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Mechanism of the Interconversions between *C*- and *N*-Bound Transition Metal α-Cyanocarbanions

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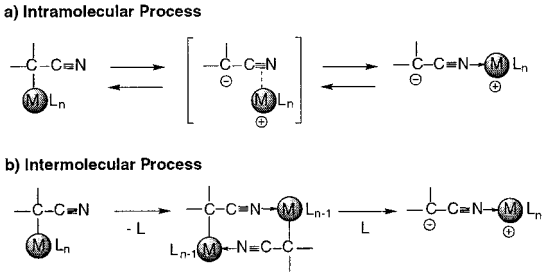
Compared to the marked progress in the chemistry of transition metal enolates,[1] much less has been made on the studies on the structure and reactivity of transition metal α-cyanocarbanions.[2,3] Recently, we reported the first interconversion between *C*- and *N*-bound transition metal α-cyanocarbanions after success in obtaining their exact isomers.[4] The elucidation of the mechanism of the *C*−*N* interconversion is a subject of great urgency, since it could be a crucial step for a new family of catalytic C−C bond formations via α-C−H activation of nitriles.[5] The movement of the metal fragments in the *C*−*N* interconversion is also of particular interest in view of linkage isomerism,[6] because of ambiguities arising from the exceptionally long distance between each binding site on the α-cyanocarbanion moieties. In this communication we describe the first mechanistic rationale on the *C*-to-*N* and *N*-to-*C* isomerizations of transition metal α-cyanocarbanions, including the intramolecular processes with the unprecedented participation of intermolecular process via self-assembly of metals as shown in Scheme 1.

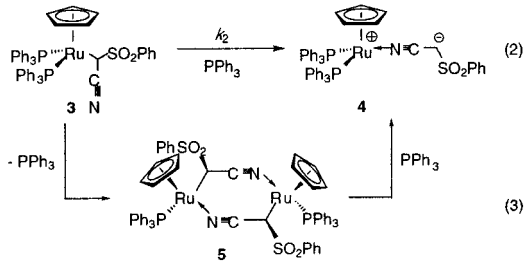
Scheme 1



As a suitable model system for the kinetic studies on the *N*-to-*C* isomerization, we designed and prepared a pair of the *C*- and *N*-bound isomers of isonitrile complexes $Ru^+Cp(NCCH^-SO_2Ph)(PPh_3)$(CN-*t*-Bu) (**1**) and $RuCp[CH(CN)SO_2Ph](PPh_3)$(CN-*t*-Bu) (**2**).[7] Due to their strong π-acidity isonitrile ligands have proven to show a remarkable acceleration effect for the *N*-to-*C* isomerizations, and the reaction of **1** to **2** proceeds irreversibly under milder conditions than those of any other *N*-bound bis-phosphine complex.[4] Kinetic studies on the isomerization of **1** in benzene-d_6 were carried out by means of ^{1}H NMR analysis using internal standard (bibenzyl). The consumption rate of **1** exhibited clean first-order dependence on the concentration of **1** at 333−348 K ($[\mathbf{1}]_0 = 2.00 \times 10^{-2}$ M), and the first-order rate constants k_1 were determined to be $8.96(2) \times 10^{-6}$ s^{-1} (333 K), $1.574(7) \times 10^{-5}$ s^{-1} (338 K), $2.89(2) \times 10^{-5}$ s^{-1} (343 K), and $4.853(3) \times 10^{-5}$ s^{-1} (348 K), respectively.[8] The rate data correlate well ($R^2 = 0.999$) with Eyring relationship of $\ln(k_1/T)$ versus $1/T$, where the activation parameters $\Delta H^‡$ and $\Delta S^‡$ were determined to be 107 ± 2 kJ·mol^{-1} and -22 ± 5 J·K^{-1}·mol^{-1}, respectively. The first-order kinetics clearly indicates that the reaction proceeds in an intramolecular manner. To gain insight into the intramolecular mechanism, kinetics on the reactions of **1** with an excess amount of external ligands such as PPh_3, CH_3-CN, and *t*-BuNC were carried out at 333 K in benzene-d_6 using similar NMR technique ($[\mathbf{1}]_0 = 2.00 \times 10^{-2}$ M, $[\text{ligand}]_0 = 8.00 \times 10^{-2}$ M). All reactions afforded exclusive formation of **2** with the clean first-order kinetics, where the observed first-order rate constants k_1 were almost same as that obtained in the absence of PPh_3 (PPh_3: $8.91(5) \times 10^{-6}$ s^{-1}; CH_3CN: $8.67(8) \times 10^{-6}$ s^{-1}; *t*-BuNC: $8.86(9) \times 10^{-6}$ s^{-1}). The reaction in $CDCl_3$ also afforded a similar k_1 value of $8.99(3) \times 10^{-6}$ s^{-1}. These results exclude the possibility of the formation and rebound of a 16-electron ion pair intermediate $[RuCp(PPh_3)(CN\text{-}t\text{-}Bu)]^+(NCCH^-SO_2Ph)$, concluding that the *N*-to-*C* isomerization proceeds intramolecularly without dissociation of any ligand.

(1)

The irreversible transformation of $RuCp[CH(CN)SO_2Ph](PPh_3)_2$ (**3**) into $Ru^+Cp(NCCH^-SO_2Ph)(PPh_3)_2$ (**4**)[4] has been investigated as a representative *C*-to-*N* isomerization. The reaction courses for the isomerization of **3** in benzene-d_6 at 313−373 K were monitored by the similar ^{1}H NMR analysis ($[\mathbf{3}]_0 = 1.00-3.00 \times 10^{-2}$ M). In all cases most of complex **3** was consumed at the early stage of the reactions, accompanying with the formation of product **4**, coordination dimer (R_{Ru}*,S_C*,R_{Ru}*,S_C*)-{$RuCp[CH(CN)SO_2Ph](PPh_3)$}$_2$ (**5**), and its minor diastereomer **6**.[9,10] Prolonged reactions at 348 and 373 K afforded faster decays of [**5**] and [**6**] with the corresponding increment of [**4**] after complete consumption of **3**, while the reaction profile at 313 K showed only a slight decline of these dimer species, suggesting temperature-dependent participation of the intermolecular process in the *C*- to-*N* isomerizations.



(2)

(3)

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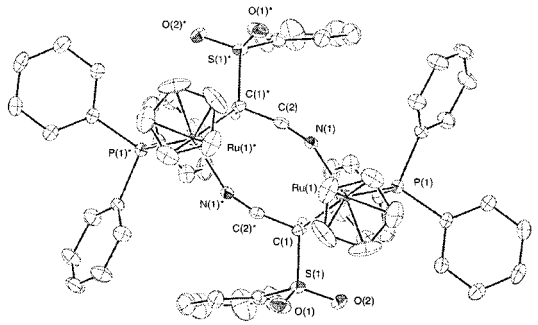

Figure 1. Molecular structure of **5**. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg.): Ru(1)−C(1), 2.220(5); C(1)−C(2)*, 1.449(8); C(2)−N(1), 1.145(7); N(1)−Ru(1), 2.073(4); Ru(1)−C(1)−C(2)*, 103.8(3); C(1)−C(2)*−N(1)*, 168.8(5); C(2)−N(1)−Ru(1), 156.7(4); N(1)−Ru(1)−C(1), 80.5(2).

To verify the presence of the intramolecular process, kinetic studies on the reaction of **3** with an excess amount of PPh_3 in benzene-d_6 (eq 2) were carried out by ^{1}H NMR analysis ($[\mathbf{3}]_0 = 2.00 \times 10^{-2}$ M, $[PPh_3]_0 = 4.00 \times 10^{-1}$ M). The formation of the coordination dimers was retarded to negligible amounts (<1%), and the consumption rate of **3** showed clean first-order dependence on [**3**] at 333−348 K. From the obtained first-order rate constants k_2: $1.31(1) \times 10^{-4}$ s^{-1} (333 K); $2.52(2) \times 10^{-4}$ s^{-1} (338 K); $4.70(7) \times 10^{-4}$ s^{-1} (343 K); $7.50(20) \times 10^{-4}$ s^{-1} (348 K), the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were estimated to be 121 ± 1 kJ·mol^{-1} and 42 ± 4 J·K^{-1}·mol^{-1} by the satisfactory Eyring relationship ($R^2 = 1.000$), indicating the intramolecular process in the *C*-to-*N* isomerization of **3**.

Cleavage of dimer species **5** (see Figure 1 for the structure of **5**) with PPh_3 was examined to clarify the suggested intermolecular pathway. When a 1.25 mM solution of **5** in benzene was heated at 373 K in the presence of PPh_3 (4 equiv), the dimeric structure was collapsed to afford *N*-bound complex **4** in a quantitative yield (eq 3). The reaction course of the cleavage of **5** with an excess amount of PPh_3 (40 equiv) at 313 K in benzene-d_6 showed that the concentrations of **3** and **4** increase with good linear time-dependence until conversion of **5** reaches up to 20%. The observed rate constants for the initial formation of **3** and **4** ($k_{obs} = d[\mathbf{3}]/dt$, $d([\mathbf{4}]/dt)$ were estimated to be $5.44(11) \times 10^{-8}$ M·s^{-1} ($R^2 = 0.996$) and $1.03(2) \times 10^{-8}$ M·s^{-1} ($R^2 = 0.998$), the latter of which is 1.5 times larger than that for the initial formation of **4** obtained in the *C*-to-*N* isomerization of **3** under similar conditions ($6.67(12) \times 10^{-9}$ M·s^{-1}, $R^2 = 0.994$).[11] These results clearly indicate the presence of both C−Ru and N−Ru scissions in the cleavage of **5**, showing the inclusion of the intermolecular process in the *C*-to-*N* isomerization of **3**.

The schematic representation of intramolecular pathways for the *C*-to-*N* and *N*-to-*C* isomerizations are shown in Scheme 1a, where the metal fragments would undergo slippage on the C−C−N surfaces and η^1-η^2 conversion on the coordinated nitriles. The wide-angle rotation of the η^1-η^2 conversion can be rationalized by assuming the bent azaallenyl intermediates (M−N═C═C). Acceleration with isonitriles could be arising from the ligand-assisted enhancement of this initiating step. The intermolecular pathway participates only in the *C*-to-*N* isomerization as shown in Scheme 1b. Due to requirement for the severe conditions in the cleavage of the coordination dimers, the intermolecular process is accompanied with the intramolecular one with high temperature dependence. This is a quite rare example of molecular transformations driven by the formation and cleavage of the molecular assemblies.

In conclusion, we have shown the first presentation of the intra- and intermolecular mechanism of *C*−*N* interconversions of transition metal α-cyanocarbanions. The results will provide significant information on the controlled generation of *N*-bound α-cyanocarbanion active species[3c−e,5b] for catalytic C−C bond forming reactions of nitriles. Further studies are currently in progress.

Supporting Information Available: Experimental details for all reactions, representative kinetic data for the isomerizations of **1** and **3**, crystallographic data for **1**, (R_{Ru}*,S_C*)-**2** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Zwitterionic and α-metalated structures of **1** and (R_{Ru}*,S_C*)-**2** (major diastereomer) have been confirmed by X-ray diffraction. **1**: orthorhombic, $P2_12_12_1$ (No. 19), $a = 17.95$ (1) Å, $b = 20.169$ (6) Å, $c = 10.467$ (5) Å, $V = 3790(2)$ Å^3, $Z = 4$, R = 0.040, wR^2 = 0.114, GOF = 1.01. (R_{Ru}*,S_C*)-**2**: triclinic, *P*-1 (No. 2), $a = 12.77$ (1) Å, $b = 13.09$ (6) Å, $c = 11.292$ (6) Å, $a = 98.67$ (6), $b = 91.78$ (7), $g = 61.87$ (4), $V = 1643$ (2) Å^3, $Z = 2$, R = 0.031, wR^2 = 0.067, GOF = 1.01.

(8) ^{1}H NMR monitoring showed that the concentration of **1** declines with constant and exclusive formation of 59:41 mixture of (R_{Ru}*,S_C*)- and (R_{Ru}*,R_C*)-**2**, which indicates that the consumption rate of **1** can be regarded as a sum of the rate of two independent isomerizations; **1** to (R_{Ru}*,S_C*)- and (R_{Ru}*,R_C*)-**2**. These diastereomers were also confirmed to be inert under the kinetic conditions.

(9) The reaction of **3** in benzene at room temperature gives a 73:27 mixture of **5** and **6**, while similar treatment in THF affords **5** (22%) as a sole diastereomer (eq 3). Selected characterization data: **5**: IR (KBr) 2195 (CN) cm^{-1}; ^{1}H NMR (270 MHz, C_6D_6) δ 2.95 (d, $J = 5.0$ Hz, 2 H, C*H*CN), 4.75 (s, 10 H, CpH); FABMS *m*/*z* 1218 [M]$^+$. **6**: ^{1}H NMR (270 MHz, C_6D_6) δ 4.18 (d $J = 1.5$ Hz, 1 H, C*H*CN), 4.22 (d, $J = 4.2$ Hz, 1 H, C*H*CN), 4.63 (s, 10 H, CpH); FABMS *m*/*z* 1218 [M]$^+$. Considering from unsymmetrical H(1) NMR signals of **6**, the stereochemistry of **6** was assigned to be (R_{Ru}*,R_C*,R_{Ru}*,S_C*) or (R_{Ru}*,R_C*,S_{Ru}*,R_C*).

(10) μ^2-*C*,*N*-Bound structure of the dimer species has been unequivocally established by X-ray analysis of **5** as shown in Figure 1, although it has been lying on the level of speculation in the literatures: (a) Cummins, D.; Higson, B. M.; McKenzie, E. D. *J. Chem. Soc., Dalton* **1973**, 414. (b) Ros, R.; Renaud, J.; Roulet, R. *Helv. Chim. Acta* **1975**, *58*, 133. (c) Oehme, G.; Röber, K.-C.; Pracejus, H. *J. Organomet. Chem.* **1976**, *105*, 127. (d) References 1d, 2c. Crystallographic data for **5**: monoclinic, *C*2/*c*, $a = 17.430$ (3) Å, $b = 16.621$ (5) Å, $c = 21.903$ (3) Å, $b = 96.88$ (1)°, $V = 6299$ (2) Å^3, $Z = 8$, R = 0.054, wR^2 = 0.136, GOF = 1.00.

(11) The kinetic data were obtained by the similar ^{1}H NMR analysis of the isomerization of **3** in the presence of excess PPh_3 in benzene-d_6 at 313 K until 10% conversion ($[\mathbf{3}]_0 = 1.71 \times 10^{-3}$ M, $[PPh_3]_0 = 6.83 \times 10^{-2}$ M).

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