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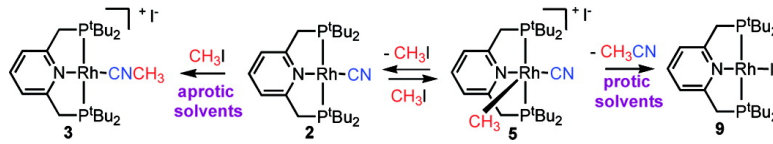

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Competitive C−I versus C−CN Reductive Elimination from a Rh^{III} Complex. Selectivity is Controlled by the Solvent

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Reductive elimination (RE) is a fundamental organometallic reaction in stoichiometric and catalytic processes, leading to the formation of new bonds.[1] Recently we reported the RE of CH_3I from a Rh^{III} complex.[2] The other few examples of directly observed RE of alkyl halides involve thermolysis of Pt^{IV} complexes,[3] including competition with C−C RE.[3b,c] Aryl halide RE was reported for Pt^{IV} and Pd^{II} complexes.[4] RE of acyl iodide is a product-forming step in the Monsanto acetic acid process.[5]

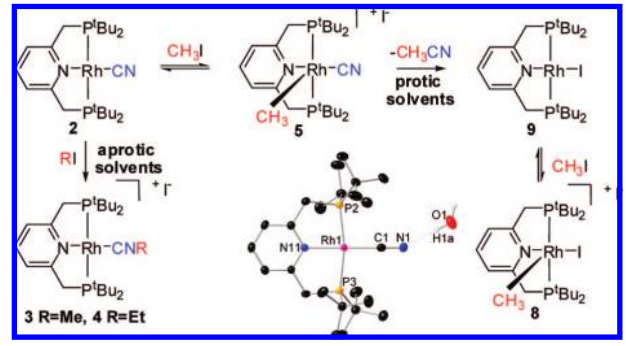
The RE of nitriles is a fundamental step in important catalytic processes, such as the hydrocyanation of butadiene in the DuPont adiponitrile process,[6] catalytic cyanation of aryl halides,[7] and carbocyanation of unsaturated carbon−carbon bonds.[8] Directly observed RE of alkyl nitriles was reported for ethyl and propyl cyanide from Ni^{II} [9] and for RCH_2CN (R = TMS, $C(CH_3)_3$) from Pd^{II}.[10] The latter was reported as a migratory RE, which is accelerated by Lewis acids.[11] The isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile by Ni^{II} also involves a RE step.[12]

Here we report the competitive RE from a $[Rh^{III}(CH_3)(CN)][I]$ complex to give exclusively CH_3CN in protic solvents and CH_3I in aprotic solvents. A rare case of selective electrophilic attack on a cyanide ligand coordinated to an unsaturated, low valent complex is also reported.

The cationic [(PNP)Rh(acetone)][BF_4] (**1**)[13] (PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine) reacts with excess KCN in methanol to give the fully characterized[14] [(PNP)Rh(CN)] (**2**). Unexpectedly, when the electron rich Rh^I complex **2** was reacted with a large excess of CH_3I or ethyl iodide (EtI) at ambient temperature in acetone or CH_2Cl_2, only the Rh^I isonitrile complexes **3** and **4**, respectively, were obtained, after 4 and 12 h respectively, with no oxidative addition (OA) being observed (Scheme 1).[14] To our knowledge, all reported cases of electrophilic attack on the terminal nitrogen of cyanide complexes occurred only with coordinatively saturated complexes or with complexes in which the metal center is in high oxidation state, making OA of the electrophile unlikely.[15,16]

Follow-up of the reaction of **2** with excess EtI by NMR did not reveal any intermediates, while in the case of excess CH_3I an OA product [(PNP)Rh(CN)(CH_3)][I] (**5**) was formed immediately in more then 65% yield. Complex **5** is stable only at low temperature (273 K) and converts into complex **3** after 4 h at room temperature (Scheme 1). **5** exhibits a doublet at 60.17 ppm ($^1J_{RhP}$ = 97.2 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The low $^1J_{RhP}$ (as compared to the Rh^I complexes **1**−**4**) indicates that **5** is a Rh^{III} complex. Using $^{13}CH_3I$, the complex exhibits a dt signal of Rh−$^{13}CH_3$ in the $^{13}C\{^1H\}$ NMR spectrum at 11.67 ppm ($^1J_{RhC}$ = 26.5 Hz, $^2J_{PC}$ = 3.8 Hz) and in the $^1H\{^{31}P\}$ NMR the methyl ligand appears as a dd at 1.65 ppm ($^2J_{RhH}$ = 2.7 Hz, $^1J_{CH}$ = 144.7 Hz). The cyano ligand appears as a ddt signal at 130.26 ppm ($^2J_{CC}$ = 2.2 Hz) confirming a cis orientation for the cyano and methyl ligands. A larger $^2J_{CC}$ of 29.5 Hz was found for the trans isomer, as described below. Crystals of **5** were obtained from a cold (253 K) solution of **2** in methanol/ether with a large excess of CH_3I. The low temperature X-ray structure of **5** confirms a cationic complex with the methyl group at the apical position.[14,17]

Scheme 1. Reaction Pathway of Complex **5** in Protic and Aprotic Solvents and an ORTEP Drawing of **2**(H_2O) at 50% Probability Level. Hydrogen Atoms (Except of Water) Were Omitted for Clarity



Complexes **2** and **5** are in equilibrium, as observed by a variable temperature $^{31}P\{^1H\}$ NMR experiment. Equilibrium constants (K_{eq} = $[\mathbf{5}]_{eq}/[\mathbf{2}]_{eq}[MeI]_{eq}$) were obtained for temperatures between 273 and 253 K, before complex **3** formed, yielding $\Delta H = -14.5 \pm 0.5$ kcal/mol, $\Delta S = -51.7 \pm 1.9$ eu and $\Delta G_{258} \approx -1.4$ kcal/mol.[14]

The reaction pathway for the conversion of **5** to **3** very likely involves RE of CH_3I from **5**, followed by its electrophilic attack on the cyano ligand of **2**. Intramolecular migration of the alkyl group to the cyano ligand is unlikely; DFT calculations give $\Delta G^{\ddagger}$ = 36.2 kcal/mol for this process, and $\Delta G^{\ddagger}$ = 25.8 kcal/mol for the external attack pathway.[14,18] In addition, an OA intermediate was not observed in the reaction of **2** with EtI. The possibility of electrophilic attack of excess CH_3I on the cyano ligand of **5** occurring prior to RE of CH_3I is unlikely, based on the observed facile RE of CH_3I from **5**, as evidenced by its equilibrium with **2**.

Reaction of $[Et_4N]CN$ with [(PNP)Rh(CH_3)I][BF_4] (**6**) (easily obtained by reaction of **1** with CH_3I[14]) at −30 °C in CH_2Cl_2 afforded complex **7**, identified as an isomer of **5**, with the methyl group trans to the cyano ligand (Scheme 2). The $^{31}P\{^1H\}$ NMR of **7** exhibits a sharp dd at 62.37 ppm ($^1J_{RhP}$ = 92.0, $^2J_{PC}$ = 6.9 Hz), and the methyl ligand appears as a dt signal at −7.65 ppm ($^1J_{RhC}$ = 15.4, $^2J_{PC}$ = 6.9 Hz) in the $^{13}C\{^1H\}$ NMR spectrum.[19] Using the $^{13}CH_3$ labeled **7**, the cyano ligand exhibits a ddt signal at 147.35 ppm with a $^2J_{CC}$ of 29.5 Hz, much larger than in the case of **5**, in line with CN trans to methyl, and is stable for more than 3 days at

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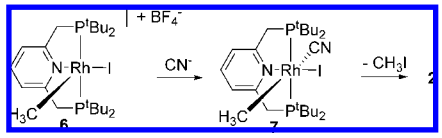
Scheme 2



−30 °C in solution, but at room temperature it reductively eliminates CH_3I (detected by $^{13}C\{^1H\}$ NMR and GC−MS) after 3 h, forming **2**, and finally **3**. Same results are obtained in the presence of excess CH_3I (Scheme 2).[20]

Surprisingly, when **2** was dissolved in protic solvents such as methanol, ethanol, isopropyl alcohol, or a water−acetone mixture, no reaction with EtI was observed. Moreover, the reaction of **2** with CH_3I in protic solvents yielded free CH_3CN and the crystallographically characterized [(PNP)Rh(CH_3)I][I] (**8**)[14] (Scheme 1). NMR follow-up of this reaction in methanol revealed that complex **2** undergoes OA of CH_3I to give complex **5**, as in methylene chloride or acetone. However, in protic solvents RE of CH_3CN takes place as evidenced by $^{13}C\{^1H\}$ NMR and GC−MS.[14] The RE of CH_3CN from **5** probably leads to formation of [(PNP)RhI] (**9**),[21] which reacts with CH_3I to give complex **8**. Complex **9** was prepared independently[14] by addition of NaI to complex **1**.[13] Addition of CH_3I to **9** resulted in immediate formation of **8**. Complex **8** is not stable and readily eliminates CH_3I upon evaporation to give **9**. The $^{31}P\{^1H\}$ NMR spectrum of **8** reveals a sharp dd at 52.08 ppm with $^2J_{CP} = 3.6$ and $^1J_{RhP} = 100.0$ Hz, the latter being typical of a Rh^{III} complex. The methyl ligand gives rise to a ddt signal at 2.31 ppm ($^1J_{CH} = 144.0$, $^2J_{RhH} = 2.8$, $^3J_{PH} = 4.4$ Hz) in the ^1H NMR spectrum and a dt signal at 8.85 ($^1J_{RhC} = 24.7$, $^2J_{PC} = 3.6$ Hz) in the $^{13}C\{^1H\}$ NMR.

Upon addition of excess CH_3I to **7** in methanol (rather than in CH_2Cl_2), **7** isomerizes to **5**, which reductively eliminates CH_3CN. The fact that RE of CH_3CN was observed only after formation of the cationic, cis cyano methyl complex **5** is in line with a concerted C−C RE from an unsaturated complex, as reported for a Pt^{IV}complex.[3b,c]

We believe that the selectivity of the reaction of **2** with CH_3I toward formation of (coordinated) methyl isonitrile in aprotic solvents or CH_3CN in protic solvents is a result of a hydrogen bond between the CN ligand and the protic solvent,[22] which hinders electrophilic attack by CH_3I on the terminal CN nitrogen.

Strong evidence for a hydrogen bond between the cyano ligand and the protic solvent was provided by crystal structures of **2** which were obtained from a mixture of acetone−water or from methanol.[14] The structures reveal a water molecule with a N(1)−O(1) distance of 2.838(3) Å (**2**(H_2O)) (Scheme 1) or a methanol molecule with a N(1)−O(1) distance of 2.731(5) Å, (**2**(CH_3OH)) which are in the range of hydrogen bonds.[23]

The large difference in the chemical shift of the cyano carbon observed in methanol versus methylene chloride ($\Delta\delta = 11.95$ ppm)[14] is in line with the existence of a hydrogen bond in solution.

In conclusion, selective and quantitative RE of CH_3I or CH_3CN was observed at ambient temperature from the complex [(PNP)Rh(CN)(CH_3)][I] (**5**) upon reaction in aprotic or protic solvents, respectively. The reductively eliminated CH_3I undergoes selective electrophilic attack on the cyano ligand of the Rh^I complex in an aprotic solvent to give the corresponding alkyl isonitrile complex. In a protic solvent a hydrogen bond between the cyano ligand and the solvent protects the cyano ligand from an electrophilic attack, resulting in selective CH_3CN RE. Further mechanistic, computational, and experimental work is in progress.

Acknowledgment. This work was supported by the Israel Science Foundation and by the Helen and Martin Kimmel Center for Molecular Design.

Supporting Information Available: Experimental procedures, characterization of complexes **2**−**9** and computational details; X-ray data for **2**, **4**, **5**, **6**, **8** and [(PNP^{i}Pr)Rh(CH_3)I][BF_4] (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Complex **5** exists in a cationic form also in solution as evidenced by the identical chemical shifts (in ^{31}P, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR) obtained by addition of CH_3Br to **2**.
(18) The reaction mixture contains only the starting complex **2**, complex **5**, and the final complex **3** until it reaches completion, rendering the addition of labeled CH_3I to the reaction mixture mechanistically noninformative.
(19) Reaction of [(PNP^{i}Pr)Rh(CH_3)I][BF_4] with CN^- gives the stable adduct [(PNP^{i}Pr)Rh(CH_3)(CN)I] in which the CH_3 and the CN are trans, as confirmed by X-ray analysis. The CH_3 chemical shifts in the ^{i}Pr complex are similar to those of complex **6** (see Supporting Information).
(20) Follow-up of CH_3I RE from **7** in the absence of added CH_3I by $^{31}P\{^1H\}$ NMR reveals formation of **2**, followed by a mixture of three more complexes, of which **3** was identified. However, in the presence of CH_3I **7** gives first complex **2** followed by formation of **3** exclusively.
(21) Addition of excess CH_3CN to **9** in methanol gave only traces of the cationic complex [(PNP)Rh(CH_3CN)][I], which reacts with CH_3I to give complex **8**: Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21*, 812.
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(23) The X-ray structure of **2**·CH_3OH reveals a second disordered methanol molecule (version A at 50.9% and version B at 49.1%). The bond distances O(40)−O(42A) and O(40)−O(42B) are in the range of a hydrogen bond (2.837(14) and 2.687(14) Å, respectively).

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