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Short Note

[(η^5-pentamethylcyclopentadienyl)(3-fluoro-*N*-methyl benzylamine-κ^1,*N*)dichlorido]iridium(III)

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Received: 17 May 2018; Accepted: 1 June 2018; Published: 5 June 2018

Abstract: A half-sandwich iridium(III) complex containing 3-fluoro-*N*-methylbenzylamine ligands has been obtained by reaction of one equivalent of [(η^5-Cp*)$IrCl_2$]$_2$ (Cp* = pentamethylcyclopentadienyl) with two equivalent of 3-fluoro-*N*-methylbenzylamine in very good yield. The structure of this complex was confirmed by X-ray crystallography, ^{1}H-NMR, ^{13}C-NMR spectroscopy, and elemental analysis.

Keywords: half-sandwich; iridium; 3-fluoro-*N*-methylbenzylamine; X-ray crystallography

1. Introduction

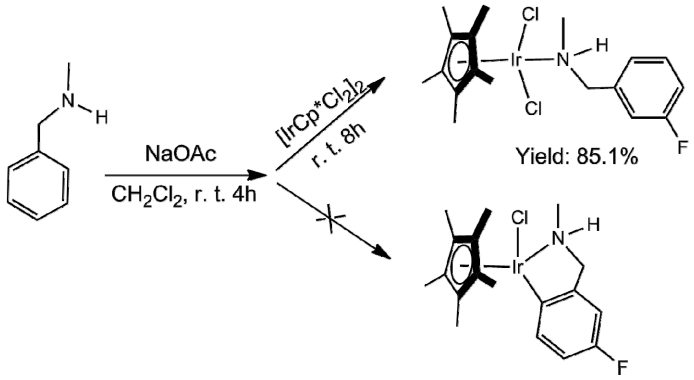
Organometallic half-sandwich iridium (Ir) complexes containing amines or imine ligands have received considerable attention in the field of catalytic chemistry [1–5] and medicinal chemistry [6–9], as these ligands can be readily modified with appropriate substituents. Most of these iridium complexes comprise cyclopentadienyl ligand, amine or imine chelating ligand, and a monodentate halide ligand. However, the Ir complexes bearing *N*-monodentate ligands are much less developed [10,11]. In the field of biology, the *N*-monodentate complexes exhibit a variety of properties that are different from those of the bidentate compounds. For example, the *N*-monodentate complexes can undergo double hydrolysis [12]. In this contribution, Ir complex containing secondary amine 3-fluoro-*N*-methylbenzylamine as *N*-monodentate ligand was prepared and characterized.

2. Results and Discussion

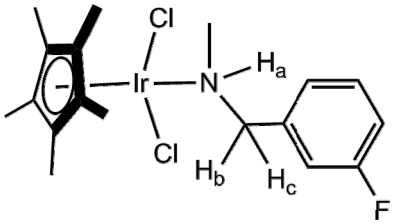
The title complex was synthesized according to the modified procedure of the reported literature [4]. As shown in Scheme 1, treating 3-fluoro-*N*-methylbenzylamine with 7.5 equiv of sodium acetate in dichloromethane at room temperature for 4 h, then adding [(η^5-Cp*)$IrCl_2$]$_2$ (0.5 equiv) to the mixture at room temperature for 8 h resulted in the form of the title complex in high yield, up to 85.1%, without other side products. The addition of sodium acetate did not result in the C-H activation of aromatic ring. In addition, we found that the same product would be obtained in absence of sodium acetate. The product was characterized by ^{1}H-NMR spectroscopy (see Supplementary Materials, Figure S1), ^{13}C-NMR spectroscopy (see Supplementary Materials, Figure S2), elemental analysis, and X-ray crystallography (see Supplementary Materials, Table S1).

In $CDCl_3$, the characteristic peak in the ^{1}H-NMR for product is at ca. δ 3.93 ppm, corresponding to the NH group. The benzylic CH_2 displays two signals, i.e., a doublet peak (δ 4.91 ppm) and a doublet of doublets (dd) peak (δ 3.48 ppm). As shown in Scheme 2, H_b-H_c is coupled to form doublet peak ($J_{Hb\text{-}Hc}$ = 12.8 Hz). However, H_b-H_a and H_b-H_c are separately coupled to form doublet of doublets peak ($J_{Hb\text{-}Hc}$ = 12.8 Hz; $J_{Ha\text{-}Hc}$ = 11.9 Hz).

The recrystallization of this compound in dichloromethane/diethyl ether solution at 289 K gave single crystals suitable for X-ray diffraction. The molecular structure of the product is shown in Figure 1. It is clear that only nitrogen atoms and iridium link, forming the title complex, and no C,N-chelating iridium complex was obtained. The title complex adopts piano-stool configuration, with Cp* acting as the seat and 3-fluoro-*N*-methylbenzylamine ligand and chloride groups as the legs. The crystal packing of the title complex is orthorhombic. The distance between iridium to the centroid of bound η^5-cyclopentadienyl ligand is 1.7852 Å. The bond length of Ir-N1 is 2.164(6) Å. The angle of C1-N1-Ir1 and C2-N1-Ir1 are 116.8(7)° and 113.0(7)°, respectively. The Cp* group and the F atom attached to C_5 showed disorder. Only one form remains with Figure 1. It had been reported that a prerequisite for the occurrence of the cyclometallation reaction of the palladium complexes was that the nitrogen had to be trisubstituted by alkyl or aryl groups (tertiary amines) [13,14]. The rational explanation for this was that the steric bulk of the substituents would weaken the N-Pd bond to such an extent that the electrophilicity of Pd(II) would remain high enough to induce the substitution of a proton [13,14]. The formation of chelated iridium complexes through C-H activation displays a process similar to the above-mentioned palladium complexes. The cyclometallation reaction of iridium(III) complexes can occur when tertiary amines was employed [15]. As a result, it seems that the production of monoligated complexes in this system is ascribed to the small size of secondary amines compared to tertiary amines.



Scheme 1. Synthesis of [(η^5-Cp*)Ir($C_6H_4FCH_2NHCH_3$)Cl_2].



Scheme 2. The mode of H-H coupling for the benzylic CH_2 group.

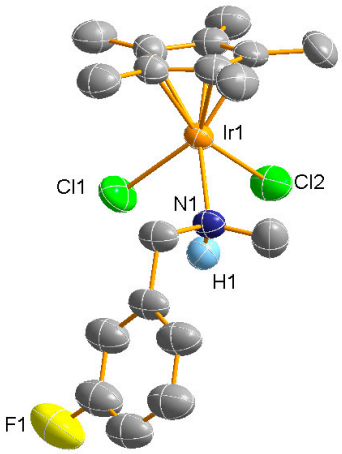


Figure 1. X-crystal structure of [(η^5-Cp*)Ir($C_6H_4FCH_2NHCH_3$)Cl_2] hydrogen atoms, except C-H, which have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. (Ir1: orange; N1: blue; H1: light blue; F1: yellow; Cl1 and Cl2: green; C: gray). H atoms attached to carbon are omitted, as are the minor components of the Cp* and 3-fluorophenyl ring disorders.

3. Materials and Methods

3.1. General Methods and Physical Measurements

All other reagents were purchased from commercial sources and used without purification. ^{1}H-NMR spectra were captured in 5 mm NMR tubes at 298 K on Bruker DPX 500 (^{1}H = 500.13 MHz) spectrometers (Bruker, Karlsruhe, Germany) using TMS as an internal standard and $CDCl_3$ as solvent. ^{13}C-NMR spectra were referenced to the residual solvent ($CHCl_3$, 77.16 ppm) for chloroform-d_1. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. X-ray diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector (Bruker, Karlsruhe, Germany) with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods, and further refinement with full-matrix least-squares on F^2 was obtained with the SHELXL program package [16,17], using SHELXS (TREF) with additional light atoms found by Fourier methods.

3.2. Synthesis of [(η^5-Cp)Ir($C_6H_4FCH_2NHCH_3$)Cl_2]*

The Ir(III) dimer [(η^5-Cp*)IrCl_2]$_2$ was prepared according to reported methods [18]. Complexes [(η^5-Cp*)Ir($C_6H_4FCH_2NHCH_3$)Cl_2] were synthesized according to the modified procedure in this work. Under a nitrogen atmosphere, a mixture solution of 3-fluoro-*N*-methylbenzylamine (0.12 mmol, 16.7 mg), NaOAc (0.9 mmol, 122.5 mg), and CH_2Cl_2 (20 mL) was stirred at temperature for 4 h, after which [(η^5-Cp*)IrCl_2]$_2$ (0.06 mmol, 47.8 mg) was added and stirred 8 h. Filter and CH_2Cl_2 were removed under reduced pressure and recrystallized from dichloromethane/diethyl ether. Yield: 54.8 g 85.1%. ^{1}H-NMR (500.13 MHz, $CDCl_3$) δ 7.34 (dd, J = 13.8, 7.8 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.05 (dd, J = 21.9, 8.8 Hz, 2H), 4.93 (d, $J_{Hb\text{-}Hc}$ = 12.8 Hz, 1H), 3.93 (s, 1H), 3.48 (dd, $J_{Hb\text{-}Hc}$ = 12.8 Hz; $J_{Ha\text{-}Hc}$ = 11.9 Hz, 1H), 2.74 (d, J = 6.1 Hz, 3H), 1.71 (s, 15H). ^{13}C-NMR (125.8 MHz, $CDCl_3$) δ 162.81 (d, $J^1_{C\text{-}F}$ = 247.8 Hz), 116.52 (d, $J^2_{C\text{-}F}$ = 21.3 Hz), 138.44 (d, $J^3_{C\text{-}F}$ = 6.8 Hz), 130.58 (d, $J^3_{C\text{-}F}$ = 8.2 Hz), 125.24 (d, $J^4_{C\text{-}F}$ = 2.8 Hz), 115.51 (d, $J^2_{C\text{-}F}$ = 21.1 Hz), 84.90 (s), 60.00 (s), 39.35 (s), 9.26 (s). Anal. Calcd. for $C_{18}H_{26}Cl_2FIrN$: C, 40.15; H, 4,87; N, 2.60; Found: C, 40.17; H, 4.85; N, 2.62.

Single crystal X-ray diffraction for $C_{18}H_{25}Cl_2FIrN$ (M_r = 537.49): Orthorhombic, space group P2(1)2(1)2(1), a = 9.0825(18) Å, b = 12.552(3) Å, c = 17.516(4) Å, α = 90°, β = 90°, γ = 90°, V =1996.9(7) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 6.961 mm^{-1}, Dcalc = 0.001788 g/cm^3, 11,650 reflections measured ($-11 \leq h \leq 8$, $-15 \leq k \leq 14$, $-21 \leq 1 \leq 21$), 3899 unique (Rint = 0.0602), which were used in all calculations. The final R1 was 0.0419(I > 2σ(I)) and ωR2 was 0.1028 (all data). The Cp* ring and

the 3-fluorophenyl ring showed disorder over two positions. The site occupancies were refined to 0.696(17):0.304(17) for the Cp* ring and 0.80(2):0.20(2) for the 3-fluorophenyl ring. CCDC 1842677 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Supplementary Materials: The following are available online. Figure S1: ^{1}H-NMR spectrum of [(η^5-Cp*)Ir($C_6H_4FCH_2NHCH_3$)Cl_2] in $CDCl_3$, Figure S2: ^{13}C-NMR spectrum of [(η^5-Cp*)Ir($C_6H_4FCH_2NHCH_3$)Cl_2] in $CDCl_3$, Table S1: Crystal data and structure refinement for [(η^5-Cp*)Ir($C_6H_4FCH_2NHCH_3$)Cl_2]. CCDC 1842677 also 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.

Author Contributions: Z.L. conceived and designed the experiments; D.K. performed the experiments; D.K., L.G., S.Z., X.L. and Z.L. analyzed the data; D.K. and Z.L. wrote the paper.

Funding: This research was funded by [the National Natural Science Foundation of China] grant number [21671118] and Taishan Scholars Program.

Acknowledgments: We thank the National Natural Science Foundation of China (Grant No. 21671118) and the Taishan Scholars Program for support.

Conflicts of Interest: The authors declare no conflict of interest.

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