of a $\mu_3$-NH group in **2**; an $^1$H NMR signal of the hydrido ligand was observed at $\delta = -23.02$ ppm.

This is the first example of a $\mu_3$-nitrido cluster complex for late transition metals, while several cubane-type complexes are known.[11] Structural parameters of **2** were quite similiar to those of isoelectronic and isostructural $\mu_3$-methylidyne analogue, $[(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHCMeCH)(\mu\text{-}H)]$ (**3**).[12] This implies that the $\mu_3$-nitrido ligand adopts an $sp^3$ configuration. In the case that the $\mu_3$-N ligand is a three-electron donor, complex **2** becomes diamagnetic and satisfies the 48-electron configuration. The Ru–N bond lengths (Ru(1)–N(1) = 2.037(5) Å, Ru(2)–N(1) = 1.922(6) Å, and Ru(3)–N(1) = 1.942(6) Å) are similar to those found for the $\mu_3$-imido complexes, $[\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}NR)]$ and $[(Cp^*Ru)_3(\mu_3\text{-}NR)(\mu_3\text{-}NR')(\mu\text{-}H)]$.[13]

As we reported recently, the reaction of **1** with benzonitrile at room temperature afforded a perpendicularly coordinated nitrile complex, $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2{:}\eta^2(\perp)\text{-}PhCN)(\mu_3\text{-}H)(\mu\text{-}H)_2]$ (**4**), exclusively [Eq. (2)].[14] Thus, it seems reasonable

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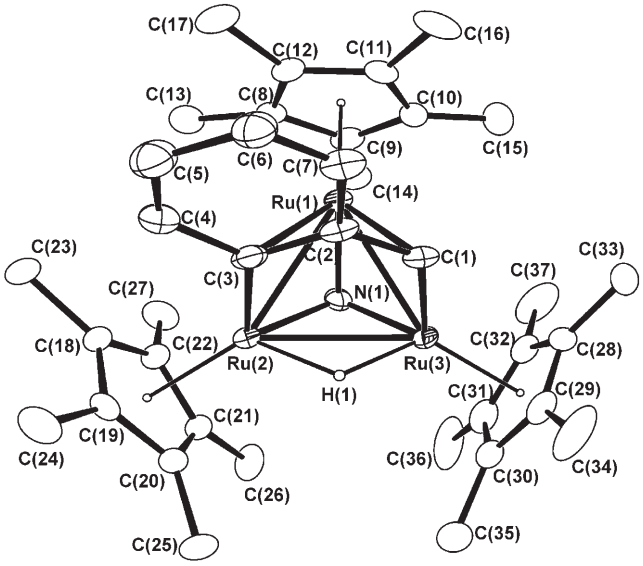
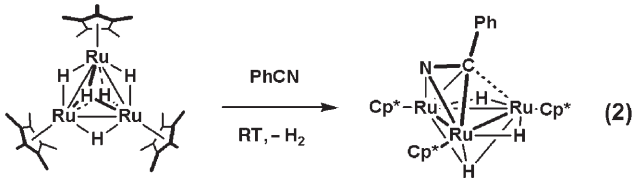
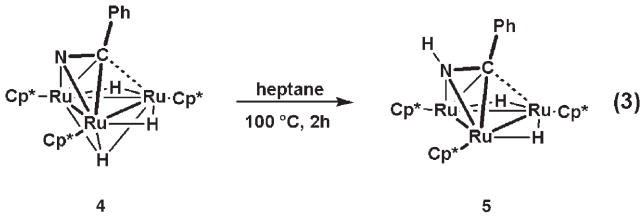



***Figure 1.*** Molecular structure and labeling scheme of **2** with thermal ellipsoids at the 30% level of probability. Selected bond lengths [Å] and angles [°]: Ru(1)–Ru(2) 2.6660(8), Ru(2)–Ru(3) 2.7432(8), Ru(1)–Ru(3) 2.6623(7), Ru(1)–N(1) 2.037(5), Ru(2)–N(1) 1.922(6), Ru(3)–N(1) 1.942(6), Ru(1)–C(1) 2.185(7), Ru(1)–C(2) 2.266(7), Ru(1)–C(3) 2.266(7), Ru(2)–C(3) 2.045(8), Ru(3)–C(1) 1.982(7), C(1)–C(2) 1.402(10), C(2)–C(3) 1.446(11), C(3)–C(4) 1.446(10), C(4)–C(5) 1.365(11), C(5)–C(6) 1.432(12), C(6)–C(7) 1.319(11), C(2)–C(7) 1.475(10); Ru(2)-Ru(1)-Ru(3) 61.97(2), Ru(1)-Ru(2)-Ru(3) 58.95(2), Ru(1)-Ru(3)-Ru(2) 59.08(2), Ru(1)-N(1)-Ru(2) 84.6(2), Ru(2)-N(1)-Ru(3) 90.4(3), Ru(1)-N(1)-Ru(3) 83.9(2), Ru(2)-C(3)-C(2) 123.2(5), Ru(3)-C(1)-C(2) 126.0(6), C(1)-C(2)-C(3) 118.5(6).




to suppose that the C≡N bond cleavage proceeds through the formation of **4**. In complex **4**, bonding interaction between metal centers and *ortho* protons at the phenyl group was negligible, which clearly indicates that orthometalation is not prerequisite for the C–N bond cleavage. Perpendicular coordination of benzonitrile seems to be rather important as shown below.

Thermolysis of **4** at 180 °C afforded complex **2**. In addition, when the reaction was carried out at a lower temperature, another intermediate for the C≡N bond cleavage was observed. Thermolysis of **4** at 100 °C in heptane resulted in the quantitative formation of a perpendicularly coordinated $\mu_3$-iminoacyl complex, $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}PhCNH)(\mu\text{-}H)_2]$ (**5**) [Eq. (3)].[15] The structure of **5** is comparable to that of the cationic $\mu_3$-iminoacyl complex, $[(Cp^*Ru)_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}PhCNH)(\mu\text{-}H)_2(\mu_3\text{-}H)][BF_4]$ (**6**), obtained by the protonation of **4**.[14] Complex **5** is soluble in nonpolar solvents, whereas cationic **6** is not.




The free nitrogen lone-pair in **4** remains uncoordinated and can be readily protonated to give **6**. Thus, the formation of the $\mu_3$-iminoacyl ligand of **5** can be understood in terms of electrophilic migration of a hydrido ligand to the nitrogen atom. The rate of the reaction, however, is comparable to that carried out in THF, which implies that the rate-determining step for the transformation from **4** into **5** is the intramolecular hydrido shift to the nitrogen atom.

A broad signal for the newly formed N–H bond of **5** was observed in the $^1$H NMR spectrum of the product at $\delta =$ 11.24 ppm. This signal immediately disappeared on addition of $CD_3OD$, which reveals the protonic character of the hydrogen bound at the iminoacyl group. In the $^{13}$C NMR spectrum of **5**, a singlet stemming from the iminoacyl carbon was observed upfield ($\delta = 96.0$ ppm) in comparison to the triply bridging carbon atom of a $\mu_3$-alkylidyne or a $\mu_3$-acetylide ligand, and the chemical shift of $\delta = 96.0$ ppm is comparable to that of the $\mu_3(\perp)$-nitrile carbon of **4** ($\delta =$ 97.8 ppm).[14]

The signal that arises from two hydrido ligands of **5** appears at $\delta = -7.89$ ppm as a singlet in the $^1$H NMR spectrum. The shape of this signal remains unchanged over the temperature range from −20 to 50 °C. In contrast, signals for the Cp* groups observed at $\delta = 1.77$ and 1.90 ppm at −10 °C coalesce into one signal at 35 °C, which shows that the $\mu_3$-iminoacyl ligand of **5** exhibits dynamic behavior similar to that of the $\mu_3$-nitrile ligand of **4**. This dynamic behavior is rationalized by the switchback motion of the $\mu_3$-iminoacyl ligand, which has been already reported for **4**[14] and the ($\perp$)-alkyne complexes.[16] The activation parameters for this motion are estimated to be $\Delta H^{\neq} = 16.4 \pm 0.2$ kcal mol$^{-1}$ and $\Delta S^{\neq} = 2.9 \pm 0.7$ cal mol$^{-1}$ K$^{-1}$ on the basis of the variable-temperature NMR studies (see Supporting Information).

The presence of perpendicular coordination of the $\mu_3$-iminoacyl ligand was established by X-ray diffraction studies of **5** on a single red crystal obtained from cold diethyl ether (see Figure 2).[10] The carbon–nitrogen bond was arranged on the crystallographic mirror plane bisecting the $Ru_3$ triangle, and the nitrogen atom was oriented outside the $Ru_3$ core. The C(1)–N(1) bond of 1.391(6) Å is longer than in **4** (1.358(6) Å)[14] and represents an intermediate value between that of a carbon–nitrogen single bond (1.45 Å) and carbon–nitrogen double bond (1.28 Å). This value lies in the range of the C–N bond lengths reported for the trimetallic $\mu_3$-iminoacyl complexes that contain an acyclic RNCR′ ligand coordinated parallel to one of the M–M bonds (1.280–1.412 Å).[3c,6b17]

Conversely, the Ru(1)–C(1) bond (2.010(5) Å) is significantly shorter than in **4** (2.124(5) Å).[14] These structural features, namely, the long C–N bond and the short Ru–C

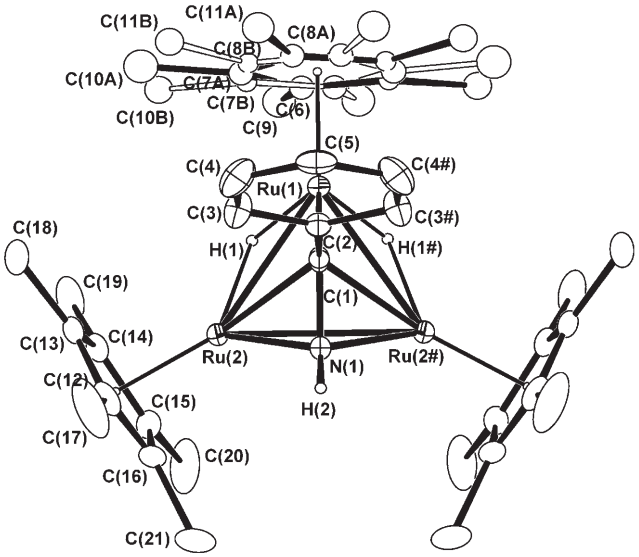
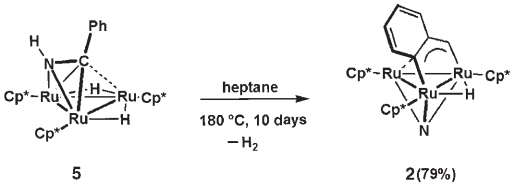



***Figure 2.*** Molecular structure and labeling scheme of **5** with thermal ellipsoids at the 30% level of probability. Selected bond lengths [Å] and angles [°]: Ru(1)–Ru(2) 2.7790(7), Ru(2)–Ru(2#) 3.0826(11), Ru(2)–N(1) 2.017(3), Ru(1)–C(1) 2.010(5), Ru(2)–C(1) 2.369(4), N(1)–C(1) 1.391(6); Ru(2)-Ru(1)-Ru(2#) 67.375(8), Ru(1)-Ru(2)-Ru(2#) 56.314(12), Ru(2)-N(1)-Ru(2#) 99.68(19), Ru(2)-C(1)-Ru(2#) 81.17(15), Ru(1)-C(1)-N(1) 120.5(4), Ru(1)-C(1)-C(2) 124.2(3), N(1)-C(1)-C(2) 115.4(4).

bond, indicate strong back-donation from the ruthenium centers to the π*(CN) orbital, and the C–N bond is liable to be cleaved by thermolysis as a result of the strong back-donation. In contrast, structural parameters of the cationic $\mu_3$-iminoacyl complex **6** were similar to those of **4**,[14] and the C–N bond of the $\mu_3$-iminoacyl ligand of **6** is not cleaved by thermolysis.

Migration of a hydride to the nitrile ligand lowers the bond order of the C–N bond. At the same time, it causes an increase in the electron density at the ruthenium centers. The carbon–nitrogen multiple bond scission on the hydrido cluster arises from such ambivalent roles of the hydrido ligand.

The $\mu_3$-nitrido complex **2** was irreversibly formed in 79% yield by the thermolysis of **5** at 180 °C [Eq. (4)]. One plausible




5 2(79%) (4)

mechanism for the carbon–nitrogen bond cleavage is the "edge" pathway, which was proposed for the carbon–carbon bond scission of a perpendicularly coordinated alkyne ligand.[18] Such perpendicular coordination seems to be effective for back-donation from metal centers to the π*(CN) orbital. In the reaction of the ditungsten complex $[W_2(OCMe_2CF_3)_6]$ with nitrile, an intermediate with a perpendicularly coordinated nitrile ligand to the W–W bond has been proposed for the formation of a nitrido complex by Chisholm and co-workers.[9d] Hidai and co-workers elucidated that strong π donation from a low-valent metal center enhances nucleophilicity of the cyano carbon atom, which causes double protonation at this atom leading to C≡N bond scission.[9e–g]

These sequential transformations from **4** into **2** provide mechanistic insight into the reductive cleavage of a carbon–nitrogen multiple bond on a polyhydrido cluster. The ambivalent nature of the hydrido ligand is essential for the activation of the substrate. The importance of the heterolytic activation of dihydrogen to generate a proton has been also noted by Rakowski DuBois and co-workers in the C≡N bond cleavage by the dimolybdenum sulfido complex.[2]

In summary, $\mu_3$-$\eta^2$:$\eta^2$(⊥)-iminoacyl complex **5** was formed upon thermolysis of the $\mu_3$-$\eta^2$:$\eta^2$(⊥)-nitrile complex **4**. Migration of a hydrido ligand to the nitrogen atom causes elongation of the carbon–nitrogen bond as well as shortening of the ruthenium–carbon bond, which facilitates the carbon–nitrogen bond cleavage leading to the formation of **2**. We are currently investigating skeletal rearrangement of the $\mu_3$-(⊥)-nitrile ligand on the $Ru_3$ plane in the presence of dihydrogen in relation to hydrogenation of the C≡N bond.

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[7] A 50 mL glass autoclave was charged with 1,3,5-trimethylcyclohexane (3 mL), benzonitrile (6.8 μL, 0.067 mmol), and **1** (47.6 mg, 0.068 mmol). The reaction mixture was then stirred at 180 °C for 9 days, during which, the solution changed from brown to brownish-yellow. The solvent was removed under reduced pressure and the residual solid was purified by column chromatography on alumina (Merck, Art. No. 1097) with tetrahydrofuran/methanol 1:1. A third brownish-yellow band which included **2** was collected, and the solvent was removed under reduced pressure. Complex **2** was obtained as an ocher solid (13.3 mg, 25% yield). NMR data for **2**: $^1$H NMR (400 MHz, [D$_6$]benzene, 23 °C, TMS): $\delta = -23.02$ (s, 1H; Ru-H), 1.33 (s, 15H; Cp*), 1.89 (s, 15H; Cp*), 1.94 (s, 15H; Cp*), 6.82 (dd, $^3J$(H,H) = 8.8, 6.0 Hz, 1H; C5-H or C6-H), 7.09 (dd, $^3J$(H,H) = 8.0, 6.4 Hz, 1H; C5-H or C6-H), 7.27 (d, $^3J$(H,H) = 8.4 Hz, 1H; C4-H or C7-H), 7.59 (d, $^3J$(H,H) = 8.4 Hz, 1H; C4-H or C7-H), 9.28 ppm (s, 1H; C1-H). $^{13}$C NMR (100 MHz, [D$_6$]benzene, 23 °C): $\delta = 10.2$ (q, $^1J$(C,H) = 128.0 Hz; C$_5$*Me*$_5$), 11.5 (q, $^1J$(C,H) = 127.1 Hz; C$_5$*Me*$_5$), 11.6 (q, $^1J$(C,H) = 127.1 Hz; C$_5$*Me*$_5$), 95.7 (s; *C*$_5$Me$_5$), 99.3 (s; *C*$_5$Me$_5$), 99.5 (s; *C*$_5$Me$_5$), 112.8 (s; C2), 119.4 (d, $^1J$(C,H) = 157.6 Hz; C5 or C6), 129.5 (d, $^1J$(C,H) = 151.8 Hz; C5 or C6), 131.9 (d, $^1J$(C,H) = 160.0 Hz; C4 or C7), 149.1 (d, $^1J$(C,H) = 158.8 Hz; C4 or C7), 166.5 (s; C3), 187.4 ppm (d, $^1J$(C,H) = 147.7 Hz; C1).

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[10] X-ray Crystallography: All data were collected on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 153 K (for **2**) and 123 K (for **5**). Cell refinement and data reduction were performed by using the Process-Auto program. The structures were solved by the Patterson method (Shelx-97) and refined by least-squares methods based on $F^2$ (Shelxl-97). Crystal data for **2**·0.5 C$_4$H$_{10}$O: empirical formula $C_{39}H_{56}NO_{0.5}Ru_3$, $M_r = 850.06$, crystal size 0.22 × 0.13 × 0.01 mm, space group $P2_1/c$ (No. 14), $a = 10.8725(13)$, $b = 31.844(4)$, $c = 20.632(3)$ Å, $\beta = 101.705(5)°$, $V = 6994.6(14)$ Å$^3$, $Z = 8$, $\rho_{calcd} = 1.614$ Mg m$^{-3}$, $\mu(Mo_{K\alpha}) = 1.308$ mm$^{-1}$, $2\theta_{max} = 60.0°$. Of the 76184 reflections that were collected, 20658 were unique ($R_{int} = 0.0953$), $R_1 = 0.0715$ [$I > 2\sigma(I)$], $wR_2 = 0.1558$ [$I > 2\sigma(I)$], max./min. residual electron densities 1.994/−3.047 e Å$^{-3}$. Crystal data for **5**: empirical formula $C_{37}H_{53}NRu_3$, $M_r = 815.04$, crystal size 0.15 × 0.15 × 0.01 mm, space group *C*2/*m* (No. 12), $a = 17.167(5)$, $b = 18.424(6)$, $c = 11.378(4)$ Å, $\beta = 104.813(13)°$, $V = 3479.2(19)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.556$ Mg m$^{-3}$, $\mu(Mo_{K\alpha}) = 1.310$ mm$^{-1}$, $2\theta_{max} = 60.0°$. Of the 20761 reflections that were collected, 5197 were unique ($R_{int} = 0.0531$), $R_1 = 0.0437$ [$I > 2\sigma(I)$], $wR_2 = 0.1060$ [$I > 2\sigma(I)$], max./min. residual electron densities 1.210/−1.610 e Å$^{-3}$. CCDC-278456 (**2**) and CCDC-283543 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[15] A 20 mL glass tube equipped with a greaseless valve was charged with heptane (10 mL) and **4** (57.2 mg, 0.070 mmol). The reaction mixture was stirred at 100 °C for 2 h, during which, the solution turned from brownish-yellow to brown. The solvent was removed under reduced pressure and complex **5** was obtained as a brown solid (52.3 mg, quantitative). NMR data for **5**: $^1$H NMR (400 MHz, [D$_6$]benzene, 23 °C, TMS): $\delta = -7.89$ (s, 2H; Ru-H), 1.77 (brs, $w_{1/2} = 9.3$ Hz, 30H; Cp*), 1.90 (brs, $w_{1/2} = 21.6$ Hz, 15H; Cp*), 6.39 (d, $^3J$(H,H) = 8.4 Hz, 2H; *o*-Ph), 6.63 (t, $^3J$(H,H) = 8.0 Hz, 2H; *m*-Ph), 6.79 (t, $^3J$(H,H) = 8.0 Hz, 1H; *p*-Ph), 11.24 ppm (brs, $w_{1/2} = 9.5$ Hz, 1H; N-H). $^{13}$C NMR (100 MHz, [D$_6$]benzene, 23 °C): $\delta = 12.2$ (brq, $w_{1/2} = 18.4$ Hz; C$_5$*Me*$_5$), 12.6 (brq, $w_{1/2} = 12.7$ Hz; C$_5$*Me*$_5$), 80.0 (brs, $w_{1/2} = 8.6$ Hz; *C*$_5$Me$_5$), 90.6 (brs, $w_{1/2} = 10.0$ Hz; *C*$_5$Me$_5$), 96.0 (s; CN), 125.9 (Ph), 126.7 (Ph), 131.9 (Ph), 151.9 ppm (s; *ipso*-Ph).

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