Dichloromethane Activation by Chlorochromium(II) Complexes with Tp^{iPr2}: Generation of an Electrophilic Cr–Methylene Species without the Action of an External Cl-Abstraction Reagent

Ken-ichiro Sugawara, Shiro Hikichi,* and Munetaka Akita*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

Five-coordinated chlorochromium(II) complexes with Tp^{iPr2} activate CH_2Cl_2 to give a metal–carbene species without the action of an external Cl-abstraction reagent, and the resulting methylene fragment is trapped by nucleophiles such as pyrazole, pyridine and olefin.

Activation of carbon–halogen bonds by transition metal compounds is involved in various organic transformation processes. From the view point of environmental chemistry, activation of the relatively stable C–Cl bond is also an important subject related to the degradation of harmful chlorinated compounds. Coordinatively unsaturated low-valent early-transition metal species are known to be effective reagents for reductive activation of haloalkanes due to their low redox potential.[1] A family of hydrotris(pyrazolyl)borates (= Tp^R) is one of the extensively utilized ligands in inorganic chemistry involving organometallic field.[2] Although a large number of early-transition metal complexes with Tp^R have been reported, chromium(II) complexes are still scarce. Recently, Theopold and co-workers reported synthesis and structural characterization of chloro- and alkylchromium(II) complexes with the highly hindered Tp^{tBu,Me} [= hydrotris(3-*tert*-butyl-5-methyl-1-pyrazolyl)borate] ligand, but their reactivity except for the oxygenation of the phenyl complex is unknown.[3] During the course of our systematic studies on synthesis and reactivity of the Tp^{R}M complexes based on bioinorganic and organometallic viewpoints,[4] we have revealed that the moderately hindered Tp^{iPr2} [= hydrotris(3,5-diisopropyl-1-pyrazolyl)borate] ligand can stabilize a coordinatively unsaturated metal center and, moreover, its somewhat structural flexibility is expected to allow further substrate activation on the vacant site. For example, highly coordinatively unsaturated alkyl complexes, Tp^{iPr2}M^{II}R' (M = Fe, Co, Ni), were carbonylated to give the corresponding acyl–carbonyl complexes, Tp^{iPr2}M^{II}[C(=O)R'](CO)$_n$ (n = 1 or 2),[5] while the analogous methylcobalt(II) complex having the highly hindered Tp^{tBu,Me} ligand did not show such a reactivity.[6] Therefore, combination of chromium(II) and Tp^{iPr2} is expected to be fruitful for the reductive activation of various substrates. Herein we report the CH_2Cl_2 activation by coordinatively

unsaturated chlorochromium(II) complexes to promote methylene transfer reaction via electrophilic Cr–methylene species under mild conditions (ambient temperature, without UV-irradiation and using of an external Cl-abstracting reagent).

Coordinatively unsaturated chlorochromium(II) complexes were prepared by metathesis between KTp^{iPr2} and CrCl$_2$ under anaerobic conditions as shown in Scheme 1.[7] The mononuclear five-coordinated complexes, Tp^{iPr2}Cr^{II}Cl(L), were formed in the presence of a 2-electron donor (= L) such as 3,5-diisopropylpyrazole (= pz^{iPr2}H; **1a**) and pyridine (= py; **1b**). The dimeric di(μ-chloro) complex, [Tp^{iPr2}Cr^{II}]$_2$(μ-Cl)$_2$ (**1c**), containing the virtually square-pyramidal Cr centers bridged by the chloride ligands, was also obtained successfully in the absence of any additives.[8]

Interestingly, **1** could activate the C–Cl bonds in CH_2Cl_2 to promote the methylene transfer without the use of an external Cl abstracting reagent. When the mononuclear complexes **1a** and **1b** were dissolved in CH_2Cl_2, a mixture of the green dichlorochromium(III) complexes, Tp^{iPr2}CrCl$_2$(L) (**2**),[9] and brown species **3** was formed (Scheme 1).[10] X-ray crystallographic analysis[11] of the pz^{iPr2}H derivative **3a** (Figure 1) revealed the progress of the methylenation of the pz^{iPr2}H ligand to form the Cr–C–N linkage. Effective magnetic moment of **3a** (3.67 μ_B; a powder sample, at 298 K) indicated **3a** was a high-spin Cr(III) species (d^3, S = 3/2: $\mu_{\text{spin only}}$ = 3.87 μ_B). The lack of counterions in the unit cell of **3a** implies formation of the zwitterionic structure of **3a** resulting from protonation of the pyrazole fragment. Moreover, such a zwitterionic character of **3a** involving the protonated pyrazolium cation moiety may be stabilized by intramolecular N–H···Cl hydrogen bonding interaction. In an IR spectrum of **3a**, slightly broad νN–H band was observed around 3165 cm^{-1}, whereas the strong νN–H of the pz^{iPr2}H ligand of **2a**, the N–H(pz^{iPr2}H) moiety of which is directed to the side opposite to the Cl ligands resulting in no hydrogen bonding interaction, appeared at 3433 cm^{-1}. In addition to the red-shifted νN–H of **3a**, moderately short N42···Cl1 distance (3.086(6) Å) evidenced the contribution of the intramolecular hydrogen bonding interaction.
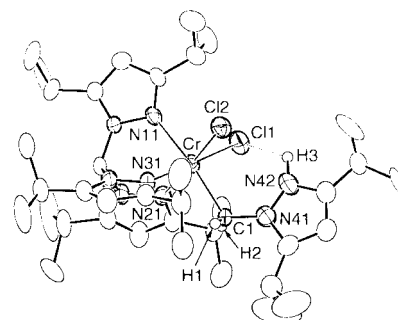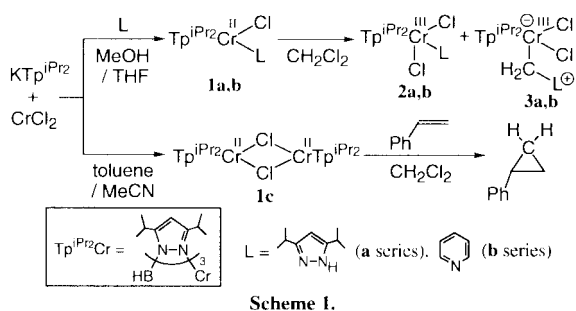

Figure 1. Molecular structure of **3a** (drawn at 50% probability). Selected bond lengths (Å) and angle (°): Cr-C1, 2.182(6); C1-N41, 1.425(6); Cr-C1-N41, 122.4(4)

Scheme 1.

In contrast to the 2e-donor containing complexes **1a** and **1c**, the base-free di-μ-chloro complex **1c** indicated the cyclopropanation capability toward external olefin upon dissolution of **1c** in CH_2Cl_2.[12] In general, electrophilic metal–carbene species are proposed to be a key intermediate for cyclopropanation as well as formation of zwitterionic complexes like **3**.[13–15] It should be noted the present cyclopropanation promoted by **1c** is a rare example via CH_2Cl_2 activation without the action of an external Cl abstracting reagent or UV-irradiation.[14]

A plausible CH_2Cl_2 activation mechanism is presented in Scheme 2. The first C–Cl bond activation yielded the dichloro-chromium(III) species **2'** and the resulting •CH_2Cl fragment was also trapped by **1** to give the chloromethyl intermediate **5**. Then, α-chloride elimination on the coordinatively unsaturated Cr(III) center of **5** yielded the carbene intermediate, $Tp^{iPr_2}Cr(=CH_2)Cl_2$ (**4**). Finally, the metal–carbene species **4** was trapped by the N-donating base (i.e. $pz^{iPr_2}H$ and py) to give **3**, or the cyclopropanation proceeded in the presence of olefin.[16]
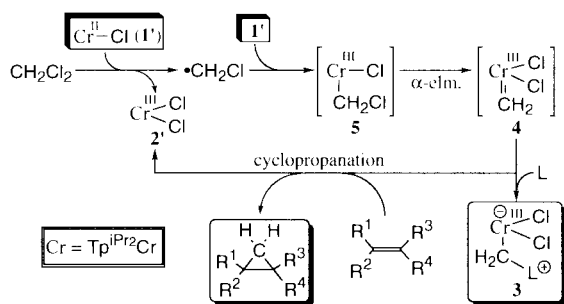
Scheme 2.

In summary, the coordinatively unsaturated chlorochromium(II) complexes with the moderately hindered Tp^{iPr_2} ligand exhibit activation capability toward CH_2Cl_2 to promote the methylene transfer reaction without the action of an external Cl abstracting reagent. The cyclopropanation using CH_2Cl_2 as the methylene source demonstrates the utility of Tp^{iPr_2} to create the coordinatively unsaturated low-valent early-transition metal complexes having the high potential for the reductive activation of small molecules. Further study on the reactivities of **1** and other $Tp^{iPr_2}Cr^{II}$ complexes, which derived from **1**, are now under way.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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6 J. D. Jewson, L. M. Liable-Sands, G. P. A. Yap, A. L. Rheingold, and K. H. Theopold, *Organometallics*, **18**, 300 (1999).
7 IR data (KBr, ν/cm^{-1}): **1a**: 3257 (NH), 2532 (BH), 1560 (C=N), **1b**: 2554 (BH), 1604 (C=N), **1c**: 2545 (BH). The molecular structures of **1** were determined by X-ray crystallography.
8 Theopold and coworkers have reported that the highly hindered $Tp^{tBu,Me}$ ligand does not give a dimeric compound like **1c** but the monomeric four-coordinated complex [i.e. (κ^3-$Tp^{tBu,Me}$)$Cr^{II}Cl$], although the molecular structure of the corresponding pyrazole-containing complex, $Tp^{tBu,Me}Cr^{II}Cl(pz^{tBu,Me}H)$, is very similar to that of **1a**. See ref 3a.
9 Previously reported $Tp^R Cr^{III}Cl_2(L)$ with the less hindered Tp^{H2} (= hydrotris(1-pyrazolyl)borate) and Tp^{Me2} (= hydrotris(3,5-dimethyl-1-pyrazolyl)borate): Tp^{H2}: a) M. J. Abrams, R. Faggiani, and C. J. L. Lock, *Inorg. Chim. Acta*, **106**, 69 (1985). b) C.-H. Li, J.-D. Chen, L.-S. Liou, and J.-C. Wang, *Inorg. Chim. Acta*, **269**, 302 (1998). Tp^{Me2}: c) T. Oshiki, K. Mashima, S. Kawamura, K. Tani, and K. Kitaura, *Bull. Chem. Soc. Jpn.*, **73**, 1735 (2000).
10 The pyrazole-adduct of the chlorochromium(II) complex **1a** (0.176 g, 0.250 mmol) was dissolved in CH_2Cl_2 (1 mL). After being stirred for 1 h at room temperature, the solvent was evaporated under vacuum. Recrystallization from MeCN (–30 °C) afforded the mixture of the green crystalline solids of **2a** (42% yield) and the brown crystals of **3a** (22% yield). Spectroscopic data: **2a**: Elemental analysis; Calcd for $C_{36}H_{62}N_8BCl_2Cr$: C, 58.38; H, 8.44; N, 15.13%. Found: C, 57.46; H, 8.05; N, 15.38%. IR (KBr, ν/cm^{-1}): 2549 (BH), 1576 (C=N). FD-MS: 739 (M$^+$). μ_{eff} (powder, 298 K, μ_B): 3.96. **3a**: Elemental analysis; Calcd for $C_{37}H_{64}N_8BCl_2Cr$: C, 58.88; H, 8.56; N, 14.85%. Found: C, 58.77; H, 8.29; N, 15.47%. IR (KBr, ν/cm^{-1}): 3165 (NH), 2549 (BH), 1576 (C=N). FD-MS: 753 (M$^+$), 718 (M–Cl$^+$), 166 ($CH_2pz^{iPr_2}H^+$). μ_{eff} (powder, 298 K, μ_B): 3.67. Dissolution of the pyridine derivative **1b** in CH_2Cl_2 resulted in formation of the dichlorochromium(III) complex **2b** (45% isolated yield). Spectroscopic data for **2b**: Elemental analysis; Calcd for $C_{32}H_{51}N_7BCl_2Cr$: C, 57.58; H, 7.70; N, 14.69%. Found: C, 57.98; H, 7.85; N, 14.12%. IR (KBr, ν/cm^{-1}): 2551 (BH), 1607 (C=N). FD-MS: 739 (M$^+$). Although we could not isolate the methylenated complex **3b**, an FD-MS spectrum of the reaction mixture indicated a peak at m/z = 94 attributed to CH_3–py$^+$ from **3b**. Molecular structures of **2a** and **2b** were also determined by X-ray crystallography.
11 The complex **3a**·(MeCN)$_3$ was crystallized in a orthorhombic space group *Pbca* (No. 61) with a = 19.115(1) Å, b = 40.473(3) Å, c = 13.0623(9) Å, V = 10105(1) Å^3, Z = 8, D_{calcd} = 1.15 g•cm^{-3}. The X-ray diffraction measurement was made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at –60 °C. The structures were solved by the direct method (SHELXS 86), and refined by full-matrix least squares method (on F^2; SHELXL 97) with anisotropic thermal parameters for all non-hydrogen atoms. The positions of the hydrogen atoms attached on C1 and N42 were refined. $R1$ = 0.0879 (for 5001 data with $I > 2.0\sigma(I)$) and w$R2$ = 0.2363 (for 9009 all unique data) with 611 parameters.
12 The base-free complex **1c** (52 mg; 0.047 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and then 17.3 mmol of styrene was added. After being stirred for 2.5 h at room temperature, the resulting reaction mixture was analyzed by GC–MS and GC. Yield of cyclopropylbenzene; 2% (based on **1c**). Carefully performed blank experiments revealed that cyclopropanation did not occur in the absence of **1c**. Also, such a methylene transfer from **3** to styrene did not occur.
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15 An example of an electrophilic carbene complex of group VI metal with the Tp^R ligand, $[Tp^{Me2}W^{II}(=CH_2)(CO)(PhCCMe)]^+$: a) T. B. Gunnoe, P. S. White, J. L. Templeton, and L. Casarrubios, *J. Am. Chem. Soc.*, **119**, 3171 (1997). b) T. B. Gunnoe, M. Surgan, P. S. White, J. L. Templeton, and L. Casarrubios, *Organometallics*, **16**, 4865 (1997). c) A. S. Jepsen, N. J. Vogeley, P. S. White, and J. L. Templeton, *J. Organomet. Chem.*, **617–618**, 520 (2001).
16 An alternate mechanism is direct methylene transfer from the Cr(III)–carbenoid species **5** to base and olefin via concerted mechanism. To date, however, no evidence has been obtained for cyclopropanation through such a direct methylen transfer from transition metal-chloromethyl (M–CH_2Cl) compounds, although the possibility of nucleophilic substitution of Cl to base on the chloromethyl ligand cannot be excluded. See ref 14a.