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Carbon monoxide activation by poly(1-pyrazolyl)boratoiridium complexes

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Abstract

The syntheses of [IrH($HBPz_3$)(COOH)(CO)] (**2**), [IrH($HBPz_3$)(COOMe)(CO)] (**5**) and [IrH($HBPz_3$)(COOEt)(CO)] (**6**) are described. They are prepared by the direct reaction of [Ir($HBPz_3$)$(CO)_2$] (**1**) with H_2O, MeOH, or EtOH, respectively. Compound (**2**) is stable in the solid state and in solution at room temperature, but decomposes in refluxing acetonitrile to give the dihydride [IrH_2($HBPz_3$)(CO)] (**3**). The protonations of **1**, **2** and **5** with $HBF_4 \cdot H_2O$ lead to the cationic complex [IrH($HBPz_3$)$(CO)_2$]BF_4 (**4**). Complex **5** is also obtained by reaction of **2** with methanol, or by treatment of **4** with KOH/MeOH. The complex [Ir(BPz_4)$(CO)_2$] (**7**) also reacts with H_2O and MeOH at room temperature, in the presence of CO; these reactions do not go to completion. The products of these reactions are most probably [IrH(BPz_4)(COOH)(CO)] and [IrH(BPz_4)(COOMe)(CO)]. Treatment of **7** with H_2O in refluxing acetonitrile leads to [IrH_2(BPz_4)(CO)] (**8**).

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 to a carbonyl group is restricted to strongly activated, usually cationic, metal carbonyl complexes [5–7], since NuH is always a much weaker nucleophile than the conjugate base. As part of our work on the chemistry of poly(1-pyrazolyl)boratoiridium complexes [8,9], we report here the unusual formation of hydroxycarbonyl and alkoxycarbonyl compounds by the direct reaction of the neutral [Ir(H_nBPz_{4-n})$(CO)_2$] ($n = 1$ or 0; Pz = pyrazolyl) complexes with water or alcohols.

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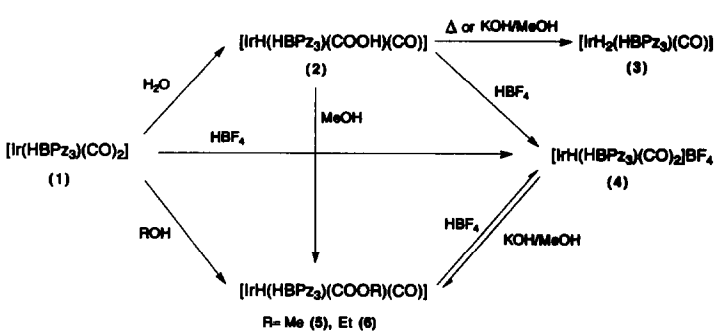
Results and discussion

Scheme 1 summarizes the reactions described below. Reaction of $[Ir(HBPz_3)(CO)_2]$ (**1**) with H_2O in acetonitrile for 4 h at room temperature leads to the hydroxycarbonyl complex $[IrH(HBPz_3)(COOH)(CO)]$ (**2**). The compound is obtained as a white, air-stable powder. The presence of the hydrido, carbonyl and hydroxycarbonyl groups is supported by its IR spectrum in CH_2Cl_2, with three bands at 2175, 2050, and 1635 cm^{-1} attributable to ν(Ir–H), ν(C≡O), and ν(C=O), respectively. The ^1H NMR spectrum shows a singlet at δ −15.89 due to the hydride proton, and several aromatic resonances (6.23–8.16 ppm) of the $HBPz_3$ ligand. These resonances indicate that the three pyrazolyl rings are non-equivalent. The ^1H NMR data of the iridium(III) (**2**) complex are in agreement with 6-coordinate structure in which $HBPz_3$ acts as a tridentate ligand.

The synthesis of the hydroxycarbonyl complex **2** is remarkable, in that it is formed by reaction of **1** directly with H_2O; free hydroxide ion is not required for the reaction. Furthermore, although hydroxycarbonyl compounds are relatively rare, most probably due to low stability [4,10,11], complex **2** is stable in the solid state and in solution at room temperature. However, decomposition of **2** occurs on heating under reflux in acetonitrile for 2 h, or at room temperature by treatment with KOH/H_2O in acetonitrile for 2 h. The product of these reactions is the dihydride, $[IrH_2(HBPz_3)(CO)]$ **3**, which is most probably formed by decarboxylation of **2**. Elemental analysis, IR and ^1H NMR data of complex **3** are in agreement with the proposed formulation.

Two principal mechanisms have been suggested for the decarboxylation of hydroxycarbonyl complexes [12,13]: (a) concerted hydrogen transfer to the metal by a β-elimination; (b) deprotonation to give a η^1-oxycarbonyl species $[L_nM]–CO_2^-$ (presumably a *C*-coordinated carbon dioxide), and subsequent dissociation of CO_2 followed by protonation of the hypothetical $[L_nM]^-$ species formed to give the hydride compound $[L_nM]–H$. As we have previously noted, acetonitrile solutions of complex **2** are stable at room temperature. However, at room temperature complex **2** undergoes decarboxylation on addition of KOH/H_2O in acetonitrile. These results suggest that mechanism (b) is dominant for the decarboxylation of **2**.

The reaction of **1** with water follows the two first steps proposed for the homogeneous catalysis of the water-gas-shift reaction [4,12]: conversion of a metal



Scheme 1.

carbonyl to a hydroxycarbonyl by reaction with H_2O (or OH^-), and the subsequent loss of CO_2. In an attempt to close a potential catalytic cycle, we have tried the reductive elimination of H_2 from **3** by reaction with CO (1 atm) in refluxing THF, but unfortunately **3** remains unchanged.

We have examined the acidic and basic properties of **2**. The reactivity of **2** towards HBF_4 and methanol demonstrates the amphoteric nature of the compound. Thus, **2** reacts with HBF_4 to give the hydride $[IrH(HBPz_3)(CO)_2]BF_4$ (**4**). As expected, treatment of **4** with KOH/H_2O in acetonitrile gives the dihydride complex **3**, most probably formed via complex **2**. The cationic complex **4** can also be prepared by reaction of **1** with HBF_4. The selective protonation of the metal centre in **1** rather than the pyrazolate nitrogen atom has also been reported for the analogous compound $[Ir(HBPz^*_3)(CO)_2]$ ($Pz^* = 3,5$-dimetylpyrazol) [14].

Reaction of **2** with methanol leads to the methyl ester $[IrH(HBPz_3)(COOMe)(CO)]$ (**5**), consistent with the acidic nature of complex **2**. Protonation of **5** with HBF_4 gives the cationic complex **4**. This reaction can be reversed by treatment of **4** with a solution of KOH in methanol. The methoxycarbonyl complex **5** is also formed by the direct reaction of **1** with methanol. Similarly, reaction of **1** with ethanol gives $[IrH(HBPz_3)(COOEt)(CO)]$ (**6**). The new complexes **5** and **6** have been characterized by elemental analyses, and IR and ^1H NMR spectroscopy. Remarkably, the formation of the alkoxycarbonyl complexes **5** and **6** by reaction of **1** directly with alcohols again demonstrates the extreme electrophilic character of the carbonyl groups in complex **1**.

The ability of the tris(pyrazolyl)borato complex (**1**) to react with water and alcohols prompted us to study the reactivity of the analogous tetrakis(pyrazolyl)-borato compound, $[Ir(BPz_4)(CO)_2]$ (**7**). Treatment of **7** with H_2O in refluxing acetonitrile leads to the formation of the dihydride $[IrH_2(BPz_4)(CO)]$ (**8**) in a reaction similar to that of **1**. However, if the reaction is carried out at room temperature, the starting compound is unaltered after 4 h; after 24 h a mixture of **7** and **8** is obtained. Interestingly, if the reaction is carried out at room temperature in the presence of CO, after 2 h **7** and a new hydride product are obtained. The proportion of this new hydride product does not increase upon leaving the mixture for a longer period. The IR and ^1H NMR data (see Experimental) of the mixture formed in the presence of CO suggest that the new hydride product is $[IrH(BPz_4)(COOH)(CO)]$. Analogously, treatment of **7** with methanol in the presence of CO at room temperature also leads to a mixture of **7** and a new hydride. This new product is most probably $[IrH(BPz_4)(COOMe)(CO)]$, as suggested by the IR and ^1H NMR data (see Experimental) of the final mixture.

Conclusions

The complex $[Ir(HBPz_3)(CO)_2]$ (**1**) has highly electrophilic coordinated carbon monoxide. This is exemplified by the reactivity of **1** towards water and alcohols, resulting in the formation of the hydroxycarbonyl or alkoxycarbonyl adducts, respectively. The nucleophilic addition of OH^- or OR^- anions to coordinated CO is relatively common, but the addition of neutral H_2O or ROH is a very unusual reaction. The formation of the hydroxycarbonyl complex **2** and its decomposition product **3** by decarboxylation, are particularly interesting since these two species have been invoked in the catalytic water-gas-shift reaction.

Experimental

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. $[Ir(HBPz_3)(CO)_2]$ [15] and $[Ir(BPz_4)(CO)_2]$ [9] were prepared as previously reported. IR spectra were recorded on a Perkin–Elmer 783 spectrophotometer. Elemental analyses were carried out with a Perkin–Elmer 240B microanalyzer. ^1H NMR spectra (internal reference $SiMe_4$) were measured at room temperature on a Varian XL 200 spectrometer.

Synthesis of $[IrH(HBPz_3)(COOH)CO)]$ (2)

A solution of $[Ir(HBPz_3)(CO)_2]$ (500 mg, 1.08 mmol) in acetonitrile: water (15 ml : 1 ml) was stirred at room temperature for 4 h. 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 (325 mg, 63%). Anal. Found: C, 27.8; H, 2.4; N, 17.7. Calc. for $C_{11}H_{12}BIrN_6O_3$: C, 27.6; H, 2.5; N, 17.5%. ^1H NMR ($CDCl_3$): δ −15.89 (s, 1H, IrH), 6.23 (br, 2H, Pz), 6.29 (br, 1H, Pz), 7.63 (d, 1H, Pz), 7.66 (m, 2H, Pz), 7.71 (d, 1H, Pz), 7.99 (br, 1H, Pz) and 8.16 (d, 1H, Pz). IR: ν(B–H) 2500 (Nujol); ν(Ir–H) 2175, ν(C≡O) 2050, ν(C=O) 1635 cm^{-1} (CH_2Cl_2).

Synthesis of $[IrH_2(HBPz_3)(CO)]$ (3)

A solution of $[IrH(HBPz_3)(COOH)(CO)]$ (100 mg, 0.21 mmol) in acetonitrile: water (15 ml : 1 ml) was heated under reflux for 2 h, and then the solution was allowed to cool to room temperature. Concentration of the solution gave a white precipitate, which was filtered off, washed with water and dried under vacuum (62 mg, 68%). Anal. Found: C, 27.5; H, 2.8; N, 18.7. Calc. for $C_{10}H_{12}BIrN_6O$: C, 27.6; H, 2.8; N, 19.3%. ^1H NMR ($CDCl_3$): δ −17.34 (s, 2H, IrH), 6.15 (t, 1H, Pz), 6.22 (t, 2H, Pz), 7.59 (d, 1H, Pz), 7.67 (d, 2H, Pz), 7.74 (d, 2H, Pz), and 7.76 (d, 1H, Pz). IR: ν(B–H) 2490 (Nujol); ν(Ir–H) 2165, ν(C≡O) 2020 cm^{-1} (CH_2Cl_2).

Synthesis of $[IrH(HBPz_3)(CO)_2]BF_4$ (4)

Tetrafluoroboric acid in diethyl ether (24 μl, 0.17 mmol) was added to a solution of $[Ir(HBPz_3)(CO)_2]$ (80 mg, 0.17 mmol) in diethyl ether (20 ml). The mixture was allowed to react for 15 min and then the white precipitate was filtered off, washed with diethyl ether and dried under vacuum (70 mg, 73%). Anal. Found: C, 24.2; H, 1.7; N, 15.9. Calc. for $C_{11}H_{11}B_2F_4IrN_6$: C, 24.1; H, 2.0; N, 15.3%. ^1H NMR (acetone-d_6): δ −13.67 (s, 1H, IrH), 6.58 (br, 3H, Pz), 8.18 (br, 3H, Pz), and 8.44 (br, 3H, Pz). IR: ν(B–H) 2520 (Nujol); ν(Ir–H) 2165, ν(C≡O) 2155 and 2115 cm^{-1} (CH_3CN). Λ_M(acetone): 106 Ω^{-1} cm^2 mol^{-1}.

Synthesis of $[IrH(HBPz_3)(COOMe)(CO)]$ (5)

A solution of $[Ir(HBPz_3)(CO)_2]$ (100 mg, 0.22 mmol) in methanol (20 ml) was allowed to react at room temperature for 30 min. 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 (40 mg, 37%). Anal. Found: C, 28.5; H, 2.6; N, 16.9. Calc. for $C_{12}H_{14}BIrN_6O_3$: C, 29.2; H, 2.8; N, 17.0%. ^1H NMR ($CDCl_3$): δ −16.04 (s, 1H, IrH), 3.67 (s, 3H, OCH_3), 6.21 (br, 2H, Pz), 6.27 (br, 1H, Pz), 7.62 (br, 2H, Pz), 7.65

(d, 1H, Pz), 7.69 (br, 1H, Pz), 7.93 (br, 1H, Pz) and 8.20 (br, 1H, Pz). IR: ν(B–H) 2495 (Nujol); ν(Ir–H) 2170, ν(C≡O) 2050, ν(C=O) 1650 cm^{-1} (CH_2Cl_2).

Synthesis of [IrH(HBPz$_3$)(COOEt)(CO)] (6)

The complex was prepared using the procedure described for 5, but by reaction of [Ir(HBPz$_3$)(CO)$_2$] (100 mg, 0.22 mmol) with ethanol (20 ml). The white complex was obtained in 32% yield (36 mg). Anal. Found: C, 31.4; H, 3.4; N, 17.4. Calc. for $C_{13}H_{16}BIrN_6O_3$: C, 30.8; H, 3.2; N, 16.6%. ^{1}H NMR ($CDCl_3$): δ −16.04 (s, 1H, IrH), 1.28 (t, 3H, OEt), 4.17 (q, 2H, OEt), 6.21 (br, 2H, Pz), 6.27 (br, 1H, Pz), 7.62 (br, 2H, Pz), 7.65 (d, 1H, Pz), 7.69 (br, 1H, Pz), 7.95 (br, 1H, Pz) and 8.22 (br, 1H, Pz). IR: ν(B–H) 2460 (Nujol); ν(Ir–H) 2170, ν(C≡O) 2050, ν(C=O) 1650 cm^{-1} (CH_2Cl_2).

Synthesis of [IrH$_2$(BPz$_4$)(CO)] (8)

A solution of [Ir(BPz$_4$)(CO)$_2$] (100 mg, 0.19 mmol) in acetonitrile: water (15 ml : 1 ml) was heated under reflux for 10 h. The solution was allowed to cool to room temperature. Concentration of the solution gave a white precipitate, which was filtered off, washed with water and dried under vacuum (10 mg, 11%). Anal. Found: C, 30.8; H, 2.5; N, 21.9. Calc. for $C_{13}H_{14}BIrN_8O$: C, 31.1; H, 2.8; N, 22.4%. ^{1}H NMR ($CDCl_3$): δ −17.29 (s, 2H, IrH), 6.14 (br, 1H, Pz), 6.24 (br, 2H, Pz), 6.61 (br, 1H, Pz), 7.37 (d, 1H, Pz), 7.82 (br, 2H, Pz), 7.87 (d, 2H, Pz), 7.91 (br, 1H, Pz) and 7.96 (d, 2H, Pz). IR: ν(Ir–H) 2165, ν(C≡O) 2015 cm^{-1} (CH_2Cl_2).

Reaction of [Ir(BPz$_4$)(CO)$_2$] with H$_2$O

Carbon monoxide was bubbled through a solution of [Ir(BPz$_4$)(CO)$_2$] (150 mg, 0.29 mmol) in acetonitrile : water (15 ml : 1 ml) for 2 h at room temperature, and the solution was then concentrated to dryness. ^{1}H NMR ($CDCl_3$): δ −15.84 (s, 1H, IrH), 6.21 (t, 1H, Pz), 6.25 (t, 1H, Pz), 6.30 (t, 1H, Pz), 6.62 (t, 1H, Pz), 7.29 (d, 1H, Pz), 7.72 (d, 1H, Pz), 7.77 (d, 1H, Pz), 7.96 (d, 2H, Pz), 8.07 (d, 1H, Pz), 8.14 (d, 1H, Pz) and 8.24 (d, 1H, Pz). IR: ν(Ir–H) 2170, ν(C≡O) 2060, ν(C=O) 1620 cm^{-1} (CH_2Cl_2). The IR and ^{1}H NMR spectra also show signals corresponding to [Ir(BPz$_4$)(CO)$_2$].

Reaction of [Ir(BPz$_4$)(CO)$_2$] with CH$_3$OH

Carbon monoxide was bubbled through a solution of [Ir(BPz$_4$)(CO)$_2$] (150 mg, 0.29 mmol) in methanol (20 ml) for 2 h at room temperature, and then the solution was concentrated to dryness. ^{1}H NMR ($CDCl_3$): δ −15.96 (s, 1H, IrH), 3.69 (s, 3H, OCH_3), 6.21 (br, 1H, Pz), 6.24 (br, 1H, Pz), 6.29 (br, 1H, Pz), 6.62 (br, 1H, Pz), 7.27 (d, 1H, Pz), 7.70 (br, 1H, Pz), 7.77 (br, 1H, Pz), 7.94 (br, 2H, Pz), 8.03 (br, 1H, Pz), 8.13 (br, 1H, Pz) and 8.29 (br, 1H, Pz). IR: ν(Ir–H) 2165, ν(C≡O) 2050, ν(C=O) 1655 cm^{-1} (CH_2Cl_2). The IR and ^{1}H NMR spectra also show the signals corresponding to [Ir(BPz$_4$)(CO)$_2$].

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