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Carbon monoxide activation in $[Ir(HBPz_3)(CO)_2]$: formation of carbamoyl complexes by direct reaction with amines

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Abstract

The carbamoyl complexes $[IrH(HBPz_3)(CONHR)(CO)]$ ($R = CH_2CH_2CH_3$ (**2**), C_6H_{11} (**3**), (R)-$CH(CH_3)C_6H_{11}$ (**4**), or (S)-$CH(CH_3)C_6H_5$ (**5**)) have been synthesized by the direct reaction of $[Ir(HBPz_3)(CO)_2]$ (**1**) with the corresponding primary amines. The carbamoyl complexes are the result of a nucleophilic attack of the amine on the coordinated CO in **1**. The compounds have been isolated in the solid state and characterized by IR and ^1H NMR spectroscopy The $^{13}C\{^1H\}$ NMR spectrum of complex **2** is also reported. The ^1H NMR spectra of **4** and **5** indicate that two diastereomers of these compounds are formed in equal proportions. Compound **2** remains unchanged when it is placed in $CH_3CH_2CH_2NH_2$. Treatment of $[IrH(HBPz_3)(CONHCH_2CH_2CH_3)(CO)]$ with HBF_4 leads to the formation of $[IrH(HBPz_3)(CO)_2]BF_4$.

Introduction

The nucleophilic activation of coordinated carbon monoxide is an important step in a variety of metal-carbonyl catalyzed reactions [1–3]. Several nucleophile-carbonyl adducts have been characterized as stable complexes [4]. These adducts are usually formed by the direct addition of a nucleophile anion Nu^- to coordinated carbon monoxide. Formation by attack of neutral NuH on a carbonyl group is restricted to strongly activated, usually cationic, metal carbonyl complexes [5–8]. In the course of our work on the chemistry of poly(1-pyrazolyl)boratoiridium complexes [9–11], we have found that $[Ir(HBPz_3)(CO)_2]$ contains coordinated carbon monoxide of high electrophilicity [11]. This was exemplified by its reactivity towards water and alcohols, resulting in the formation of hydroxycarbonyl and alkoxycarbonyl adducts, respectively. The extreme electrophilicity of the carbonyl

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group in [Ir(HBPz$_3$)(CO)$_2$] prompted us to study its reactivity towards other nucleophiles such as amines. We report here the results.

Results and discussion

Treatment of [Ir(HBPz$_3$)(CO)$_2$] (**1**) with $CH_3CH_2CH_2NH_2$ in tetrahydrofuran for 7 h at room temperature results in the formation of the carbamoyl compound [IrH(HBPz$_3$)(CONHCH$_2$CH$_2$CH$_3$)(CO)] (**2**) according to the following equation.

$$[Ir(HBPz_3)(CO)_2] + CH_3CH_2CH_2NH_2 \longrightarrow [IrH(HBPz_3)(CONHCH_2CH_2CH_3)(CO)]$$

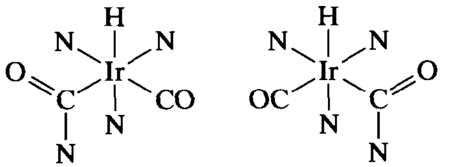
Complex **2** is obtained as a white powder. It is stable in the solid state and in solution at room temperature. The presences of hydrido, carbonyl and carbamoyl groups are supported by the IR spectrum in CH_2Cl_2 which shows three bands, at 2150, 2030 and 1600 cm^{-1}, attributable to ν(Ir–H), ν(C≡O), and ν(C=O), respectively. The IR spectrum in Nujol shows a sharp band at 3440 cm^{-1} due to ν(N–H). The ^1H NMR spectrum shows a broad signal at δ 5.47 attributable to the proton of the CONH group and a singlet at −16.53 due to the hydride proton in addition to the aliphatic ($CH_2CH_2CH_3$) and aromatic (Pz) resonances. The $^{13}C\{^1H\}$ NMR spectrum shows two signals at δ 159.93 and δ 166.24 corresponding to the carbon nuclei of the CO and CONH groups as well as the aliphatic and aromatic resonances, but the similarity of the chemical shifts has precluded an exact assignment. The pyrazolyl proton and carbon resonances indicate that the three pyrazolyl rings are non-equivalent. The NMR data of the iridium(III) complex **2** are in agreement with an octahedral structure in which HBPz$_3$ acts as a tridentate ligand.

Although some carbamoyl complexes derived from primary amines decompose on treatment with a base, leading to the formation of isocyanates [4,12,13], **2** remains unchanged when it is placed in $CH_3CH_2CH_2NH_2$. Treatment with HBF_4 leads to the formation of [IrH(HBPz$_3$)(CO)$_2$]BF$_4$, a reaction similar to that found with the hydroxycarbonyl [IrH(HBPz$_3$)(COOH)(CO)] compound [11].

We have also studied the reactions of [Ir(HBPz$_3$)(CO)$_2$] (**1**) with $C_6H_{11}NH_2$ and with amines containing a chiral carbon, (*R*)-$C_6H_{11}(CH_3)CHNH_2$ and (*S*)-$C_6H_5(CH_3)CHNH_2$. The products of these reactions are the carbamoyl compounds [IrH(HBPz$_3$)(CONHR)(CO)] (R = C_6H_{11} (**3**), (*R*)-CH(CH$_3$)C$_6$H$_{11}$ (**4**), (*S*)-CH(CH$_3$)C$_6$H$_5$ (**5**)). The new complexes **3**, **4** and **5** have been characterized by elemental analyses and IR and ^1H NMR spectroscopy. The ^1H NMR data of complexes **3**, **4** and **5** are also consistent with an octahedral structure in which HBPz$_3$ acts as a tridentate ligand with three pyrazolyl rings non-equivalent.

As expected, the reaction of **1** with the amines containing a chiral carbon gives two diastereomers in approximately equal proportions. The reaction of **1** with a non-optically active amine would lead to the formation of a racemic mixture of the two enantiomers shown in Scheme 1, in which the iridium atom is the chiral centre. The presence of a chiral carbon in the amine converts these enantiomers into two diastereomers.

The presence of two diastereomers in **4** and **5** is supported by their ^1H NMR and IR spectra. For example, the ^1H NMR spectrum of **5** has two signals at δ



Scheme 1

-16.56 and -16.53 due to the hydride protons, at 1.43 and 1.45 due to methyl protons and at 5.69 and 5.72 due to the NHCO group protons. It also shows several pyrazolyl proton resonances, corresponding to the two diastereomers. The IR spectra of **4** and **5** show one ν(N–H) band for each diastereomer. The ν(Ir–H), ν(C≡O) and ν(C=O) values of the two diastereomers must be very similar since the IR spectra have only one band attributable to these stretching absorptions.

These and previous results [11] show that coordinated carbon monoxide in $[Ir(HBPz_3)(CO)_2]$ is highly electrophilic, and the complex forms stable adducts by direct reaction with neutral nucleophiles. They are also an example of the versatility of the chemistry of poly(1-pyrazolyl)boratoiridium complexes.

Experimental

All reactions were carried out under nitrogen by Schlenk techniques. $[Ir(HBPz_3)(CO)_2]$ was prepared as previously reported [14]. IR spectra were recorded on a Perkin–Elmer 783 spectrophotometer. Elemental analyses were carried out with a Perkin–Elmer 240B microanalyzer. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured in $CDCl_3$ at room temperature on a Varian UNITY 300 spectrometer; chemical shifts are given relative to $SiMe_4$ as external reference.

General procedure for the preparation of the carbamoyl compounds

The carbamoyl complexes $[IrH(HBPz_3)(CONHR)(CO)]$ were prepared by similar methods. As a typical example, a mixture of $[Ir(HBPz_3)(CO)_2]$ (75 mg, 0.16 mmol) and $C_6H_{11}NH_2$ (92 μl, 0.81 mmol) in tetrahydrofuran (10 ml) was stirred for two days. The resulting colourless solution was concentrated to dryness and then pentane (10 ml) was added. The white precipitate formed was removed by filtration, washed with pentane and dried under vacuum. Yield 49 mg (54%).

Characterization of the carbamoyl compounds

$[IrH(HBPz_3)(CONHC_6H_{11})(CO)]$. White. Anal. Found: C, 36.4; H, 4.5; N, 17.3. Calc. for $C_{17}H_{23}BIrN_7O_2$: C, 36.4; H, 4.1; N, 17.5(%). ^1H NMR: δ -16.63 (s, 1H, IrH), 1.0–1.9 (m, 10H, C_6H_{11}), 3.86 (m, 1H, C_6H_{11}), 5.33 (d, 1H, NH), 6.16 (br, 2H, Pz), 6.23 (br, 1H, Pz), 7.57 (br, 2H, Pz), 7.61 (br, 1H, Pz), 7.63 (br, 1H, Pz), 7.81 (br, 1H, Pz) and 7.94 (br, 1H, Pz). IR: ν(N–H) 3375 cm^{-1}, ν(B–H) 2485 cm^{-1} (Nujol); ν(Ir–H) 2160 cm^{-1}, ν(C≡O) 2035 cm^{-1}, ν(C=O) 1595 cm^{-1} (CH_2Cl_2).

$[IrH(HBPz_3)(CONHCH_2CH_2CH_3)(CO)]$. White. Anal. Found: C, 32.5; H, 3.9; N, 18.9. Calc. for $C_{14}H_{19}BIrN_7O_2$: C, 32.3; H, 3.7; N, 18.9%. ^1H NMR: δ -16.53 (s, 1H, IrH), 0.91 (t, 3H, $CH_2CH_2\mathit{CH_3}$), 1.51 (m, 2H, $CH_2\mathit{CH_2}CH_3$), 3.23 (m, 2H, $\mathit{CH_2}CH_2CH_3$), 5.47 (br, 1H, NH), 6.20 (br, 2H, Pz), 6.28 (t, 1H, Pz), 7.62 (d, 2H,

Pz), 7.65 (d, 1H, Pz), 7.67 (d, 1H, Pz), 7.85 (d, 1H, Pz) and 7.99 (d, 1H, Pz). $^{13}C\{^1H\}$ NMR: δ 11.52 (1C, $CH_2CH_2\mathit{CH_3}$), 23.54 (1C, $CH_2\mathit{CH_2}CH_3$), 42.14 (1C, $\mathit{CH_2}CH_2CH_3$), 106.09 (1C, Pz), 106.20 (1C, Pz), 106.24 (1C, Pz), 134.68 (1C, Pz), 134.94 (1C, Pz), 135.15 (1C, Pz), 143.10 (1C, Pz), 144.04 (1C, Pz), 144.24 (1C, Pz), 159.93 (1C, CON or CO) and 166.24 (1C, CON or CO). IR: ν(N–H) 3440 cm^{-1}, ν(B–H) 2490 cm^{-1} (Nujol); ν(Ir–H) 2150 cm^{-1}; $\nu(C\equiv O)$ 2030 cm^{-1}, ν(C=O) 1600 cm^{-1} (CH_2Cl_2).

$[IrH(HBPz_3)(CONHCH(CH_3)C_6H_{11})(CO)]$ (*R-diastereomer*). White. Anal. Found: C, 38.3; H, 4.8; N, 16.8. Calc. for $C_{19}H_{27}BIrN_7O_2$: C, 38.8; H, 4.6; N, 16.7%. ^1H NMR: δ −16.60 (s, 1H, IrH), −16.52 (s, 1H, IrH), 0.9–2.0 (m, 28H, CH_3 and C_6H_{11}), 3.9 (m, 2H, CH), 5.26 (d, 1H, NH), 5.32 (d, 1H, NH), 6.18 (br, 4H, Pz), 6.25 (br, 2H, Pz), 7.59–7.66 (m, 8H, Pz), 7.82 (d, 1H, Pz), 7.84 (d, 1H, Pz), 7.93 (d, 1H, Pz) and 7.98 (d, 1H, Pz). IR: ν(N–H) 3440 and 3340 cm^{-1}, ν(B–H) 2480 cm^{-1} (Nujol); ν(Ir–H) 2145 cm^{-1}, $\nu(C\equiv O)$ 2030 cm^{-1}, ν(C=O) 1600 cm^{-1} (CH_2Cl_2).

$[IrH(HBPz_3)(CONHCH(CH_3)C_6H_5)(CO)]$ (*S-diastereomer*). White. Anal. Found: C, 38.2; H, 3.5; N, 16.3. Calc. for $C_{19}H_{21}BIrN_7O_2$: C, 39.2; H, 3.6; N, 16.8%. ^1H NMR: δ −16.56 (s, 1H, IrH), −16.53 (s, 1H, IrH), 1.43 (d, 3H, CH_3), 1.45 (d, 3H, CH_3), 5.27 (m, 2H, CH), 5.69 (d, 1H, NH), 5.72 (d, 1H, NH), 6.04 (t, 1H, Pz), 6.17 (m, 3H, Pz), 6.22 (t, 1H, Pz), 6.24 (t, 1H, Pz), 7.25–7.34 (m, 10H, Pz), 7.41 (d, 1H, Pz), 7.54 (d, 1H, Pz), 7.57 (d, 2H, Pz), 7.58 (d, 2H, Pz), 7.59 (d, 2H, Pz), 7.64 (d, 1H, Pz), 7.78 (d, 1H, Pz), 7.88 (d, 1H, Pz) and 7.94 (d, 1H, Pz). IR: ν(N–H) 3440 and 3365 cm^{-1}, ν(B–H) 2490 cm^{-1} (Nujol); ν(Ir–H) 2160 cm^{-1}, $\nu(C\equiv O)$ 2035 cm^{-1}, ν(C=O) 1605 cm^{-1} (CH_2Cl_2).

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