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Synthesis of Rh(I) Complexes Bearing *N*-*p*-Toluenesulfonyl-substituted *N*-Heterocyclic Carbenes

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We have synthesized Rh(I) complexes bearing a 1,2,4-triazol-3-ylidene or imidazol-2-ylidene substituted *N*-*p*-toluenesulfonyl (*N*-Ts) group. Structural characterizations of the Rh(I) complexes revealed that, because of its mesomeric and inductive electron-withdrawing effects, the *N*-Ts substituent increased π-accepting ability and decreased σ-donating ability of carbenes compared to *N*-mesityl substituents.

N-Heterocyclic carbenes (NHCs) have attracted great attention as organometallic ligands[1] and organocatalysts[2] owing to their strong σ-donating ability and high flexibility in the molecular design. At the same time, electron-deficient NHCs with increased π-accepting ability have also been developed in the last decade.[3] Recently, we have reported *N*-2,4-dinitrophenyl (*N*-DNP)-substituted 1,2,4-triazol-3-ylidene **A**[4] and imidazol-2-ylidene **B**[5] with stronger π-accepting ability than typical NHCs (Figure 1). However, the electronic properties of the DNP substituent arise exclusively from inductive electron-withdrawing effect, because it can hardly conjugate with the NHC framework. Herein, we describe the synthesis and structural characterizations of Rh(I) complexes bearing *N*-*p*-toluenesulfonyl (*N*-Ts)-substituted 1,2,4-triazol-3-ylidene and imidazol-2-ylidene. Because of its mesomeric effect, the *N*-Ts group is expected to conjugate with the NHC framework and act as an effective electron-withdrawing group.

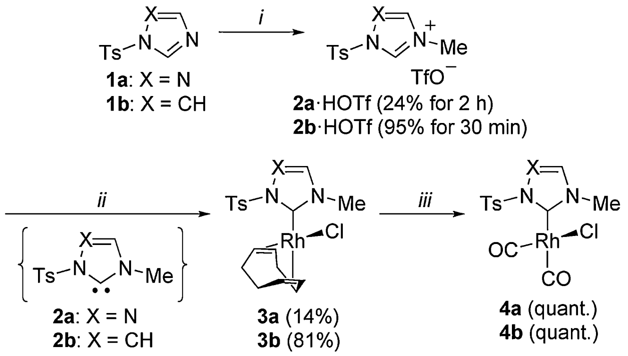
The incorporation of electronegative elements to the NHC framework decreases the σ-donating ability of carbenes. Methylation of 1-(*p*-toluenesulfonyl)-1,2,4-triazole (**1a**) and 1-(*p*-toluenesulfonyl)imidazole (**1b**) with methyl triflate at 0 °C (2 h for **1a** and 30 min for **1b**) afforded azolium salts **2a**•HOTf in 24% yield and **2b**•HOTf in 95% yield (Scheme 1). Reaction of [{RhCl(cod)}$_2$] (cod: 1,5-cyclooctadiene) with **2a**•HOTf and **2b**•HOTf in the presence of sodium bis(trimethylsilyl)amide (NaHMDS) afforded Rh(I)–cod complex [RhCl(**2a**)(cod)] (**3a**) in 14% and [RhCl(**2b**)(cod)] (**3b**) in 81% yield, respectively, with in situ generation of free NHC **2a** and **2b**. Furthermore, **3a** and **3b** were converted to Rh(I)–carbonyl complexes [RhCl(**2a**)(CO)$_2$] (**4a**) and [RhCl(**2b**)(CO)$_2$] (**4b**), respectively, in quantitative yields by bubbling CO gas through their solutions in CH$_2$Cl$_2$ or CDCl$_3$.

A **B**

DNP = 2,4-(NO$_2$)$_2$C$_6$H$_3$

Figure 1. *N*-DNP-substituted *N*-heterocyclic carbene.

To evaluate the electronic properties of *N*-Ts-substituted NHCs **2a** and **2b**, we compared the properties of the Rh(I) complexes **3a** and **3b**, and **4a** and **4b** with those of corresponding Rh(I) complexes bearing 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) **3c** and **4c**. First, we investigated σ-donating ability of the NHCs from the infrared (IR) spectra of complexes **4a**–**4c** (Table 1 and Figure 2). Average CO stretching frequencies of **4a**–**4c** (ν_{av}(CO)) increased in the order: **4c** (2037.0 cm^{-1}) < **4b** (2046.1 cm^{-1}) < **4a** (2050.5 cm^{-1}); these ν_{av}(CO) could be converted to Tolman electronic parameter (TEP) values as described in the literature, i.e., 2050 cm^{-1} for **4c**, 2057 cm^{-1} for **4b**, and 2061 cm^{-1} for **4a**. Thus, NHC **2a** showed the weakest σ-donating ability among the examined NHCs.



Scheme 1. Syntheses of Rh(I)–NHC complexes; reaction conditions: (*i*) MeOTf, CH$_2$Cl$_2$, 0 °C; (*ii*) [{RhCl(cod)}$_2$], NaHMDS, −78 °C to rt, 12 h; (*iii*) CO gas (bubbling), CH$_2$Cl$_2$ or CD$_3$Cl, rt, 30 min (NaHMDS: sodium bis(trimethylsilyl)amide; NHC: *N*-heterocyclic carbene; *N*-Ts: *N*-*p*-toluenesulfonyl).

Table 1. IR ν(CO) stretching frequencies of [RhCl(L)(CO)$_2$] (**4a**–**4c**) in CH$_2$Cl$_2$ and TEP values

Complex	ν (CO)[a]	ν_{av}(CO)[b]	TEP[c]
4a (L = **2a**)	2012.4, 2088.5	2050.5	2061
4b (L = **2b**)	2008.5, 2083.7	2046.1	2057
4c (L = IMes)	1995.0, 2078.9	2037.0	2050

[a]IR CO stretching frequencies in cm^{-1} (CH$_2$Cl$_2$). [b]The average of ν(CO) in cm^{-1}. [c]Tolman electronic parameter (TEP) in cm^{-1} calculated using the equation TEP (cm^{-1}) = 0.8001ν_{av}(CO) (cm^{-1}) + 420.0 (cm^{-1}).[1b]

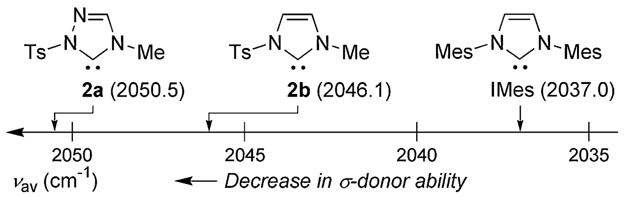


Figure 2. Comparison of the ν_{av}(CO) values of [RhCl(NHC)(CO)$_2$] **4a**–**4c**.

Table 2. ^{13}C NMR chemical shifts of carbenic carbons and carbonyls in [RhCl(L)(cod)] **3a**–**3c** in CDCl$_3$

Complex	^{13}CN$_2$/ppm	*trans*-^{13}CH$_{COD}$/ppm
3a (L = **2a**)	197.6	99.3, 99.7
3b (L = **2b**)	191.2	98.0, 98.3
3c (L = IMes)[6]	183.6	96.3

Next, the ^{13}C NMR spectra of Rh(I)–cod complexes **3a**–**3c** were examined to support the IR spectral analysis (Table 2). As the TEP values of NHCs increased, both the signals of carbenic carbons and alkene moieties of cod *trans* to the NHC ligands shifted downfield. This deshielding can be explained by (i) the decrease in the N → C$_{carbene}$ π-overlaps caused by the *N*-Ts substituent and incorporated N atoms into the NHC frameworks and (ii) the decrease in the π-backbonding interactions from the electron-deficient metal centers to the alkene moieties of cod.[3b,7]

Moreover, single-crystal X-ray diffraction analyses of **3a**–**3c** also supported the aforementioned trend between the TEP values of the NHCs and their π-accepting ability. ORTEP representations of **3a** and **3b** are shown in Figures 3[8] and 4,[9] respectively; Figure 3 shows one of the two crystallographically independent molecules. Based on the increase in the TEP values, it can be observed that the Rh–C$_{carbene}$ crystallographic distance shortened in the order: **3c** (2.0494(16) Å)[10] > **3b** (2.010(2) Å) > **3a** (average 1.997 Å). It can be construed that the contraction of Rh–C$_{carbene}$ bond distance is caused by the increase in the bond order because of the Rh → C$_{carbene}$ π-backbonding interaction. Notably, the NHC frameworks could be conjugated with one of the S=O bonds in the sulfonyl group; the dihedral angle between the NHC framework and the S=O bond for **3a** is either 12.29(16) or 11.42(17)°, whereas that for **3b** is 15.8(3)°. Incidentally, the dihedral angle between the NHC framework and DNP ring for [RhCl(**B**)(cod)] is 136.78(19)°.[5] Therefore, it is assumed that the *N*-Ts substituent acts as electron-withdrawing group because of both inductive and mesomeric effects.

To evaluate the electronic properties of NHCs, the energies of σ-donor orbital (E_σ) and π-acceptor orbital (E_π) and natural atomic charges of the carbenic carbon atoms (δ_C) were calculated (Table 3).[11] E_σ is the energy of an occupied carbene lone pair and E_π is the energy of a vacant p orbital on the carbene carbon atom. Both the values of E_σ and E_π decreased with increasing the TEP values, indicating that the σ-donating ability of the NHCs decreased, whereas the π-accepting ability increased. Furthermore, the δ_C values positively increased with increasing downfield shifts of the ^{13}C NMR signals.

In conclusion, we synthesized novel Rh(I) complexes coordinated to *N*-Ts-substituted 1,2,4-triazol-3-ylidene **2a** and imidazol-2-ylidene **2b**. Experimental and computational analyses of [RhCl(**2**)(cod)] **3** and [RhCl(**2**)(CO)$_2$] **4** revealed that the σ-donating ability of the NHCs decreased and the π-accepting ability increased in the order IMes, **2b**, and **2a**. Furthermore, X-ray diffraction analysis made it obvious that the *N*-Ts substituent could utilize its mesomeric electron-withdrawing effect.[12]

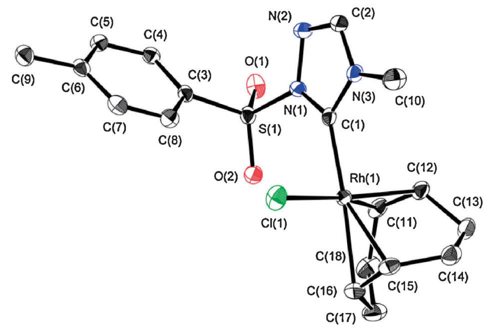


Figure 3. ORTEP representation of **3a** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. One of the two crystallographically independent molecules is shown.

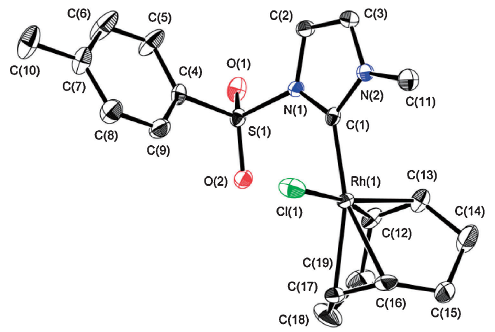


Figure 4. ORTEP representation of **3b** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Table 3. Summary of computational analysis of NHCs

NHC	E_σ/eV[a]	E_π/eV[b]	δ_C[c]
2a	−8.19 (HOMO−4)	−1.68 (LUMO)	0.147
2b	−7.86 (HOMO−4)	−1.41 (LUMO)	0.131
IMes	−7.47 (HOMO−8)	−1.17 (LUMO)	0.122

[a] Energies of σ-donor orbital. [b] Energies of π-acceptor orbital. [c] Natural atomic charges of carbenic carbon atoms.

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8 Selected crystallographic data of **3a**. $C_{18}H_{23}ClN_3O_2RhS$, $M_r = 483.81$, $T = 120(2)\,K$, triclinic, $P\bar{1}$, $a = 11.629(14)\,Å$, $b = 13.037(15)\,Å$, $c = 13.720(16)\,Å$, $\alpha = 67.309(12)°$, $\beta = 81.675(18)°$, $\gamma = 87.45(3)°$, $V = 1899(4)\,Å^3$, $Z = 4$, $D_{calcd} = 1.693\,g\,cm^{-3}$, $F_{000} = 984$, $\mu(\mathrm{Mo\,K\alpha}) = 1.168\,mm^{-1}$, 21168 reflections collected, 8493 unique ($R_{int} = 0.0199$), $GOF = 1.063$, $R1 = 0.0206$ ($I > 2\sigma(I)$) and $wR_2 = 0.0530$ (all data). CCDC 943330 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

9 Selected crystallographic data of **3b**. $C_{19}H_{24}ClN_2O_2RhS$, $M_r = 482.82$, $T = 100(2)\,K$, monoclinic, Cc, $a = 10.105(2)\,Å$, $b = 17.149(4)\,Å$, $c = 11.381(3)\,Å$, $\alpha = 90°$, $\beta = 96.918(3)°$, $\gamma = 90°$, $V = 1957.9(8)\,Å^3$, $Z = 4$, $D_{calcd} = 1.638\,g\,cm^{-3}$, $F_{000} = 984$, $\mu(\mathrm{Mo\,K\alpha}) = 1.131\,mm^{-1}$, 5354 reflections collected, 3019 unique ($R_{int} = 0.0170$), $GOF = 1.057$, $R1 = 0.0183$ ($I > 2\sigma(I)$) and $wR_2 = 0.0481$ (all data). CCDC 943329.

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11 All calculations were performed at the M06/cc-pVTZ level using the Gaussian 09 program package and NBO analysis was carried out with the NBO version 3.1 program. For details of the calculations see the Supporting Information.

12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.