Crystal Structure of a Rhodium(I) Complex with a Chelating Bidentate Isonitrile Ligand Containing Nitrogen Bridging Groups

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A rhodium(I) complex with a chelating bidentate isonitrile ligand, 1,2-bis(4-*tert*-butyl-2-isocyanophenylmethylamine)ethane ($\text{Rh}[t\text{-BuDinMeNC}]_2\text{BF}_4$), was synthesized and characterized by X-ray crystallography. The complex crystallizes in a triclinic crystal system under the space group $P\bar{1}$ and $Z = 2$ with $a = 10.3165(6)\text{\AA}$, $b = 15.5162(9)\text{\AA}$, $c = 19.0534(11)\text{\AA}$, $\alpha = 68.166(1)^\circ$, $\beta = 78.973(1)^\circ$, $\gamma = 89.329(1)^\circ$, $V = 2773.0(3)\text{\AA}^3$. The complex is square-planar, and the BF_4^- anion exists as a counter ion. This is the first structural example of a bidentate isonitrile-containing complex having a square-planar structure.

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The syntheses and characterizations of bidentate isonitrile ligand-containing complexes were first summarized by Angelici *et al.*¹ Ligands containing ethereal oxygen bridging groups² and thioetheral sulfur bridging groups³ were also reported. Though these ligands contain four coordination sites, namely two oxygen atoms or two sulfur atoms in the bridging group and two carbon atoms in the isonitrile groups, metal ions are only coordinated through the carbon atoms of the isonitrile groups. However, the metal ions are coordinated to two carbons of the isonitrile to form a thirteen-membered ring structure, and the isonitrile can also act as a bidentate ligand to form a square-planar complex. Herein, we report on our latest investigation of a bidentate isonitrile ligand containing amine bridging groups. 1,2-Bis(4-*tert*-butyl-2-isocyanophenylmethylamine)ethane (*t*-BuDinMeNC) was synthesized for the first time. A rhodium(I) complex with the ligand ($\text{Rh}[t\text{-BuDinMeNC}]_2\text{BF}_4$) was prepared and characterized by X-ray crystallography.

t-BuDinMeNC was synthesized as shown in Scheme 1. It was fully characterized by elemental analysis, mass and infrared and ^1H NMR spectroscopy. Bis(1,5-cyclooctadiene)dichlororhodium(I) (0.030 g, 0.0608 mmol) was dissolved in dichloromethane (5 ml) under a nitrogen atmosphere. After this solution was stirred for 5 min, a solution of *t*-BuDinMeNC (0.098 g, 0.243 mmol) in dichloromethane (6 ml) was added. The reaction solution was stirred at room

temperature for 5 h, and was then filtrated. The volume of the filter liquor was reduced to half by evaporation. When the product precipitated from the solution after hexane was added, the solution was kept at 5°C for 12 h. A green-yellow powder of complex $\text{Rh}[t\text{-BuDinMeNC}]_2\text{Cl}$ was obtained by filtration, and was fully washed with diethyl ether. The title complex, $\text{Rh}[t\text{-BuDinMeNC}]_2\text{BF}_4$, was gained by the anion-exchange reaction of $\text{Rh}[t\text{-BuDinMeNC}]_2\text{Cl}$ and NaBF_4 in dichloromethane. Red crystals of $\text{Rh}[t\text{-BuDinMeNC}]_2\text{BF}_4$ (Fig. 1) containing one molecule of hexane (used in the synthetic process) and one molecule of ethanol, which were suitable for X-ray crystal structure analysis, were obtained by recrystallization from hexane and ethanol (vol/vol, 1:1) in a yield of 38%. *Anal.* Found: H, 7.46; C, 63.38; N, 10.27. *Calc.* for $\text{C}_{57}\text{H}_{81}\text{BF}_4\text{N}_8\text{ORh}$: H, 7.53; C, 63.16; N, 10.34%.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Most of the hydrogen atoms were located at calculated positions and/or at positions found from difference Fourier maps. Crystal data and details associated with data collection are summarized in Table 1. Figure 2 shows an ORTEP view of the title complex without a solvent. Selected bond lengths and angles are listed in Table 2. In the complex, the Rh(I) atom is coordinated with four carbon atoms of two isonitrile ligands to form a square-planar complex cation, while it is not coordinated with two nitrogen atoms of the amine bridging group in the isonitrile to form a thirteen-membered

Scheme 1 Synthesis of *t*-BuDinMeNC

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Fig. 1 Chemical structure of the title complex.

Table 1 Crystal and experimental data

Formula	$C_{52}H_{68}BF_4N_8R \cdot 0.5(C_6H_{14}) \cdot C_2H_6O$
Formula weight	1084.02
Temperature	100(2)K
Crystal size	$0.31 \times 0.12 \times 0.12$ mm
Crystal color	red
Crystal description	prismatic
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
Cell dimensions	$a = 10.3165(6)\text{\AA}$ $b = 15.5162(9)\text{\AA}$ $c = 19.0534(11)\text{\AA}$ $\alpha = 68.166(1)^\circ$ $\beta = 78.973(1)^\circ$ $\gamma = 89.329(1)^\circ$
V	$2773.0(3)\text{\AA}^3$
D_{calc}	1.298 g cm^{-3}
Radiation	$0.71073\text{\AA}$ (Mo K_α)
$\mu(\text{Mo } K_\alpha)$	0.368 mm^{-1}
Monochromator	graphite
No. of reflections used	11313
No. of parameters	699
$2\theta_{\text{max}}$	52.74°
R	0.0623
Goodness of fit	1.051
$(\Delta\sigma)_{\text{max}}$	4.096
$(\Delta\rho)_{\text{max}}$	$0.949\text{ e\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$	$-0.800\text{ e\AA}^{-3}$
Measurement	Bruker SMART CCD-1000
Program system	SADABS
Structure determination	SHELXS-97 (Sheldrick, 1990)
Refinement	SHELXL-97 (Sheldrick, 1997)

CCDC 269313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fig. 2 ORTEP drawing of the title complex. The thermal ellipsoids are drawn at the 50% probability level. The H atoms are omitted for clarity.

ring structure.³ BF_4^- exists as an anion. The Rh atom and four carbon atoms are almost in the same plane. The angle of C(1)-Rh(1)-C(27) is $168.39(16)^\circ$ and the angle of C(18)-Rh(1)-C(44) is $171.86(16)^\circ$. Furthermore, the angles of N(1)-C(1)-Rh(1), N(4)-C(18)-Rh(1), N(5)-C(27)-Rh(1),

Table 2 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

C(1)-N(1)	1.152(5)	C(27)-N(5)	1.153(6)
C(1)-Rh(1)	1.949(4)	C(27)-Rh(1)	1.976(5)
C(18)-N(4)	1.167(6)	C(44)-N(8)	1.165(5)
C(18)-Rh(1)	1.944(5)	C(44)-Rh(1)	1.959(4)
C(2)-N(1)	1.387(5)	C(28)-N(5)	1.393(6)
C(17)-N(4)	1.390(5)	C(43)-N(8)	1.396(5)
C(9)-C(10)	1.521(7)	C(35)-C(36)	1.523(7)
N(1)-C(1)-Rh(1)	172.4(3)	N(5)-C(27)-Rh(1)	172.9(4)
N(4)-C(18)-Rh(1)	174.3(4)	N(8)-C(44)-Rh(1)	174.6(3)
C(1)-N(1)-C(2)	170.7(4)	C(27)-N(5)-C(28)	174.8(5)
C(18)-N(4)-C(17)	173.8(4)	C(44)-N(8)-C(43)	172.4(4)
N(2)-C(9)-C(10)	112.1(3)	N(6)-C(35)-C(36)	111.8(4)
C(7)-N(2)-C(8)	115.6(4)	C(33)-N(6)-C(34)	115.8(5)
C(7)-N(2)-C(9)	114.1(3)	C(33)-N(6)-C(35)	114.9(4)
C(8)-N(2)-C(9)	111.8(4)	C(34)-N(6)-C(35)	116.2(5)
N(3)-C(10)-C(9)	111.5(3)	N(7)-C(36)-C(35)	113.1(4)
C(12)-N(3)-C(11)	114.2(4)	C(38)-N(7)-C(37)	113.4(4)
C(12)-N(3)-C(10)	112.0(3)	C(38)-N(7)-C(36)	114.7(4)
C(11)-N(3)-C(10)	112.4(4)	C(37)-N(7)-C(36)	115.0(4)
C(18)-Rh(1)-C(1)	89.05(18)	C(44)-Rh(1)-C(27)	90.59(17)
C(18)-Rh(1)-C(44)	171.86(16)	C(1)-Rh(1)-C(27)	168.39(16)
C(1)-Rh(1)-C(44)	89.70(16)	C(18)-Rh(1)-C(27)	89.03(18)

N(8)-C(44)-Rh(1) are $172.4(3)^\circ$, $174.3(4)^\circ$, $172.9(4)^\circ$, and $174.6(3)^\circ$, respectively. This also determines the square-planar structure of the complex. The mean bond length between the Rh atom and carbon atoms is $1.957\text{\AA}$. The mean bond length between the isocyanato groups and the phenyl groups is $1.392\text{\AA}$. Two of them are longer than the mean bond length of $C\equiv N$, which is $1.159\text{\AA}$. Two carbon atoms of bridging groups are at two sides of the square-planar structure. Though the angles of N(2)-C(9)-C(10) and N(3)-C(10)-C(9) ($112.1(3)^\circ$ and $111.5(3)^\circ$, respectively) are similar to those of N(6)-C(35)-C(36) and N(7)-C(36)-C(35) ($111.8(4)^\circ$ and $113.1(4)^\circ$, respectively), two bridging groups in two ligands show different configurations. One of them is a boat form (N(6)-C(35)-C(36)-N(7)), and the other is a chair form (N(2)-C(9)-C(10)-N(3)). This disordered structure may be due to the interaction among the complex cation, the BF_4^- anion and the solvents. Furthermore, the maximum shift in the last refinement ($(\Delta\sigma)_{\text{max}}$) did not converge, though the least-squares technique was used (Table 1). This may be due to the disordered structure.

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