Linkage Isomerism of Nitriles in Rhodium Half-Sandwich Metallacycles

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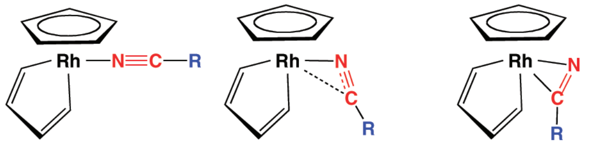
Summary: A systematic analysis of the linkage isomerism of nitriles in half-sandwich five-membered rhodacycles is presented for 15 nitriles of the general formula RCN. The hitherto elusive transition states connecting the two isomers have been located using advanced DFT methods.

Linkage isomerism is common to transition-metal complexes with ligands capable of bonding in different modes. Among these ligands, the nitrile group (CN) has paramount importance in numerous catalytic processes in which easily available nitriles RCN are utilized as feedstock to produce amines, amides, and N-acyl amino acids and in which CN activation is the key step.[1] The most common coordination mode of nitriles to transition metals is end-on, through formation of a metal−nitrogen σ bond involving the nitrogen lone pair. Alternatively, side-on coordination is possible which involves the metal d and nitrile π orbitals. This is illustrated in Chart 1 for end-on (**1R**) and side-on (**2R**) rhodacycle−nitrile model complexes of the present study, as well as the corresponding isomerization transition states (**TS-R**), with R = H, Me, Et, CFH_2, CF_2H, CF_3, CBr_3, CN, F, Cl, Br, I, AcO, Ph, $(C_4H_8)N$.

Numerous examples of end-on RCN−[M] complexes can be found in the Cambridge Structural Database (CSD), but much fewer of the corresponding side-on complexes have been crystallographically characterized.[2] Combined experimental and theoretical studies[3] have shown that end-on complexes are energetically favored, albeit less activated than side-on complexes. For example, we have recently shown[4] that the end-on 16-electron rhodacycle−nitrile complex, involved in the CpRh-catalyzed synthesis of 2-methylpyridine from acetylene and acetonitrile, is about 10 kcal/mol more stable than the corresponding side-on complex. However, the energy barrier for conversion into the subsequent intermediate along the catalytic pathway was estimated to be 2 times lower for the latter.

Herein, we report on a computational exploration of the occurrence and feasibility of linkage isomerism in the catalytic cycle of CpRh-catalyzed cyclotrimerization pathways. This investigation is prompted by our own results (vide supra) but also by the fact that linkage isomerism has been postulated already, but not proven, by others for analogous reactions.[3a,5] Jiao et al.[6] described how to control the relative stability of end-on and side-on nitrile coordination in a series of tetrahedral cobalt catalysts by tailoring the ancillary ligands, but no mechanistic investigation into their interconversion was undertaken. Thus, we have analyzed the end-on and side-on complexes of the rhodacycle with 15 nitriles RCN, mentioned above and shown in Chart 1, using relativistic density functional theory (DFT) at the ZORA-BLYP/TZ2P level as implemented in the Amsterdam density functional (ADF) program.[7–9] For the first time, the transition states connecting the two isomers have been determined and the height of the barrier is analyzed in terms of the activation strain model (vide infra). Our purpose, in addition to elucidating the isomerization mechanism, is to understand how the nature of the substituent R in the substrate RCN affects the isomerization energy and barrier.

Chart 1. End-on (1R) and Side-on (2R) Nitrile Model Complexes and Isomerization Transition State (TS-R)



1R **TS-R** **2R**

Bending of the nitrile's R−C−N angle occurs both in side-on and, more remarkably, also in end-on isomers, with loss of

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Table 1. Geometry (in Å) and PES and Activation-Strain Analysis (in kcal/mol) of Model Rhodacycle + RCN Complexes[a]

	distance			ΔE_{strain}					
species	N−Rh	C−Rh	C−N	RCN	[Rh]	total	ΔE_{int}	ΔE	ΔE_{rel}[b]
1H	1.97	3.13	1.16	0.1	3.1	3.2	−27.6	−24.4	0.0
2H	2.24	2.12	1.21	8.8	3.4	12.2	−31.0	−18.8	5.6
TS-H	2.26	2.80	1.17	0.1	1.4	1.5	−10.3	−8.7	15.7
1F	3.17	2.01	1.19	10.0	3.7	13.7	−33.5	−19.8	0.0
2F	2.04	2.25	1.22	18.0	5.1	23.1	−49.8	−26.8	−6.9
TS-F	2.72	2.31	1.17	0.8	1.4	2.2	−10.9	−8.8	11.1
1Cl	1.98	3.15	1.17	0.0	2.9	2.9	−25.8	−22.9	0.0
2Cl	2.23	2.08	1.22	15.7	4.6	20.3	−41.9	−21.5	1.4
TS-Cl	2.28	2.70	1.18	0.9	1.9	2.8	−10.8	−8.0	14.9
1Br	1.98	3.15	1.17	0.4	3.0	3.4	−26.5	−23.2	0.0
2Br	2.25	2.08	1.22	14.9	4.7	19.6	−42.2	−22.6	0.7
TS-Br	2.27	2.71	1.18	0.9	1.9	2.8	−10.7	−7.9	15.3
1I	1.97	3.14	1.18	2.9	3.4	6.3	−30.3	−24.0	0.0
2I	2.25	2.09	1.21	13.2	4.5	17.7	−39.7	−22.0	2.0
TS-I	2.25	2.72	1.18	1.6	2.0	3.6	−11.8	−8.1	15.9
1Me	2.00	33.16	1.16	0.0	2.9	2.9	−27.0	−24.1	0.0
2Me	2.21	2.18	1.21	9.7	3.7	13.4	−29.0	−15.6	8.5
TS-Me	2.28	2.57	1.18	1.3	2.4	3.7	−14.5	−10.8	13.3
1CFH$_2$	1.97	3.13	1.17	0.2	3.2	3.4	−29.0	−25.6	0.0
2CFH$_2$	2.22	2.14	1.21	9.4	4.2	13.6	−32.0	−18.5	5.1
TS-CFH$_2$	2.24	2.44	1.18	2.7	2.8	5.5	−17.4	−11.8	14.6
1CF$_2$H	1.95	3.12	1.17	0.4	3.4	3.8	−30.0	−26.1	0.0
2CF$_2$H	2.22	2.11	1.21	11.2	4.0	15.2	−36.2	−21.0	7.1
TS-CF$_2$H	2.25	2.69	1.18	0.7	1.8	2.5	−13.9	−11.5	13.7
1CF$_3$	1.94	3.11	1.17	0.6	3.6	4.2	−30.1	−25.9	0.0
2CF$_3$	2.21	2.09	1.22	12.8	4.2	17.0	−38.9	−21.8	4.0
TS-CF$_3$	2.18	2.12	1.24	20.0	5.7	25.7	−41.4	−15.6	10.3
1Et	2.00	3.16	1.16	0.0	2.9	2.9	−27.2	−24.3	0.0
2Et	2.21	2.18	1.21	8.9	3.7	12.6	−28.4	−15.7	8.6
TS-Et	2.28	2.57	1.18	1.3	2.4	3.7	−14.6	−10.9	13.4
1CBr$_3$	1.95	3.12	1.17	1.1	3.9	5.0	−33.0	−28.1	0.0
2CBr$_3$	2.18	2.14	1.22	15.0	5.0	20.0	−37.1	−17.0	11.1
TS-CBr$_3$	2.22	2.89	1.18	1.0	2.0	3.0	−10.3	−7.3	20.8
1Ph	1.98	3.15	1.17	0.1	3.2	3.3	−29.3	−26.0	0.0
2Ph	2.19	2.17	1.21	11.1	3.9	15.0	−30.3	−15.3	10.7
TS-Ph	2.23	2.61	1.18	2.7	3.4	6.1	−14.4	−8.3	17.7
1CN	1.93	3.11	1.18	0.4	4.1	4.5	−35.8	−31.2	0.0
2CN	2.19	2.12	1.22	11.1	3.7	14.8	−36.5	−21.7	9.5
TS-CN	2.17	2.59	1.19	1.7	2.4	4.1	−15.2	−11.2	20.0
1(C$_4$H$_8$)N	2.01	3.16	1.17	0.1	3.4	3.5	−28.4	−24.8	0.0
2(C$_4$H$_8$)N	2.18	2.15	1.23	13.5	5.0	18.5	−36.5	−18.0	6.9
TS-(C$_4$H$_8$)N	2.20	2.49	1.20	3.9	2.8	6.7	−21.0	−14.4	10.5
1AcO	2.01	3.17	1.16	0.0	2.7	2.7	−25.0	−22.3	0.0
2AcO	2.21	2.08	1.22	18.0	4.9	22.9	−43.5	−20.7	1.6
TS-AcO	2.27	2.59	1.18	3.0	3.2	6.2	−16.2	−9.9	12.3

[a] Computed at the ZORA-BLYP/TZ2P level, without ZPE. [b] Energies relative to end-on complex **1X**: $\Delta E_{rel} = 0$, ΔE_{iso} and $\Delta E^{\ddagger}$ for **1X**, **2X**, and **TS-X**.

the degeneracy of the π and π* sets of MOs and mixing of the in-plane orbitals with σ.[5c] As a result, the end-on nitriles bind as σ donors or weak π donors. In contrast, in side-on nitriles, the σ donor component involves a π level and there is also back-donation from the metal to π*, so that the nitrile becomes a π acceptor. Although the phase of π* in end-on nitriles would still be good for back-bonding, this does not occur because of a smaller amplitude on N.

The end-on/side-on isomerism involves shortening of the Rh−C bond and concerted lengthening of the Rh−N bond (see Table 1) and the displacement of the CN bond. This bond lies initially nearly in the C_s symmetry plane of the rhodacycle (except for R = F, Br, I) and shifts, through an approximately 90° rotation, to an orthogonal plane, almost parallel to the Cp ring. In fact, in side-on complexes with the CN bond in the rhodacycle symmetry plane, back-bonding would be less efficient.

The variation of ΔE_{iso} and $\Delta E^{\ddagger}$ (i.e., the relative energy of the isomers and the isomerization barrier relative to the end-on complex, indicated as ΔE_{rel} in Table 1) as a function of R has been investigated through an activation strain analysis.[8] According to this model the energy is decomposed into strain energy (ΔE_{strain}) of the rhodacycle and the nitrile that are deformed in the complex and the interaction energy (ΔE_{int}) between these two deformed fragments.[8] The interaction energy is the sum of three contributions: Pauli repulsion (ΔE_{Pauli}), electrostatic interaction (ΔV_{elstat}), and orbital interaction (ΔE_{oi}).[7b,d]

As expected, the values of ΔE_{int} are always more stabilizing in side-on than in end-on complexes, mainly because of the back-donation from rhodium to the π*-LUMO on RCN. This backdonation is much less favorable for the end-on complexes.

The barrier decreases as the halogen substituent becomes more electronegative, i.e., along R = I, Br, Cl, F. Interestingly, the end-on isomers containing the halonitriles, with the exception of **1Cl**, show significant out-of-symmetry-plane distortion of the CN group already in the end-on complex. When R = H, Cl the $\Delta E^{\ddagger}$ values are almost identical, but the energy difference ΔE_{iso} of **2Cl** relative to **1Cl** is smaller than that of **2H** relative to **1H**, because in **2H** only ΔE_{strain} increases, while in **2Cl** also ΔE_{int} becomes larger due to the presence of the electronegative chlorine. The reverse stability of the isomers **1F** and **2F** is due to significant bending of the nitrile fragment FCN in the former, which translates into large strain energy ΔE_{strain} in **1F**. The presence of the strongly electronegative fluorine makes FCN a

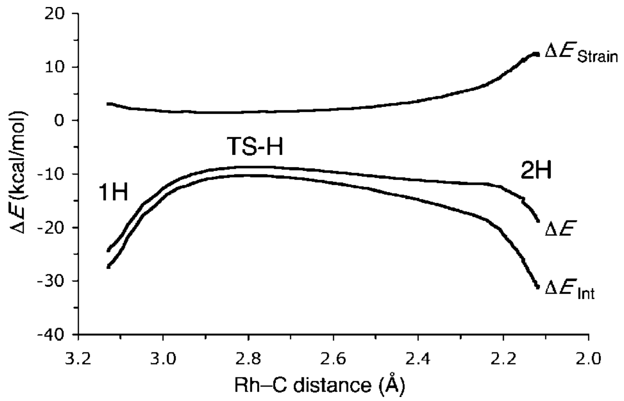

Figure 1. Activation strain analysis of the **1H** → **2H** isomerization.

very good π acceptor, and **2F** is stabilized. Despite the change in geometries of **1R** and **TS-R** along the series R = Cl, Br, I, $\Delta E^{\ddagger}$ is unaffected because the increase of $\Delta E_{\mathrm{strain}}$ is counterbalanced by the increase of ΔE_{int}.

For the isomerization **1H** → **2H** the potential energy surface was calculated via an intrinsic reaction coordinate (IRC) calculation. The activation strain analysis is shown as a function of the Rh−C distance in Figure 1.

The transition from **1H** to **2H** is smooth. The rotation of the CN group out of the symmetry plane of the rhodacycle occurs between 2.1 and 2.2 Å, the same interval where strain becomes important. A more detailed analysis shows that the out-of-plane movement of the CN moiety is purely relief of Pauli repulsive interactions which dominate in **2H**.

Interestingly, similar ΔE_{iso} and $\Delta E^{\ddagger}$ values are computed for very different nitriles, i.e., for R = CBr_3, Ph or for R = CF_3, $(C_4H_8)N$. In the former couple, the close matching of the ΔE_{iso} values occurs because in both coordination modes, **1** and **2**, the ΔE_{int} and $\Delta E_{\mathrm{strain}}$ terms decrease from R = CBr_3 to R = Ph. In contrast, both ΔE_{int} and $\Delta E_{\mathrm{strain}}$ are larger in **TS-Ph** than in **TS-CBr$_3$**; thus, the computed $\Delta E^{\ddagger}$ values are again similar. In the latter couple, compounds **1** and **2** have similar ΔE_{int} and $\Delta E_{\mathrm{strain}}$ values, but the strong interaction and large strain in **TS-CF$_3$** and the weak interaction and small strain in **TS-(C$_4$H$_8$)N** result in similar $\Delta E^{\ddagger}$ values. These examples suggest that simplified predictions of ΔE_{iso} and $\Delta E^{\ddagger}$ based on the electron-donating/electron-withdrawing character of R and/or on purely geometrical features might be misleading.

Note that in many cases $\Delta E^{\ddagger}$ is comparable to or even lower than the energy barrier of the rate-determining step identified for the cocyclization of acetylene and RCN: i.e., the formation of the rhodacycle ($\Delta E^{\ddagger} = 12.7$ kcal/mol).[4] This implies that end-on/side-on linkage isomerism might indeed be a viable step of this specific catalytic cycle, provided a suitable RCN is chosen as reactant.

The present analysis can be easily extended to other processes in which nitrile activation at a metal center is a key step. This represents a tool for fine-tuning the PES as a function of the metal as well as the nitrile reactant.

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Supporting Information Available: Tables giving Cartesian coordinates and energies of all species in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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