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Facile C–N cleavage reactions of secondary and tertiary alkyl amines by P,O chelating rhodium and iridium complexes

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Abstract

The reactions of Cp*MCl(MDMPP-*P*,*O*) (**1**: M = Rh; **3**: M = Ir; MDMPP-*P*, *O* = *P*Ph$_2$(C$_6$H$_3$-2-*O*-6-MeO)) with secondary or tertiary alkyl amine (R$_2$NH or R$_3$N) in the presence of KPF$_6$ underwent a C–N cleavage of amine to afford primary amine complex [Cp*M(MDMPP-*P*,*O*) (RNH$_2$)](PF$_6$) (**2**: M = Rh; **4**: M = Ir).

Keywords: C–N cleavage; Rhodium; Iridium; P,O chelating ligand

Transition-metal-assisted C–X (X = S, N) bond cleavage [1] plays an important role for several industrial processes. Desulfurization [2] and denitrogenation [3] of crude oil are the examples of the C–X bond cleavage. Among them, there are a few examples of cleavage of a C–N single bond of amines. For example, it has been reported that Pt, Ni and Ru complexes promote the cleavage of the allyl-N bond of allylamines with subsequent transfer of the allyl group to the metal center [4]. Aryl amines (XC$_6$H$_4$NH$_2$) were activated by (silox)$_3$Ta (silox = ^{t}Bu$_3$SiO) to afford (silox)$_3$HTa {NH(C$_6$H$_4$X)} and/or (silox)$_3$(H$_2$N)Ta(C$_6$H$_4$X) depending on the substituent [5].

Recently we reported that compounds, Cp*MCl (MDMPP-*P*,*O*) and Cp*MCl(BDMPP-*P*,*O*) (M = Rh [a] and Ir [b]; Cp* = C$_5$Me$_5$; MDMPP-*P*, *O* = *P*Ph$_2$(C$_6$H$_3$-2-*O*-6-MeO), BDMPP-*P*,*O* = *P*Ph{C$_6$H$_3$-2,6-(MeO)$_2$}(C$_6$H$_3$-2-*O*-6-MeO)), derived from demethylation of one of the *ortho*-methoxy groups in (2,6-dimethoxyphenyl)diphenylphosphine and bis(2,6-dimethoxyphenyl)phenylphosphine gave novel six- or seven-membered metallacycles arising from single or double insertion of alkyne into the M–O or P–C bond on treatment with 1-alkyne or disubstituted alkyne in the presence of KPF$_6$ or NaPF$_6$ [7]. When complexes Cp*MCl(MDMPP-*P*,*O*) and Cp*Ir(TDMPP-*P*,*O*,*O*′) (TDMPP-*P*,*O*,*O*′ = *P*{C$_6$H$_3$-2,6-(MeO)$_2$}(C$_6$H$_3$-2-*O*-6-MeO)$_2$) were treated with electron-deficient olefins such as tetracyanoethylene (tcne) and 7,7,8,8-tetracyano-*p*-quinodimethane (tcnq), olefin inserted into weakly activated C–H bond on the phenyl ring of the phosphine ligand [8]. During a series of our research on interaction of these complexes with small molecule, we found the C–N bond cleavage reaction of tertiary and secondary amines to give primary amine complexes. We here report the facile metal-assisted C–N bond cleavage reactions of alkyl amines.

When Cp*RhCl(MDMPP-*P*,*O*) **1** was treated with diethylamine in the presence of KPF$_6$ at room temperature, orange complex formulated as [Cp*Rh(NH$_2$Et)(MDMPP-*P*,*O*)](PF$_6$) **2a** based on elementary analysis and FAB mass spectrometry, was generated in high yield (Scheme 1). The IR spectrum showed two bands at 3323 and 3273 cm^{-1} due to N–H groups and a band at 885 cm^{-1} due to a PF$_6$ group. The ^{1}H NMR spectrum showed four characteristic resonances at δ 0.69(t), 1.48(d), 2.09(br), and 3.35(s), due to methyl, Cp*, methylene and methoxy protons, respectively. The ^{31}P{^{1}H} NMR spectrum showed a doublet at δ 50.3 together with a septet at δ-143.7 due to a PF$_6$ group. This complex **2a** can be prepared by the reaction of

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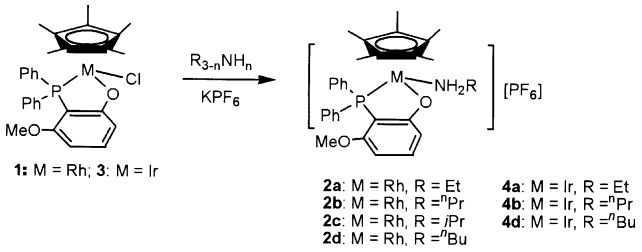


Scheme 1. Reactions of Cp*MCl(MDMPP-*P*,*O*) (**1**: M = Rh; **3**: M = Ir) with alkyl amine.

Cp*RhCl(MDMPP-*P*,*O*) with ethylamine in the presence of KPF_6. These results showed that the C–N bond cleavage occurred in secondary amine, whereas did not proceed in the primary amine. A similar C–N bond cleavage occurred in an iridium (III) analog **3** to generate the corresponding [Cp*Ir(NH_2Et)(MDMPP-*P*,*O*)](PF_6) complex **4a**. It was confirmed by X-ray analysis of **4a** that ethylamine coordinated to the iridium metal (Fig. 1) [9].

When secondary amines such as di-*n*-propylamine, di-*iso*-propylamine and di-*n*-butylamine were used, the corresponding primary alkyl amine complexes, [Cp*M(NH_2R)(MDMPP-*P*,*O*)](PF_6) (M = Rh; **2b**: R = ^{n}Pr; **2c**: R = ^{i}Pr; **2d**: R = ^{n}Bu; M = Ir; **4b**: R = ^{n}Pr; **4d**: R = ^{n}Bu) were generated. Secondary aromatic amine such as Ph_2NH did not undergo a C–N bond cleavage, suggesting the requirement for the presence of the NCH_2 or NCH groups in amine molecules.

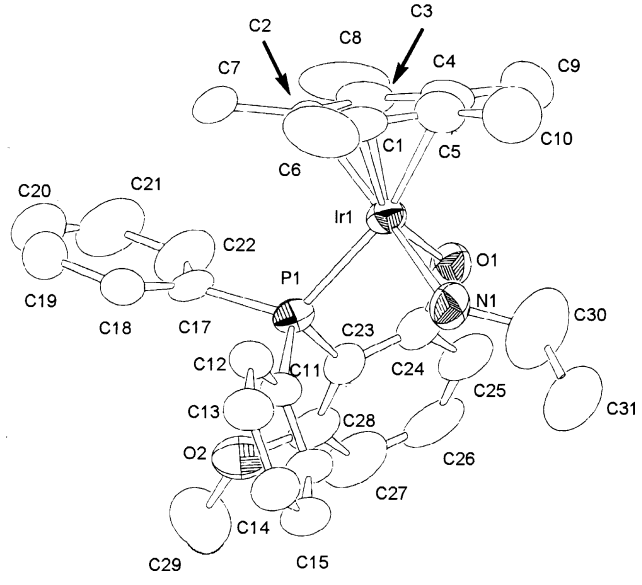
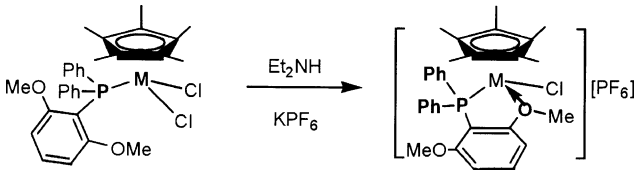


Fig. 1. Molecular structure of complex cation [Cp*IrCl(MDMPP-*P*,*O*)($EtNH_2$)](PF_6) **4a**. The anion was omitted for clarity. Selected bond length (Å) and angles (°): Ir–P(1) 2.304(3), Ir–O(1) 2.074(7), Ir–N 2.158(8); P(1)–Ir–O(1) 82.3(2), P(1)–Ir–N(1) 87.9(2), O(1)–Ir–N(1) 85.1(3).



Scheme 2. Reactions of Cp*MCl [$PPh_2\{C_6H_3$-2, 6-$(MeO)_2\}$] (M = Rh or Ir) with diethyl amine.

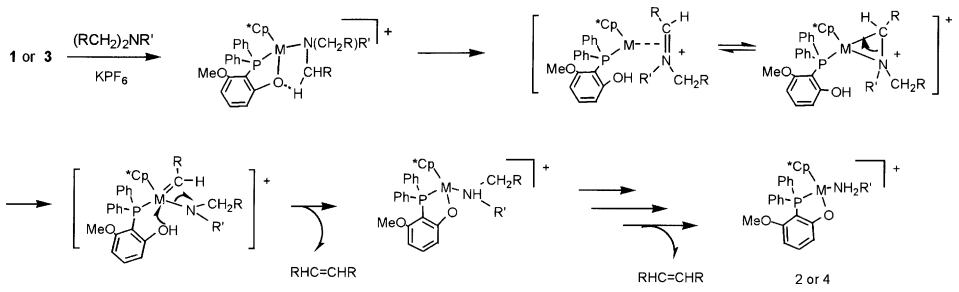
The reactions of **1** or **3** with triethylamine also gave **2a** and **4a**, respectively, whereas tertiary amines such as ^{n}Pr$_3$N and ^{n}Bu$_3$N did not undergo a C–N bond cleavage. No C–N cleavage reaction occurred in the monodentate complexes such as Cp* MCl_2(L) (M = Rh, Ir; L = PPh_3, $PPh_2\{C_6H_3$-2, 6-$(MeO)_2\}$); especially in the latter complex, an ether-O coordinated complex [Cp*MCl{PPh_2(C_6H_3-2-*O*Me-6-MeO) }](PF_6) (M = Rh, Ir) [6] was isolated, suggesting the unique specificity of the P,O chelate complexes (Scheme 2).

In order to examine a fate of fragments for amines, the ^{1}H NMR spectrum of a mixture of Cp*RhCl (MDMPP-*P*,*O*), *i*-Pr$_2$NH and KPF_6 was monitored in a mixture of $CDCl_3$ and $(CD_3)_2CO$, and showed a singlet at δ 1.04 together with resonance corresponding to **2c**, suggesting the presence of 2,3-dimethylbut-2-ene, followed by identification of 2,3-dibromo-2, 3-dimethylbutane derived from its bromination. A similar reaction using *n*-Bu_2NH was carried out, and the GC-MS spectrum of the reaction mixture showed the presence of octene.

A tentative C–N cleavage route for secondary or tertiary amines is shown in Scheme 3. Since no η^1-complexes led to the C–N cleavage, the P,σO-coordination is assumed to be indispensable. The reaction consists of an initial coordination of alkyl amine to a metal, accompanying with the transfer of α-hydrogen of alkyl amine to the phenolate, forming a metallaaziridine. The resulting carbene-imine species by the C–N bond cleavage rearranges to a primary amine complex and olefin arising from a dimerization of carbene.

The present reactions provide a mild C–N cleavage of alkyl amines by P,O chelating complexes of pentamethylcyclopentadienylrhodium(III) and -iridium(III). We are currently investigating the catalytic application of the reaction.

Satisfactory analytical data were obtained for new complexes. The representative reaction is described: *Preparation* of **2a**: A solution of (54 mg, 0.093 mmol), diethyl amine (0.5 ml) and $NaPF_6$ (54.1 mg, 0.322 mmol) was stirred in CH_2Cl_2 (7.5 ml) and acetone (7.5 ml) at rt. After 4 h, the solvent was removed, and residue was extracted with CH_2Cl_2. The CH_2Cl_2 was concentrated, and diethyl ether was added to give orange



Scheme 3. A possible pathway for the C–N cleavage reaction. The PF_6 anion was omitted for clarity.

brown crystals of **2a** (55.2 mg, 80.8%). IR(nujol): 3325, 3285(N–H), 839(PF_6) cm^{-1}; ^1H NMR($CDCl_3$): δ 0.69 (t, $J_{HH} = 7.0$ Hz, Me, 3H), 1.48 (d, $J_{PH} = 3.0$ Hz, Cp*, 15H), 2.09 (br, CH_2, 2H), 3.35 (s, OMe, 3H), 3.40 (b, NH_2, 2H), 6.0–7.6 (m, 13H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 50.3 (d, $J_{PRh} = 137$ Hz), −143.7 (sep, $J_{PF} = 712$ Hz). (Yield of **2a** from Et_3N: 61.6%). **2b** (80%, from $^n Pr_2NH$): IR(nujol): 3327, 3285 (NH), 839 (PF_6) cm^{-1}; ^1H NMR($CDCl_3$): δ 0.43 (t, $J_{HH} = 7.5$ Hz, Me, 3H), 0.95 (m, CH_2, 2H), 1.48 (d, $J_{PH} = 3.0$ Hz, Cp*, 15H), 1.99 (br, CH_2, 2H), 3.35 (s, OMe, 3H), 6.0–7.6 (m, 13H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 50.0 (d, $J_{PRh} = 125$ Hz), −143.8 (sep, $J_{PF} = 713$ Hz). **2c** (%, from $^i Pr_2NH$): FAB mass (m/z): 606 ($[M]^+$). IR(nujol): 3314, 3274 (NH), 839 (PF_6) cm^{-1}; ^1H NMR($CDCl_3$): δ 0.36 (d, $J_{HH} = 6.5$ Hz, $^i Pr$, 3H), 0.95 (d, $J_{HH} = 6.5$ Hz, $^i Pr$, 3H), 1.47 (d, $J_{PH} = 3.5$ Hz, Cp*, 15H), 2.13 (b, NH_2, 2H), 3.34 (s, OMe, 3H), 6.0–7.7 (m, 13H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 50.8 (d, $J_{PRh} = 125$ Hz), −143.8 (sep, $J_{PF} = 713$ Hz). **2d** (orange, 48.3% from $^nBu_2NH$): IR(nujol): 3319, 3277 (NH), 835 (PF_6) cm^{-1}; ^1H NMR($CDCl_3$): δ 0.62 (t, $J_{HH} = 7.0$ Hz, Me, 3H), 0.85 (b, CH_2, 6H), 1.48 (d, $J_{PH} = 3.0$ Hz, Cp*, 15H), 2.02 (b, CH_2), 2.35 (b, NH_2, 2H), 3.35 (s, OMe, 3H), 6.0–7.7 (m, 13H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 49.9 (d, $J_{PRh} = 139$ Hz), −143.8 (sep, $J_{PF} = 714$ Hz). **4a** (yellow, 16.2% from Et_3N; 57.2% from Et_2NH): FAB mass (m/z): 694 ($[M]^+$); IR(nujol): 3312, 3265(N–H), 844 (PF_6) cm^{-1}; ^1H NMR($CDCl_3$): δ 0.72 (t, $J_{HH} = 7.0$ Hz, Me, 3H), 1.52 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 2.16 (q, $J_{HH} = 7.0$ Hz, CH_2, 2H), 3.36 (s, OMe, 3H), 6.0–7.6 (m, 13H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 26.3 (s), −143.7 (sep, $J_{PF} = 712$ Hz). **4b** (yellow, 71.1%, from $^n Pr_2NH$): IR(nujol): 3302, 3260 (NH), 839 (PF_6) cm^{-1}; ^1H NMR($CDCl_3$): δ 0.43 (t, $J_{HH} = 7.5$ Hz, Me, 3H), 1.00 (br, CH_2, 2H), 1.52 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 2.11 (br, CH_2, 2H), 2.28 (b, NH_2, 2H), 3.37 (s, OMe, 3H), 6.0–7.6 (m, 13H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 26.3 (d, $J_{PRh} = 125$ Hz), −143.6 (sep, $J_{PF} = 713$ Hz). **4d** (orange, 51.1% from $^nBu_2NH$): IR(nujol): 3310, 3273 (NH), 837 (PF_6) cm^{-1}; ^1H NMR($CDCl_3$): δ 0.63 (t, $J_{HH} = 7.0$ Hz, Me, 3H), 0.90 (b, CH_2, 6H), 1.52 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 2.14 (b, CH_2, and NH_2, 8H), 3.37 (s, OMe, 3H), 6.0–7.2 (m, 13H). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 26.2 (s), −143.8 (sep, $J_{PF} = 711$ Hz).

Monitoring of the reaction mixture by the ^1H *NMR spectrum*: 2,3-dimethylbut-2-ene was estimated as ca. 55% yields based on the intensity of the methyl resonance.

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[9] Crystal data for **4a**: $C_{31}H_{38}NOP_2F_6Ir$, $M = 808.8$, monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, $a = 12.541(2)$, $b = 14.708(4)$, $c = 17.539(3)$ Å, $\beta = 92.19(1)°$, $V = 3232.9(9)$ Å^3, $D = 1.662$ g/cm^3. Data were collected on a Rigaku AFC5S diffractometer. The structure was solved by Patterson methods and refined anisotropically using full-matrix least-square techniques based on F^2 for all unique reflections (5914) to give $R = 0.117$ and $Rw = 0.149$ $[w = 1/\sigma^2(Fo)]$ for 5914 reflections, and $R1 = 0.056$ (for 4134 reflections $I > 2.0\sigma(Io)$). GOF = 1.48.