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Synthesis and Characterization of *C*- and *N*-Bound Isomers of Transition Metal α-Cyanocarbanions

Takeshi Naota,* Akio Tannna, and Shun-Ichi Murahashi*

Department of Chemistry
Graduate School of Engineering Science
Osaka University, Machikaneyama
Toyonaka, Osaka 560-8531, Japan

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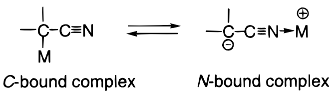
Transition metal α-cyanocarbanions are the subjects of considerable attention in relation to the enolate chemistry of transition metals,[1] and also as a key intermediate for a family of catalytic carbon−carbon bond forming reactions of nitriles with electrophiles under neutral conditions.[2,3] According to numerous studies on the preparation of transition metal α-cyanocarbanions, two types of structures, *C*-[1,4] and *N*-bound ones,[2b,5,6] are known as stable forms. The *C*-bound complexes have been widely used as α-cyanoalkylating reagents,[1] while the *N*-bound ones, derived by α-C−H activation of nitriles, have recently proven to be active species for catalytic aldol and Michael reactions of nitriles.[2b,5a] The basic studies on the dynamic behavior of *C*- and *N*-bound complexes, e.g., reactivities toward electrophiles and interconversions, are of particular importance since they will provide significant information on the design and creation of novel C−C bond forming process of nitriles via α-C−H activation.[2,3] Synthesis of both exact isomers will lead us directly to the systematic investigations; however, difficulties in obtaining the isomers have long been preventing such a study.



As a part of the program aiming at the development of novel catalytic C−C bond forming reactions of nitriles,[2] we are investigating the structure and reactivity of transition metal α-cyanocarbanion intermediates. We have designed a model system for ruthenium phosphine complexes of α-cyanocarbanion bearing an α-sulfonyl group, whose small contribution to the resonance structure of enolate enables both isomers to be present in a stable form. In this paper, we describe the first synthesis of *C*- and *N*-bound isomers of transition metal α-cyanocarbanion, $\mathrm{RuCp[CH(CN)SO_2Ph](PR_3)_2}$ (**1**) and $\mathrm{Ru^+Cp(NCCH^-SO_2Ph)(PR_3)_2}$ (**2**), and the first observation of their specific isomerizations.

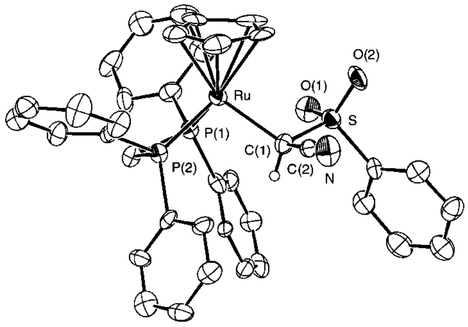


Figure 1. Molecular structure of **1b**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru−P(1), 2.290(3); Ru−P(2), 2.289(3); Ru−C(1), 2.17(1); S−C(1), 1.80(1); C(1)−C(2), 1.45(2); C(2)−N, 1.17(1); S−O(1), 1.429(8); S−O(2), 1.445(8); P(1)−Ru−P(2), 71.8(1); P(1)−Ru−C(1), 92.0(3); P(2)−Ru−C(1), 101.7(3); Ru−C(1)−S, 112.4(5); Ru−C(1)−C(2), 113.1(8); S−C(1)−C(2), 107.7(8).

The reaction of $\mathrm{RuCpCl(PPh_3)_2}$ with the sodium salt of (phenylsulfonyl)acetonitrile in EtOH/toluene (1:1) under argon atmosphere at 25 °C gave the corresponding *N*-bound complex, $\mathrm{Ru^+Cp(NCCH^-SO_2Ph)(PPh_3)_2}$ (**2a**), as the sole product in 89% yield. When a similar reaction was carried out in EtOH/hexane (1:1), the corresponding *C*-bound isomer, $\mathrm{RuCp[CH(CN)SO_2Ph]}$-$\mathrm{(PPh_3)_2}$ (**1a**), was formed as a 59:41 mixture of **1a** and **2a**. Filtration of the precipitate under argon atmosphere gave pure **1a** in 37% yield. Various *N*- and *C*-bound complexes of tertiary phosphines can be prepared either by a similar treatment of $\mathrm{RuCpCl(PR_3)_2}$ or the ligand exchange of **1a** or **2a** with phosphines. These complexes are characterized by ^{1}H, ^{13}C NMR, IR, mass spectra, and elemental analyses.

The almost complete α-metalated and zwitter ionic structures of the *C*- and *N*-bound complexes have been unequivocally established by X-ray analysis. Figure 1 shows the molecular structure of $\mathrm{RuCp[CH(CN)SO_2Ph](dppm)}$ (**1b**, dppm = $\mathrm{Ph_2PCH_2}$-$\mathrm{PPh_2}$).[7] The Ru−C(1) bond distance (2.12 Å) lies in the range of a normal metal−carbon single bond of $\mathrm{MCH_2CN}$ (2.1−2.2 Å).[4d,f,g] The bond angles around the C(1) atom indicate sp^3 configuration of C(1). The C(2)−N bond distance (1.18 Å) is within the normal range of the CN triple bond of free nitrile, and the C(1)−C(2)−N bond angle is almost linear (178°). These observations show the carbon−metal bond of **1b** has complete σ-character and any contribution to η^2-coordination is negligible. The molecular structure of *N*-bound complex **2a** is illustrated in Figure 2.[7] The

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(6) Linear zwitter ion ($\mathrm{M^+{-}NC{-}C^-R^1R^2}$) and bent azaallene ($\mathrm{M{-}N{=}C{=}CR^1R^2}$) structures have been an argument for the *N*-bound complex of transition metals; however, the reported X-ray analyses indicate a strong contribution of zwitter ionic structure.[2b,5a−h]

(7) Crystallographic data. **1b**: orthorhombic, *Pbca*, $a = 42.400(1)$ Å, $b = 19.648(7)$ Å, $c = 17.943(8)$ Å, $V = 14947(8)$ Å^3, $Z = 16$, $R = 0.055$, $R_w = 0.069$, GOF = 1.74. **2a**: monoclinic, $P2_1/n$, $a = 10.298(2)$ Å, $b = 22.889(4)$ Å, $c = 17.333(1)$ Å, $\beta = 95.06(1)°$, $V = 4069.5(10)$ Å^3, $Z = 4$, $R = 0.038$, $R_w = 0.039$, GOF = 1.33.

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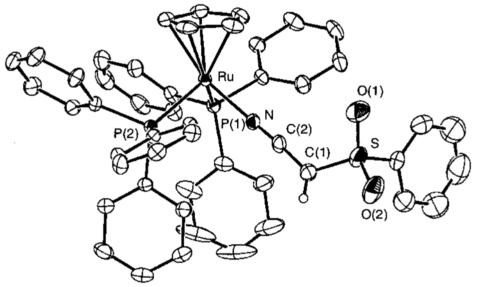
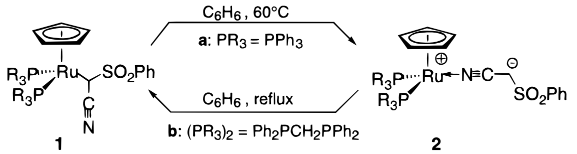


Figure 2. Molecular structure of **2a**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru−N, 2.050(4); Ru−P(1), 2.313(1); Ru−P(2), 2.333(1); N−C(2), 1.150(6); C(2)−C(1), 1.367(7); S−C(1), 1.662(6); S−O(1), 1.452(4); S−O(2), 1.430(4); P(1)−Ru−P(2), 100.59(4); P(1)−Ru−N, 88.2(1); P(2)−Ru−N, 91.1(1); Ru−N−C(2), 171.9(4); N−C(2)−C(1), 176.1(5); C(2)−C(1)−S, 122.9(4).

linearity of the Ru−N−C(2)−C(1) atoms and the C(2)−C(1)−S bond angle of 123° indicate the strong contribution of zwitter ionic structure[2b,5a−h] including η^1-coordination of α-cyanocarbanion, rather than the bent structure of azaalenyl metal.

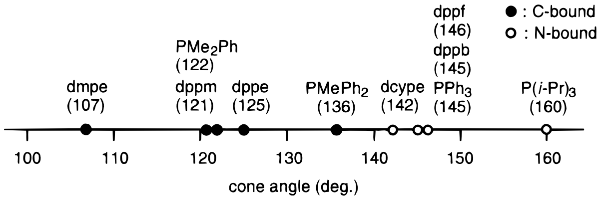
The *C*-bound PPh_3 complex **1a** is less stable and readily converted into the *N*-bound isomer **2a** in solution. Upon heating a 1.25 mM solution of **1a** in benzene at 60 °C under argon atmosphere, complex **1a** is converted quantitatively into **2a** after 3 h, while complex **2a** is thermally stable in various boiling solvents such as benzene, THF, and EtOH. Relative thermal stabilities of the *C*- and *N*-bound complexes have proven to be changed drastically depending on the choice of phosphine ligands. In sharp contrast to the PPh_3 complexes, *C*-bound dppm complex **1b** is inert in various boiling solvents, while *N*-bound complex **2b** undergoes quantitative *N*-to-*C* isomerization upon refluxing in benzene for 24 h.



1 **2**

To obtain a perspective view of the influence of phosphines for thermal stabilities of *C*- and *N*-bound complexes, we investigated the isomerization of **1** and **2** by the ligand exchange reactions with various tertiary phosphines. A 1.25 mM solution of thermally stable $RuCp[CH(CN)SO_2Ph](PMePh_2)_2$ (**1c**) or **2a** in benzene was refluxed for 24 h in the presence of mono- and diphosphines **3** (monophosphine, 4 equiv; diphosphine, 2 equiv) under argon atmosphere. Yields of the products were determined by ^1H NMR analysis of the reaction mixtures using internal standard. The reactions of inert *C*-bound complex **1c** with phosphines such as dppb (**3d**, dppb = $Ph_2P(CH_2)_4PPh_2$), dppf (**3e**, dppf = 1,1′-bis(diphenylphosphino)ferrocene), and dcype (**3f**, dcype = 1,2-bis(dicyclohexylphosphino)ethane) afford the corresponding *N*-bound complexes **2d**−**f** as a sole product in 79, 75, and 71% yields, respectively. On the contrary, similar treatment with dppm (**3b**), dppe (**3g**, dppe = $Ph_2PCH_2CH_2PPh_2$), dmpe (**3h**, dmpe = $Me_2PCH_2CH_2PMe_2$), and PMe_2Ph (**3i**) gives rise to only ligand exchange reactions to afford *C*-bound complexes **1b**,**g**−**i**. Almost the same preferences of *C*- and *N*-bound structures have been observed in the *N*-to-*C* isomerizations. Thus, treatment of inert *N*-bound complex **2a** with **3d**−**f** and P(*i*-Pr)$_3$ (**3j**) gives the corresponding *N*-bound complexes **1d**−**f**,**j**, while addition of **3b**,**c**,**g**−**i** affords the *C*-bound complexes **1b**,**c**,**g**−**i** selectively in 51, 85, 72, 90, and 82% yields.

Scheme 1



One plausible factor for determining the stable structures is the steric circumstance around the metal center, where ligation of bulky phosphines would favor the end-on coordination of the *N*-bound complexes rather than the carbon−metal bond formation of the *C*-bound ones. Indeed, the order of cone angles[8,9] of tertiary phosphines is well in accord with the tendency of relative thermal stabilities of *C*- and *N*-bound complexes as shown in Scheme 1. π-Basicity of ligands is not a major factor, as is clearly indicated by the fact that two bidentate trialkyl phosphines, dmpe and dcype, show different preferences. These isomerizations would proceed intramolecularly via η^2-coordination[10] of nitriles, although the intermolecular process including assembly of metals by bridging α-cyanocarbanion moieties is also under consideration.

In conclusion, we have shown the first synthesis and characterization of *C*- and *N*-bound isomers of α-cyanocarbanions. Reactivity and catalysis of the *C*- and *N*-bound complexes toward carbon electrophiles have been investigated.[2] Catalytically active species will be readily controlled by steric factors of external ligands, overcoming their original stabilities mainly arising from α-substituent of nitriles. These studies will serve as a new approach for exploitation of novel and fundamental catalytic C−C bond-forming reactions of nitriles fulfilling the future requirement toward efficiency, selectivity, and atom economy.[11] Efforts are currently underway to provide the full scope of the reactions and definitive mechanistic information and to apply the present reactions to other systems.

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Supporting Information Available: Experimental details for all compounds and crystallographic data for **1b** and **2a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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