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Protonation Reactions of Dinuclear Pyrazolato Iridium(I) Complexes

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The complex $[\{Ir(\mu\text{-Pz})(CNBu^t)_2\}_2]$ (**1**) undergoes double protonation reactions with HCl and with HO_2CCF_3 to give the neutral dihydride complexes $[\{Ir(\mu\text{-Pz})(H)(X)(CNBu^t)_2\}_2]$ (X = Cl, $\eta^1\text{-}O_2CCF_3$), in which the hydride ligands were located *trans* to the X groups and in the boat of the complexes, both in the solid state and in solution. The complex $[\{Ir(\mu\text{-Pz})(H)(Cl)(CNBu^t)_2\}_2]$ evolves in solution to the cationic complex $[\{Ir(\mu\text{-Pz})(H)(CNBu^t)_2\}_2(\mu\text{-Cl})]Cl$. Removal of the anionic chloride by reaction with methyltriflate allows the isolation of the triflate salt $[\{Ir(\mu\text{-Pz})(H)(CNBu^t)_2\}_2(\mu\text{-Cl})]OTf$. This complex undergoes a metathesis reaction of hydride by chloride in $CDCl_3$ under exposure to the direct sunlight to give the complex $[\{Ir(\mu\text{-Pz})(Cl)(CNBu^t)_2\}_2(\mu\text{-Cl})]OTf$. Protonation of both metal centers in $[\{Ir(\mu\text{-Pz})(CO)_2\}_2]$ with HCl occurs at low temperature, but eventually the mononuclear compound $[IrCl(HPz)(CO)_2]$ is isolated. The related complex $[\{Ir(\mu\text{-Pz})(CO)(P\{OPh\}_3)\}_2]$ reacts with HCl and with HO_2CCF_3 to give the neutral Ir(III)/Ir(III) complexes $[\{Ir(\mu\text{-Pz})(H)(X)(CO)(P\{OPh\}_3)\}_2]$, respectively. Both reactions were found to take place stepwise, allowing the isolation of the intermediate monohydrides. They are of different natures, i.e., the metal–metal-bonded Ir(II)/Ir(II) compound $[(P\{OPh\}_3)(CO)(Cl)Ir(\mu\text{-Pz})_2Ir(H)(CO)(P\{OPh\}_3)]$ and the mixed-valence Ir(I)/Ir(III) complex $[(P\{OPh\}_3)(CO)Ir(\mu\text{-Pz})_2Ir(H)(\eta^1\text{-}O_2CCF_3)(CO)(P\{OPh\}_3)]$.

Introduction

Dinuclear complexes are excellent candidates for new reactivity patterns and unusual chemical transformations unavailable for mononuclear complexes. Some examples found in the chemistry of rhodium and iridium are the transference of ligands between metals,[1] the formation and breaking of metal−metal bonds,[2] and the reactions of one metallic center with organic fragments coordinated to the second metal.[3] This cooperative bimetallic reactivity has been facilitated by the use of flexible and firmly bonded bridging ligands that prevent the fragmentation of the dinuclear core during the course of the reactions. Regarding the diiridium(I) compounds, the result of an oxidative addition reaction has been dominated by the formation of Ir(II)/Ir(II) metal−metal bonded derivatives.[4] Exceptions to this general trend are exemplified by the mixed-valence Ir(I)/Ir(III) complexes $[(CO)_2Ir(\mu\text{-NH}\{p\text{-tolyl}\})_2Ir(I)(Me)(CO)_2]$[5] and $[(CO)Ir(\mu\text{-PNNP})(\mu\text{-PPh}_2)Ir(I)(Me)(CO)]$[6] and the Ir(III)/Ir(III) compounds $[\{Ir(\mu\text{-Pz})(CH_2R)(CNBu^t)_2\}_2(\mu\text{-X})]X$ (Pz = pyra-

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zolate, X = Cl, I) coming from the double-oxidative-addition reaction of haloalkanes to the complex [{Ir(μ-Pz)(CNBu^t)$_2$}$_2$].[7] Moreover, we have found that the complexes [{Ir(μ-Pz)$_2$(CNBu^t)$_2$}$_2$(Cl)(R)] (R = CH_2Ph, $CH_2-CH=CH_2$), characterized in the solid state as the Ir(II)/Ir(II) species [(CNBu^t)$_2$(R)Ir(μ-Pz)$_2$Ir(Cl)(CNBu^t)$_2$], undergo a tautomeric equilibrium in solution with the mixed-valence Ir(I)/Ir(III) species [(CNBu^t)$_2$Ir(μ-Pz)$_2$Ir(Cl)(R)(CNBu^t)$_2$].[8] These results suggest that there might be a delicate balance between the formally Ir(II)/Ir(II) and Ir(I)/Ir(III) compounds in some instances. Furthermore, molecular compounds displaying two-electron mixed-valence cores in rhodium and iridium chemistry are unusual and may result from an internal disproportionation.[9] The original behavior of complex [{Ir(μ-Pz)(CNBu^t)$_2$}$_2$], as well as its rhodium counterpart,[10] has been attributed to the presence of four strong σ-donor CNBu^t ligands, which probably enhance the electronic density of the metal centers. Therefore, we have decided to investigate the basic properties of [Ir(μ-Pz)(CNBu^t)$_2$}$_2$], as well as some related complexes, by reacting them with protic acids. Previous examples of the protonation reactions of dinuclear iridium complexes include the reactions of [Ir$_2$(μ-L)$_x$(CO)$_2$(PR$_3$)] (L = Pz, x = 2; L = 1,8-diamidonaphthalene, x =1) with HBF_4. The resulting cationic mono-hydride compounds were found to be active species for the addition of dihydrogen,[11] water,[12] and methanol.[12] We describe in this paper the preparation of unusual dihydride Ir(III)/Ir(III) complexes and the striking influence of the chloride versus trifluoroacetic anions in the stabilization of intermediate Ir(II)/Ir(II) or Ir(I)/Ir(III) monoprotonated complexes.

Experimental Section

Starting Materials and Physical Methods. All reactions were carried out under argon using standard Schlenk techniques. [{Ir(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) was prepared according to literature methods.[7] Solvents were dried and distilled under argon before use by standard methods. Carbon, hydrogen, and nitrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode. Ions were produced with the standard Cs^+ gun at ca. 30 KV, and 3-nitrobenzyl alcohol (NBA) was used as matrix. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on a Bruker ARX 300 and on a Varian UNITY 300 spectrometers operating at 300.13 and 299.95 MHz for ^{1}H, respectively. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the residual signal of the deuterated solvent as reference. NOESY experiments were carried out using the standard noesyst pulse sequence on the Bruker spectrometer. Conductivities were measured in 4−5 × 10^{-4} M in acetone solutions using a Philips PW 9501/01 conductimeter.

Synthesis of the Complexes. [{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CNBu^t)$_2$}$_2$] (2). To a solution of [{Ir(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) (153.0 mg, 0.18 mmol) in ethyl acetate (10 mL) was added trifluoroacetic acid (28 μL, 0.36 mmol). The initial orange solution turned purple and then red, to give finally a new orange solution. Orange microcrystals suitable from X-ray analysis were deposited leaving the solution in the fridge overnight. The solution was decanted, and the crystals were washed with hexane and then vacuum-dried. Yield: 248 mg (85%). Anal. Calcd for $C_{30}H_{44}N_8F_6O_4Ir_2$: C, 33.39; H, 4.11; N, 10.38. Found: C, 33.39; H, 3.80; N, 10.34. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2214 (s), 2181 (s). ^{1}H NMR (25 °C, $CDCl_3$) δ: 7.41 (d, 2.3 Hz, 4H, H^{3,5}Pz), 6.10 (t, 2.3 Hz, 2H, H^{4}Pz), 1.52 (s, 36H, CNBu^t), − 20.98 (s, 2H, H−Ir). ^{19}F{^{1}H} NMR (25 °C, $CDCl_3$) δ: − 75.1. ^{13}C{^{1}H} NMR (25 °C, HDA) δ: 141.6 (C^{3,5}Pz), 105.9 (C^{4}Pz), 59.0 (*C*-(CH$_3$)$_3$), 30.0 (C−(*C*H$_3$)$_3$). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 965, 100% (M − CF_3COO^+). Λ_M (4.99 × 10^{-4} M in acetone) = 21 S cm^2 mol^{-1}.

[{Ir(μ-Pz)(H)(Cl)(CNBu^t)$_2$}$_2$] (3) was prepared in a similar way as that described for complex **2** starting from [{Ir(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) (196.0 mg, 0.23 mmol) and hydrochloric acid (12 M in water, 39 μL, 0.46 mmol) to render white crystals. Yield: 196 mg (92%). Anal. Calcd for $C_{26}H_{44}N_8Cl_2Ir_2\cdot(H_2O)_2$: C, 32.53; H, 5.04; N, 11.67. Found: C, 32.54; H, 5.10; N, 11.91. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2210 (s), 2179 (s). ^{1}H NMR (25 °C, CD_2Cl_2) δ: 7.71 (d, 2.2 Hz, 4H, H^{3,5}Pz), 6.09 (t, 2.2 Hz, 2H, H^{4}Pz), 1.56 (s, 36H, CNBu^t), − 17.55 (s, 2H, H−Ir). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2) δ: 144.9 (C^{3,5}Pz), 108.9 (C^{4}Pz), 61.2 (*C*−(CH$_3$)$_3$), 32.3 (C−(*C*H$_3$)$_3$). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 889, 100% (M − Cl$^+$). Λ_M (5.04 × 10^{-4} M in acetone) = 18 S cm^2 mol^{-1}.

[{Ir(μ-Pz)(H)(CNBu^t)$_2$}$_2$(μ-Cl)]CF$_3$SO$_3$ ([4]OTf). To a pale yellow suspension of [{Ir(μ-Pz)(H)(Cl)(CNBu^t)$_2$}$_2$] (**3**) (92.4 mg, 0.10 mmol) in ethyl acetate (5 mL) was added $MeCF_3SO_3$ (11 μL, 0.10 mmol). A colorless solution was formed immediately. After 30 min, the solution was carefully layered with diethyl ether (20 mL) to render white crystals in 2 days. The crystals were isolated by filtration, washed with cold diethyl ether, and dried under vacuum. Yield: 68 mg (66%). Anal. Calcd for $C_{27}H_{44}N_8ClF_3O_3SIr_2$: C, 31.25; H, 4.27; N, 10.80; S, 3.09. Found: C, 31.25; H, 4.27; N, 10.83; S, 2.73. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2212 (s), 2189 (s). ^{1}H NMR (25 °C, $CDCl_3$) δ: 7.44 (d, 2.4 Hz, 4H, H^{3,5}Pz), 6.05 (t, 2.4 Hz, 2H, H^{4}Pz), 1.51 (s, 36H, CNBu^t), − 20.24 (s, 2H, H−Ir). ^{19}F{^{1}H} NMR (25 °C, $CDCl_3$) δ: −78.4. ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2) δ: 142.5 (C^{3,5}Pz), 108.3 (br, CN), 106.7 (C^{4}Pz), 60.3 (*C*−(CH$_3$)$_3$), 30.5 (C−(*C*H$_3$)$_3$). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 889, 100% (M$^+$). Λ_M (5.01 × 10^{-4} M in acetone) = 80 S cm^2 mol^{-1}.

[{Ir(μ-Pz)(Cl)(CNBu^t)$_2$}$_2$(μ-Cl)]CF$_3$SO$_3$ ([5]OTf). The white complex [{Ir(μ-Pz)(H)(CNBu^t)$_2$}$_2$(μ-Cl)]CF$_3$SO$_3$ ([**4**]OTf) (51.9 mg, 0.05 mmol) was dissolved in $CDCl_3$ (1 mL) in a sealed NMR tube and irradiated with the direct sun light, and the reaction was monitored by ^{1}H NMR. The resulting yellow solution was layered with diethyl ether to give yellow crystals in 2 days. The crystals were separated by filtration, washed with cold diethyl ether, and vacuum-dried. Yield: 49.8 mg (90%). Anal. Calcd for $C_{27}H_{42}N_8Cl_3F_3O_3SIr_2$: C, 29.31; H, 3.83; N, 10.13; S, 2.90. Found: C, 29.92; H, 3.59; N, 9.60; S, 2.74. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2220 (s), 2193 (s). ^{1}H NMR (25 °C, $CDCl_3$) δ: 7.75 (d, 2.4 Hz, 4H, H^{3,5}Pz), 6.30 (t, 2.4 Hz, 2H, H^{4}Pz), 1.60 (s, 36H, CNBu^t). ^{19}F{^{1}H} NMR

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(25 °C, $CDCl_3$) δ: −78.4. $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$) δ: 139.7 ($C^{3,5}Pz$), 106.4 (C^4Pz), 60.6 ($C-(CH_3)_3$), 30.5 ($C-(CH_3)_3$). MS (FAB^+, CH_2Cl_2, *m*/*z*): 957, 100% (M^+). Λ_M (4.98×10^{-4} M in acetone) = 80 S cm^2 mol^{-1}.

[IrCl(CO)$_2$(HPz)] (7). Hydrochloric acid (12 M in water, 8 μL, 0.10 mmol) was added to a solution of [{Ir(μ-Pz)(CO)$_2$)}$_2$] (**6**) (126.1 mg, 0.20 mmol) in acetone (10 mL) to give a pale yellow solution in a few minutes. This solution was concentrated to ca. 1 mL and layered with hexane to render a microcrystalline solid, which was separated by decantation, washed with hexane, and vacuum-dried. Yield: 112.5 mg (80%). Anal. Calcd for $C_5H_4N_2ClO_2Ir$: C, 17.07; H, 1.15; N, 7.63. Found: C, 17.31; H, 1.20; N, 7.56. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2073 (s), 1994 (s). ^1H NMR (25 °C, C_6D_6) δ: 12.25 (br s, 1H, HN), 7.74 (br s, 1H, H^5Pz), 7.64 (br s, 1H, H^3Pz), 6.47 (t, 2.2 Hz, 1H, H^4Pz).

[{Ir(μ-Pz)(CO)(P{OPh}$_3$)}$_2$] (8). Triphenylphosphite (417.0 μL, 1.59 mmol) was added dropwise to a solution of [{Ir(μ-Pz)(CO)$_2$}$_2$] (**6**) (500.0 mg, 0.79 mmol) in diethyl ether (20 mL). A yellow microcrystalline solid precipitated almost immediately. The reaction mixture was stirred for 1 h and then concentrated to ca. 10 mL. The solid was filtered under argon, washed with cold diethyl ether, and vacuum-dried. Yield: 834.1 mg (88%). Anal. Calcd for $C_{44}H_{36}N_4O_8P_2Ir_2$: C, 44.22; H, 3.04; N, 4.69. Found: C, 43.78; H, 3.32; N, 4.86. $^1H\{^{31}P\}$ NMR (25 °C, C_6D_6) δ: 7.45 (d, 8.3 Hz, 12H, $H^oP\{OPh\}_3$), 7.37 (d, 2.1 Hz, 4H, $H^{3,5}Pz$), 7.05 (t, 8.1 Hz, 12H, $H^mP\{OPh\}_3$), 6.85 (t, 7.6 Hz, 6H, $H^pP\{OPh\}_3$), 5.83 (t, 2.2 Hz, 2H, H^4Pz). $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6) δ: 176.6 (d, $^2J_{C-P}$ = 19 Hz, CO), 151.8 (d, J_{C-P} = 7 Hz, $C^iP\{OPh\}_3$), 140.9 (dd, J_{C-P} = 5.2, 1.5 Hz, C^3Pz), 140.8 (d, J_{C-P} = 4.5 Hz, C^5Pz), 129.9 ($C^pP\{OPh\}_3$), 124.9 (d, J_{C-P} = 0.75, $C^mP\{OPh\}_3$), 121.3 (d, J_{C-P}= 5.2 Hz, $C^oP\{OPh\}_3$), 105.9 (d, J_{C-P} = 4 0.5 Hz, C^4Pz).

[{Ir(μ-Pz)(H)(Cl)(CO)(P{OPh}$_3$)}$_2$] (9). Hydrochloric acid (12 M in water, 20 μL, 0.24 mmol) was added to a suspension of [{Ir(μ-Pz)(CO)(P{OPh}$_3$)}$_2$] (**7**) (120.0 mg, 0.10 mmol) in acetone (15 mL). The initial yellow suspension gave an orange solution in a few minutes and then turned to pale yellow. This solution was concentrated to ca. 1 mL and layered with diethyl ether to render an orange microcrystalline solid in 2 days. The crystals were separated by decantation, washed with hexane, and vacuum-dried. Yield: 101.8 mg (80%). Anal. Calcd for $C_{44}H_{38}N_4Cl_2O_8P_2Ir_2$: C, 41.67; H, 3.02; N, 4.12. Found: C, 41.42; H, 3.51; N, 4.43. ^1H NMR (−40 °C, CD_2Cl_2) δ: 7.83 (br s, 2H, H^3Pz), 7.67 (br s, 2H, H^5Pz), 7.33 (t, 7.5 Hz, 12H, $H^mP\{OPh\}_3$), 7.22 (t, 7.2 Hz, 6H, $H^pP\{OPh\}_3$), 7.03 (d, 7.8 Hz, 12H, $H^oP\{OPh\}_3$), 6.15 (q, 1.5 Hz, 2H, H^4Pz), −14.35 (d, J_{H-P} = 17.4 Hz, 2H, H−Ir). $^{13}C\{^1H\}$ NMR (−40 °C, CD_2Cl_2) δ: 162.3 (d, J_{C-P} = 14 Hz, CO), 150.8 (d, J_{C-P} = 10 Hz, $C^iP\{OPh\}_3$), 144.0 (d, J_{C-P} = 5 Hz, C^3Pz), 143.9 (m, C^5Pz), 130.6 ($C^mP\{OPh\}_3$), 126.5 ($C^pP\{OPh\}_3$), 120.9 (d, J_{C-P} = 4 Hz, $C^oP\{OPh\}_3$), 107.0 (m, C^4Pz).

[{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CO)(P{OPh}$_3$)}$_2$] (10). To a solution of [(P{OPh}$_3$)(CO)Ir(μ-Pz)$_2$Ir(H)(η^1-O_2CCF_3)(CO)(P{OPh}$_3$] (**12**) (130.9 mg, 0.10 mmol) in dichloromethane (5 mL) was added trifluoroacetic acid (7.8 mL, 0.10 mmol). The initial yellow solution turned colorless almost immediately. The solution was concentrated to ca. 2 mL and layered with hexane affording white microcrystals overnight. The solution was decanted, and the crystals were washed with hexane and vacuum-dried. Yield: 128.1 mg (90%). Anal. Calcd for $C_{48}H_{38}N_4F_6O_{12}P_2Ir_2$: C, 40.51; H, 2.69; N, 3.94. Found: C, 39.99; H, 3.10; N, 3.93. ^1H NMR (25 °C, HDA) δ: 7.78 (t, 2.4 Hz, 2H, H^3Pz), 7.43 (m, 14H, H^5Pz+ $H^mP\{OPh\}_3$), 7.29 (t, 7.3 Hz, 6H, $H^pP\{OPh\}_3$), 7.06 (d, 7.50 Hz, 12H, $H^oP\{OPh\}_3$), 6.32 (q, 2.4 Hz, 2H, H^4Pz), −18.18 (d, J_{H-P} = 20.6 Hz, 2H, H−Ir). ^{19}F NMR (25 °C, HDA) δ: −73.5. $^{13}C\{^1H\}$ NMR (25 °C, HDA) δ: 161.3 (d, $^2J_{C-P}$ = 15 Hz, CO), 150.9 (d, J_{C-P} = 11 Hz, $C^iP\{OPh\}_3$), 142.8 (d, J_{C-P} = 4 Hz, H^3Pz), 142.6 (dd, J_{C-P} = 7, 2 Hz, C^5Pz), 130.7 ($C^mP\{OPh\}_3$), 126.6 ($C^pP\{OPh\}_3$), 120.7 (d, J_{C-P} = 4 Hz, $C^oP\{OPh\}_3$), 106.9 (d, J_{C-P} = 5 Hz, C^4Pz).

[(P{OPh}$_3$)(CO)(Cl)Ir(μ-Pz)$_2$Ir(H)(CO)(P{OPh}$_3$)] (11) was prepared as described for **9** but by adding 8 μL (0.10 mmol) of hydrochloric acid (12 M in water). Orange microcrystals were obtained from acetone−hexane. Yield: 86.5 mg (70%). Anal. Calcd for $C_{44}H_{37}N_4ClO_8P_2Ir_2$: C, 42.91; H, 3.03; N, 4.55. Found: C, 42.74; H, 3.27; N, 4.55. ^1H NMR (25 °C, HDA) (assigned from H,H-COSY spectrum) δ: 7.69 (br s, 1H, H^3Pz), 7.42 (br s, 1H, $H^{3'}Pz$), 7.38 (t, 8.1 Hz, $H^mP^1\{OPh\}_3$), 7.25 (m, 9H, $H^pP^1\{OPh\}_3$+$H^mP^2\{OPh\}_3$), 7.18 (m, 9H, $H^{o+p}P^2\{OPh\}_3$), 7.15 (br s, 1H, $H^{5'}Pz$), 7.03 (d, 6H, $H^oP^1\{OPh\}_3$), 6.99 (br s, 1H, H^5Pz), 5.93 (q, 2.1 Hz, 1H, H^4Pz), 5.74 (q, 2.1 Hz, 1H, $H^{4'}Pz$), −12.34 (d, J_{H-P} = 21.6 Hz, H−Ir). $^{13}C\{^1H\}$ NMR (25 °C, HDA) δ: 173.3 (d, $^2J_{C-P}$ = 17 Hz) and 171.5 (d, $^2J_{C-P}$ = 15 Hz) (CO); 151.9 (d, J_{C-P} = 11 Hz) and 151.6 (d, J_{C-P} = 11 Hz) ($C^iP\{OPh\}_3$); 141.8 (d, J_{C-P} = 4 Hz), 141.6 (d, J_{C-P} = 10 Hz), 136.9 (d, J_{C-P} = 6 Hz) and 136.6 (d, J_{C-P} = 8 Hz) ($H^{3,3',5,5'}Pz$), 130.4 and 129.9 ($C^mP\{OPh\}_3$); 126.0 and 125.4 ($C^pP\{OPh\}_3$); 121.4 (d, J_{C-P} = 4 Hz) and 121.3 (d, J_{C-P} = 4 Hz) ($C^oP\{OPh\}_3$); 105.9 (d, J_{C-P} = 6 Hz) and 105.3 (d, J_{C-P} = 6 Hz) ($H^{4,4'}Pz$).

[(P{OPh}$_3$)(CO)Ir(μ-Pz)$_2$Ir(H)(η^1-O$_2$CCF$_3$)(CO)(P{OPh}$_3$)] (12). Neat trifluoacetic acid (11.5 μL, 0.15 mmol) was added to a suspension of [{Ir(μ-Pz)(CO)(P{OPh}$_3$)}$_2$] (**8**) (167.3 mg, 0.14 mmol) in acetone (5 mL). The resulting suspension was stirred for ca. 1 h affording an orange solution, which was concentrated to ca. 2 mL and layered with hexane (15 mL) to render a pale yellow crystalline solid. The solution was decanted and the solid washed with hexane and vacuum-dried. Yield: 137.5 mg (75%). Anal. Calcd for $C_{46}H_{37}N_4F_3O_{10}P_2Ir_2$: C, 42.20; H, 2.85; N, 4.28. Found: C, 42.49; H, 3.00; N, 4.05. $^1H\{^{31}P\}$ NMR (25 °C, HDA) (assigned from the H,H-COSY spectrum) δ: 7.87 (d, 2.3 Hz, 1H, H^3Pz), 7.43 (d, 2.2 Hz, 1H, H^5Pz), 7.42 (t, 7.8 Hz, 6H, $H^mP^1\{OPh\}_3$), 7.33 (m, 9H, $H^pP^1\{OPh\}_3$+$H^mP^2\{OPh\}_3$), 7.30 (d, 8.8 Hz, 6H, $H^oP^2\{OPh\}_3$), 7.27 (d, 2.3 Hz, 1H, $H^{3'}Pz$), 7.18 (t, 6.1 Hz, 3H, $H^pP^2\{OPh\}_3$), 7.12 (d, 2.2 Hz, 1H, $H^{5'}Pz$), 7.09 (d, 8.4 Hz, 6H, $H^oP^1\{OPh\}_3$), 7.38 (t, 8.1 Hz, $H^mP^1\{OPh\}_3$), 7.25 (m, 9H, $H^pP^1\{OPh\}_3$+$H^mP^2\{OPh\}_3$), 7.18 (m, 9H, $H^{o+p}P^2\{OPh\}_3$), 7.15 (br s, 1H, $H^{5'}Pz$), 7.09 (d, 6H, $H^oP^1\{OPh\}_3$), 6.22 (t, 2.2 Hz, 1H, H^4Pz), 6.04 (t, 2.3 Hz, 1H, $H^{4'}Pz$), −17.29 (d, J_{H-P} = 19.51 Hz, H−Ir). ^{19}F NMR (25 °C, HDA) δ: −73.5. $^{13}C\{^1H\}$ NMR (25 °C, HDA) δ: 180.4 (d, J_{C-P} =19 Hz) and 166.7 (d, J_{C-P} =14 Hz) (CO); 156.3 (d, J_{C-P} = 6 Hz) and 155.6 (d, J_{C-P} = 11 Hz) ($C^iP\{OPh\}_3$); 148.24 (d, J_{C-P} = 3 Hz), 148.21 (dd, J_{C-P} = 6.0, 2.2 Hz), 145.09 (d, J_{C-P} = 6 Hz) and 145.01 (dd, J_{C-P} = 4.5, 2.2 Hz) ($C^{3,3',5,5'}Pz$); 135.4 (d, J_{C-P} = 1.5 Hz) and 134.9 (d, J_{C-P} = 0.8 Hz) ($C^mP\{OPh\}_3$); 131.2 (d, J_{C-P} = 1.5 Hz) and 130.2 (d, J_{C-P} = 1.5 Hz) ($C^pP\{OPh\}_3$); 125.9 (d, J_{C-P} = 5.2 Hz) and 125.6 (d, J_{C-P} = 4.5 Hz) ($C^oP\{OPh\}_3$); 110.8 (d, J_{C-P} = 4.5 Hz) and 110.7 (d, J_{C-P} = 3.0 Hz) ($C^{4,4'}Pz$).

[{Ir(μ-Pz)(CO){P(*p*-tolyl)$_3$}$_2$] (13). Tris(*p*-tolyl)phosphine (484.0 mg, 1.59 mmol) was added to a diethyl ether solution (20 mL) of [{Ir(μ-Pz)(CO)$_2$}$_2$] (**6**) (500.0 mg, 0.79 mmol). After stirring for 1 h, an orange microcrystalline solid precipitated. The reaction mixture was concentrated to ca. 10 mL, and hexane (10 mL) was added. The solid was filtered under argon, washed with cold hexane, and vacuum-dried. Yield: 655 mg (70%). Anal. Calcd for $C_{50}H_{48}N_4O_2P_2Ir_2$: C, 50.75; H, 4.09; N, 4.73. Found: C, 50.60; H, 4.10; N, 4.62. $^1H\{^{31}P\}$ NMR (25 °C, C_6D_6) δ: 7.9 (sh, 2H, H^3Pz), 7.87 (d, 7.9 Hz, 12H, $C^oP\{p\text{-tolyl}\}_3$), 6.98 (d, 7.9 Hz, 12H, $C^mP\{p\text{-tolyl}\}_3$), 6.90 (d, 2.1 Hz, 2H, H^5Pz), 5.85 (t, 2.1 Hz, 2H, H^4Pz), 1.990 (s, 18H, Me P{*p*-tolyl}$_3$). $^{13}C\{^1H\}$ NMR (25 ×bbC, C_6D_6)

δ: 179.4 (d, $^2J_{C-P}$ = 12 Hz, CO), 140.4 (dd, J_{C-P} = 3.5, 1 Hz, C^3Pz), 140.3 (d, J_{C-P} = 2.5 Hz, C^5Pz), 138.8 (d, $^4J_{C-P}$ = 2 Hz, C^pP{*p*-tolyl}$_3$), 134.8 (d, $^2J_{C-P}$ = 11 Hz, C^oP{*p*-tolyl}$_3$), 131.3 (d, J_{C-P} = 58 Hz, C^iP{*p*-tolyl}$_3$), 129.2 (d, $^3J_{C-P}$ = 10 Hz, C^mP{*p*-tolyl}$_3$), 105.8 (d, J_{C-P} = 2.7 Hz, C^4Pz), 20.9 (Me P{*p*-tolyl}$_3$).

[(P{*p*-tolyl}$_3$)(CO)Ir(μ-Pz)$_2$Ir(H)(η^1-O$_2$CCF$_3$)(CO)(P{*p*-tolyl}$_3$)] (14). The addition of neat HO_2CCF_3 (17.0 μL, 0.22 mmol) to a suspension of [{Ir(μ-Pz)(CO)(P{*p*-tolyl}$_3$)}$_2$] (**13**) (100.0 mg, 0.08 mmol) in acetone gave an orange solution in 10 min. The solution was concentrated to ca. 2 mL, and hexane (15 mL) was added. An orange microcrystalline solid is deposited overnight. The solid was decanted, washed with cold hexane, and vacuum-dried. Yield: 90.0 mg (65%). Anal. Calcd for $C_{52}H_{49}N_4F_3O_4P_2Ir_2$: C, 48.13; H, 3.81; N, 4.32. Found: C, 48.20; H, 3.70; N, 4.29. ^{1}H{^{31}P} NMR (25 °C, HDA) δ: 7.48 (d, 2.2 Hz, 1H, H^3Pz), 7.47 (d, 8.1 Hz, 6H, C^oP^1{*p*-tolyl}$_3$), 7.46 (d, 8.0 Hz, 6H, C^oP^2{*p*-tolyl}$_3$), 7.34 (d, 2.2 Hz, 1H, $H^{3'}$Pz), 7.26 (d, 7.4 Hz, 12H, C^mP{*p*-tolyl}$_3$), 7.19 (d, 2.2 Hz, 1H, H^5Pz), 6.51 (d, 2.2 Hz, 1H, $H^{5'}$Pz), 5.92 (t, 2.22 Hz, 1H, H^4Pz), 5.78 (t, 2.2 Hz, 1H, $H^{4'}$Pz), 2.38 (s, 18H, Me P{*p*-tolyl}$_3$), −16.14 (s, 1H, H−Ir). ^{19}F NMR (25 °C, HDA) δ: −73.3. ^{13}C{^{1}H} NMR (−56 °C, HDA) δ: 178.0 (d, $^2J_{C-P}$ = 12 Hz) and 165.4 (d, $^2J_{C-P}$ = 10 Hz) (CO); 142.8 (br s) and 142.3 (br s) ($H^{3,3'}$Pz); 142.3 and 141.4 (C^pP{*p*-tolyl}$_3$); 139.9 (br s) and 138.4 (br s) ($H^{5,5'}$Pz); 134.1 (d, J_{C-P} = 10 Hz) and 133.4 (d, J_{C-P} = 10 Hz) (C^mP^2{*p*-tolyl}$_3$); 130.6 (d, J_{C-P} = 56 Hz) and 126.3 (d, J_{C-P} = 63 Hz) (C^iP{*p*-tolyl}$_3$); 129.9 (d, J_{C-P} = 11 Hz) and 129.6 (d, J_{C-P} = 11 Hz) (C^oP{*p*-tolyl}$_3$); 106.1 (br s, $H^{4,4'}$Pz), 20.9 (s, Me P{*p*-tolyl}$_3$).

[{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CO)(P{*p*-tolyl}$_3$)}$_2$] (15). Neat HO_2CCF_3 (15 μL, 0.2 mmol) was added to an orange suspension of [{Ir(μ-Pz)(CO)(P{*p*-tolyl}$_3$)}$_2$] (**13**) (100.0 mg, 0.08 mmol) in acetone (10 mL). After stirring for 10 min, an orange solution was formed which turned yellow and finally pale yellow in ca. 3 h. The reaction mixture was concentrated to ca. 2 mL and carefully layered with hexane (20 mL) to render white microcrystals overnight. The crystals were separated by decantation, washed with cold hexane, and vacuum-dried. Yield: 102.6 mg (86%). Anal. Calcd for $C_{54}H_{50}N_4F_6O_6P_2Ir_2$: C, 45.94; H, 3.57; N, 3.97. Found: C, 45.70; H, 3.90; N, 3.90. ^{1}H{^{31}P} NMR (25 °C, HDA) δ: 7.61 (d, 2.1 Hz, 2H, H^3Pz), 7.41 (d, 8.2 Hz, 12H, C^oP{*p*-tolyl}$_3$), 7.33 (d, 8.2 Hz, 12H, C^mP{*p*-tolyl}$_3$), 6.97 (d, 2.1 Hz, 2H, H^5Pz), 5.97 (t, 2.1 Hz, 2H, H^4Pz), 2.40 (s, 18H, MeP{*p*-tolyl}$_3$), −17.09 (s, 2H, H−Ir). ^{19}F NMR (25 °C, HDA) δ: −73.8. MS (FAB$^+$, acetone, *m*/*z*): 1410, 16% (M^+ − H).

Crystal Structure Determination of Compounds 2 and 9. A summary of crystal data and refinement parameters is given in Table 4. Data were collected on a Bruker Smart APEX with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Corrections for Lorentz and polarization effects were applied. The structures were solved by Patterson method (SHELXS97)[13] and difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL97).[13] Scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

Crystal Data for [{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CNBu^t)$_2$}$_2$] (2). An orange irregular block of approximately 0.08 × 0.12 × 0.14 mm^3 was used for data collection. Reflections (24987)were integrated in the range $3 \leq 2\theta \leq 57°$ from ω scans, and 9000 were unique (R_i = 0.0658); a multiscan absorption correction based on this multiplicity was performed,[14] with min/max transmission factors of 0.403/0.578. Non-hydrogen atoms were refined with anisotropic displacement parameters, except those involved in disorder; one tert-butyl and one trifluoroacetate ligands of this molecule were disordered in two positions and were refined with restraints in the bond distances and without hydrogens in the model. The geometry of the remaining organic hydrogen atoms was calculated and refined riding on the corresponding atoms. The hydride ligands were observed in the final difference Fourier maps included in the refinement as free isotropic atoms. They refined at geometrically reasonable positions although the final Ir−H bond distances were slightly shorter than expected, probably due to the limitations in the absorption correction. Final agreement factors were R1 = 0.0469 (7117 observed reflections) and wR2 = 0.1058 (9000 reflections) for 460 parameters and 54 restraints; GOF = 1.034. Largest peak and hole in the final difference map: 1.816 and −2.366 e Å^{-3}. The calculated weighting scheme is $1/[\sum^2(F_o^2) + (0.0368P)^2 + 5.8224P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Crystal Data for [{Ir(μ-Pz)(H)(Cl)(CO)(P{OPh}$_3$)}$_2$] (9). A colorless crystal of approximately 0.05 × 0.16 × 0.31 mm^3 was used for data collection. Reflections (26900) were integrated in the range $4.3 \leq 2\theta \leq 57.4°$ from ω scans, and 10287 were unique (R_i = 0.0407); a multiscan absorption correction based on this multiplicity was performed,[14] with min/max transmission factors of 0.245/0.743. All non-hydrogen atoms were refined with anisotropic displacement parameters; organic hydrogens were introduced in the calculated positions and refined riding on the corresponding atoms. Both hydride ligands were located in a difference Fourier map and refined as free isotropic atoms, but with restriction in their bond distances. Final agreement factors were R1 = 0.0288 (8361 observed reflections) and wR2 = 0.0575 (10287 reflections) for 567 parameters and 2 restraints; GOF = 0.931. Largest peak and hole in the final difference map: 1.563 and −0.920 e Å^{-3}. The calculated weighting scheme is $1/[\sum^2(F_o^2) + (0.0207P)^2]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Results and Discussion

(i) Isocyanide Complexes. The addition of 2 molar equiv of HO_2CCF_3 to [{Ir(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) produced an immediate reaction to yield the neutral dihydride complex [{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CNBu^t)$_2$}$_2$] (**2**), which incorporates 2 molar equiv of HO_2CCF_3 according to the elemental analyses. Complex **2** was isolated as a sole stereoisomer of C_{2v} symmetry in solution, as deduced from the fairly simple ^{1}H and ^{13}C{^{1}H} NMR spectra (see Experimental Section). The oxidation of both iridium atoms to Ir(III) was evidenced by a shift of the ν(CN) stretchings, ca. 100 cm^{-1} to higher frequencies relative to **1**, and the hydride ligands were located inside the pocket of the complex because the lack of nOe enhancement of the hydride signal upon irradiation of the $H^{3,5}$ pyrazolate protons (and vice versa). This disposition of the hydrido ligands has also been found in the solid state by an X-ray crystallographic study on complex **2**.

Figure 1 shows the molecular structure of **2** along with the atomic labeling scheme used. Selected bond distances and angles are collected in Table 1. The molecule exhibits a central "Ir(μ-Pz)$_2$Ir" metallacycle framework, constituted by two iridium atoms bridged through two *exo*-bidentate pyrazolate ligands, which adopts the typical boat conforma-

(13) Sheldrick, G. M. *Programs for Crystal Structure Analysis (Release 97-2)*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

(14) *SADABS: Area-Detector Absorption Correction*; Siemens Industrial Automation, Inc.: Madison, WI, 1996.

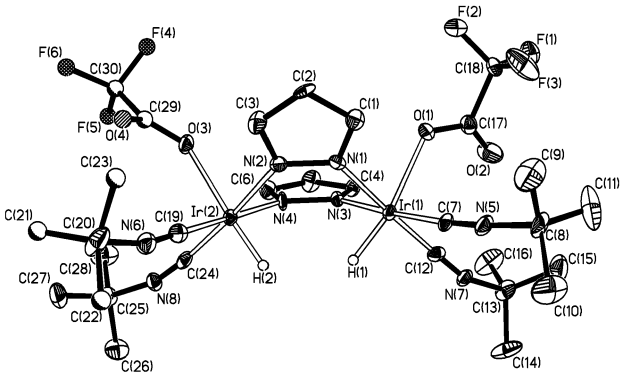

Figure 1. Representation of the molecular structure of complex **2** showing the atomic scheme used.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Compound **2**

Ir(1)···Ir(2)	3.8031(8)		
Ir(1)−O(1)	2.182(5)	Ir(2)−O(3)	2.204(5)
Ir(1)−N(1)	2.065(6)	Ir(2)−N(2)	2.065(6)
Ir(1)−N(3)	2.074(6)	Ir(2)−N(4)	2.062(6)
Ir(1)−C(7)	1.940(8)	Ir(2)−C(19)	1.923(8)
Ir(1)−C(12)	1.921(8)	Ir(2)−C(24)	1.920(8)
Ir(1)−H(1)	1.44(7)	Ir(2)−H(2)	1.41(7)
O(1)−Ir(1)−N(1)	81.6(2)	O(3)−Ir(2)−N(2)	89.1(2)
O(1)−Ir(1)−N(3)	88.3(2)	O(3)−Ir(2)−N(4)	84.1(2)
O(1)−Ir(1)−C(7)	88.4(3)	O(3)−Ir(2)−C(19)	96.1(3)
O(1)−Ir(1)−C(12)	96.7(3)	O(3)−Ir(2)−C(24)	87.6(3)
O(1)−Ir(1)−H(1)	168(3)	O(3)−Ir(2)−H(2)	173(3)
N(1)−Ir(1)−N(3)	89.4(2)	N(2)−Ir(2)−N(4)	89.9(2)
N(1)−Ir(1)−C(7)	90.8(3)	N(2)−Ir(2)−C(19)	89.0(3)
N(1)−Ir(1)−C(12)	178.2(3)	N(2)−Ir(2)−C(24)	176.2(3)
N(1)−Ir(1)−H(1)	89(3)	N(2)−Ir(2)−H(2)	93(3)
N(3)−Ir(1)−C(7)	176.6(3)	N(4)−Ir(2)−C(19)	178.9(3)
N(3)−Ir(1)−C(12)	90.7(3)	N(4)−Ir(2)−C(24)	91.7(3)
N(3)−Ir(1)−H(1)	83(3)	N(4)−Ir(2)−H(2)	89(3)
C(7)−Ir(1)−C(12)	89.1(3)	C(19)−Ir(2)−C(24)	89.4(3)
C(7)−Ir(1)−H(1)	100(3)	C(19)−Ir(2)−H(2)	91(3)
C(12)−Ir(1)−H(1)	92(3)	C(24)−Ir(2)−H(2)	91(3)

tion. Each iridium center completes an essentially octahedral environment with two terminal $CNBu^t$ ligands located *trans* to the pyrazolate bridges and a trifluoroacetate group *trans* to the hydride ligand, which was located inside the pocket of the complex. The long iridium−iridium distance of 3.8031(8) Å reflects the opening of the dihedral angle formed by the "$Ir(N-N)_2Ir$" framework to provide enough space to accommodate both terminal hydride ligands in the boat conformation. Nevertheless, the hydride−hydride distance of 2.1(1) Å is slightly shorter that the sum of the van der Waals radii but beyond the range found for the dihydrogen complexes.[15] Most probably there is not room enough to accommodate two other monoatomic ligands larger than the hydride in the pocket of this type of complex.

In a similar way, the reaction of **1** with 2 molar equiv of HCl afforded the related diiridium(III) compound $[\{Ir(\mu\text{-Pz})(H)(Cl)(CNBu^t)_2\}_2]$ (**3**), which was isolated as a white solid in excellent yield. The spectroscopic data of freshly prepared solutions of complex **3** (see Experimental Section) clearly indicated the formation of a single stereoisomer with a stereochemistry identical to **2**, i.e., with the hydride ligands located inside the pocket of the complex and *trans* to the chloride groups. However, complex **3** evolves in solution to the cationic complex $[\{Ir(\mu\text{-Pz})(H)(CNBu^t)_2\}_2(\mu\text{-Cl})]Cl$ ([**4**]Cl) after 48 h in CD_2Cl_2, and in 2 h in acetone (Scheme 1). Nevertheless, this isomerization is reversible since neutral complex **3** is isolated again from these solutions. Removal of the anionic chloride in **3** by reaction with methyltriflate allows the isolation of the ionic species as the triflate salt $[\{Ir(\mu\text{-Pz})(H)(CNBu^t)_2\}_2(\mu\text{-Cl})]OTf$ ([**4**]OTf) as a white crystalline solid in good yield (Scheme 1).

Complex [**4**]Cl showed identical NMR spectra compared to those of the isolated [**4**]OTf. The equivalence of the two hydrido, two pyrazolato, and four isocyanide ligands, detected by the ^1H and $^{13}C\{^1H\}$ NMR spectra, clearly indicated a C_{2v} symmetry of the cation $[\mathbf{4}]^+$. Furthermore, the *cis* disposition of the two equivalent hydrido ligands relative to the pyrazolato groups was evidenced by a large nOe enhancement of the hydride signal upon irradiation of the $H^{3,5}$ pyrazolate protons. Therefore, the structure of cation $[\mathbf{4}]^+$ is that depicted in Scheme 1.

Dihydride complexes **2** and **3** are rare examples of the double protonation of a dinuclear complex. The data indicate that the protonation of the complex $[\{Ir(\mu\text{-Pz})(CNBu^t)_2\}_2]$ (**1**) with coordinating acids corresponds to a selective *trans* addition on each metal center with both hydrido ligands located in the boat formed by the "$Ir(\mu\text{-Pz})_2Ir$" dimetallacycle. This selectivity could be the result of the double electrophilic attack of H^+ to the external faces of the complex followed by a boat to boat inversion,[16] which allows the coordination of the anions through the external face of the intermediates. Previously reported double protonations in dirhodium complexes led to hydrogen elimination[17] or to the formation of symmetrical dihydrides located at the external face of the complexes.[18] Moreover, in contrast with the double protonation of $[\{Cp^*Ir(\mu\text{-CO})\}_2]$[19] and of $[Ir_2(\mu\text{-1,8-}(NH)_2naphth)(CO)_2(PPr^i_3)_2]$,[11] no bridging hydride results from the reactions of **1** with protic acids.

The evolution of chloro complex **3** to the cationic chloride-bridged isomer [**4**]Cl in polar solvents probably occurs by dissociation of a chloride ligand along with a ring boat inversion.[16] Complex [**4**]Cl undergoes a further reaction with chloroform consisting of a hydride/chloride metathesis, which is associated with the transformation of $CDCl_3$ into $CDHCl_2$. In a similar way, a solution of $[\{Ir(\mu\text{-Pz})(H)(CNBu^t)_2\}_2(\mu\text{-Cl})]OTf$ ([**4**]OTf) in $CDCl_3$ evolves quantitatively into the complex $[\{Ir(\mu\text{-Pz})(Cl)(CNBu^t)_2\}_2(\mu\text{-Cl})]OTf$ ([**5**]OTf) (Scheme 1). Monitoring this reaction by ^1H NMR spectroscopy, we detected that the time required for this transformation to be completed varied noticeably from one sample to another at room temperature. The reason for this behavior

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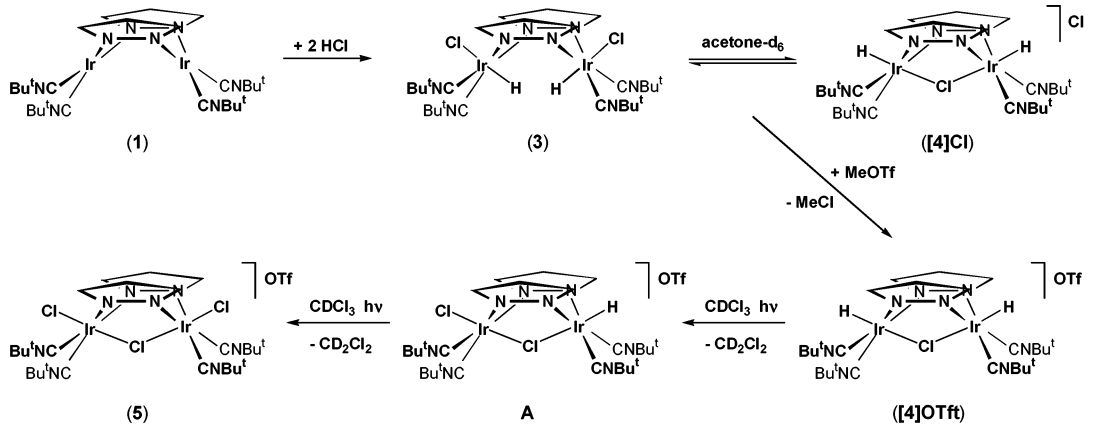
Scheme 1

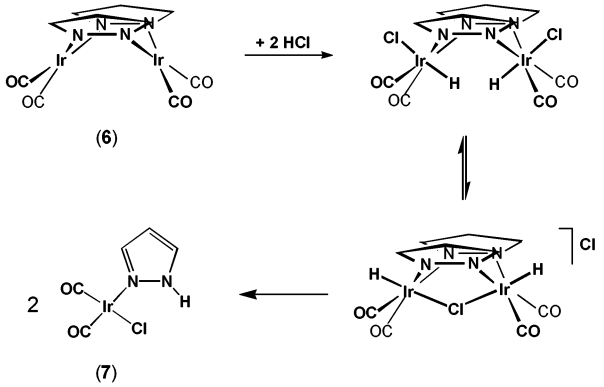


is that the reaction requires the direct sunlight irradiation to progress, and it stops in the darkness. From these chloroform solutions, the yellow complex [{Ir(μ-Pz)(Cl)(CNBu^t)$_2$}$_2$(μ-Cl)]OTf ([**5**]OTf) was isolated by crystallization with diethyl ether and further characterized (see Experimental Section). Moreover, the transformation of the dihydride complex [**4**]-OTf into [**5**]OTf was found to proceed stepwise through the monohydride intermediate [(CNBu^t)$_2$(H)Ir(μ-Pz)$_2$(μ-Cl)Ir-(Cl)(CNBu^t)$_2$]OTf (**A**, Scheme 1), which was identified by its ^{1}H NMR spectrum. We believe that a radical mechanism, probably associated with the decomposition of $CDCl_3$ upon sunlight exposure, was responsible for this exchange reaction.

(ii) Carbonyl Complexes. The addition of 2 molar equiv of HCl to the complex [{Ir(μ-Pz)(CO)$_2$}$_2$] (**6**), isoelectronic with **1**, gave the mononuclear compound [IrCl(HPz)(CO)$_2$] (**7**) according to analytical and spectroscopic data. At first glance, the result of this reaction could be rationalized by assuming that the strong π-acceptor properties of the CO relative to the isocyanide ligand decrease the basicity of the iridium(I) centers in such a way that the nitrogen atoms are preferentially protonated. However, this is not right, because hydride signals, but no NH resonances, were observed by monitoring the reaction of **6** with HCl at low temperature by ^{1}H NMR spectroscopy. On raising the temperature, the hydride signals disappeared to give new NH resonances at ca. 10 ppm. Eventually, the resulting mixture cleanly evolved to mononuclear complex **7** in a few minutes at room temperature. Therefore, the iridium(I) centers are basic enough in the tetracarbonyl complex **6** to react with the proton, but the resulting hydride complexes were not stable above -50 °C, and they evolved to **7** by a reductive elimination reaction leading to the observed N$-$H bond formation. Moreover, this reaction implies the formation of species containing the pyrazolate and hydride ligands in a mutually *cis* disposition. A plausible sequence of reactions considering the results already described for complex **3** is shown in Scheme 2.

Furthermore, these results suggest that strong π-acceptor ligands such as CO are unable to stabilize H$-$Ir(III) bonds in complexes containing the binuclear "Ir(μ-Pz)$_2$Ir" framework. However, it is also important to consider that if the complexes with the hydride ligands inside the pocket of the complex are the products, the boat ring inversion is a

Scheme 2



noninnocent process, since it allows the required stereochemistry for the reductive elimination reaction.

The basic properties of the related complex [{Ir(μ-Pz)-(CO)(P{OPh}$_3$)}$_2$] (**8**), incorporating a bulkier and more basic ancillary ligand, were also investigated. Complex **8** was obtained by adding P{OPh}$_3$ to diethyl ether solutions of [{Ir(μ-Pz)(CO)$_2$}$_2$] (**6**). Upon these conditions, complex **8** was isolated as the pure *transoid* isomer (C_2 symmetry). If hexane is added to complete the crystallization of the product, the overall yield increases, but the *cisoid* isomer (C_s symmetry) crystallizes too, as found for related rhodium complexes.[2a] To prevent further complications, the pure *transoid*-**8** isomer was used as the starting material in the following reactions.

Complex **8** was reacted with HCl and with HO_2CCF_3 (1:2 molar ratio) to give the neutral Ir(III)/Ir(III) complexes [{Ir-(μ-Pz)(H)(X)(CO)(P{OPh}$_3$)}$_2$] (X = Cl (**9**), η^1-O_2CCF_3 (**10**)), respectively. They were isolated as white crystalline materials, suitable for X-ray diffraction studies in the case of complex **9**. The structure of **9** is shown in Figure 2 together with the atomic labeling scheme used. Selected bond distances and angles are collected in Table 2. The molecular structure is similar to that described for complex **2** and represents a second example of a complex showing a boat conformation of the "Ir(N$-$N)$_2$Ir" metallacycle with two terminal hydrides located inside the boat. The coordination environments around the metal atoms are similar to those found for complex **2**. In this case, the iridium$-$iridium

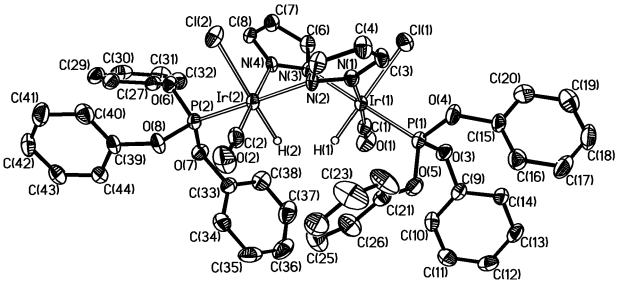


Figure 2. Representation of the molecular structure of complex **9** showing the atomic scheme used.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compound **9**

Ir(1)···Ir(2)	3.7701 (3)		
Ir(1)−Cl(1)	2.4659(11)	Ir(2)−Cl(2)	2.4773(11)
Ir(1)−P(1)	2.2238(11)	Ir(2)−P(2)	2.2290(10)
Ir(1)−N(1)	2.086(3)	Ir(2)−N(2)	2.096(3)
Ir(1)−N(3)	2.092(3)	Ir(2)−N(4)	2.082(3)
Ir(1)−C(1)	1.858(4)	Ir(2)−C(2)	1.866(5)
Ir(1)−H(1)	1.48(3)	Ir(2)−H(2)	1.52(3)
Cl(1)−Ir(1)−P(1)	89.81(4)	Cl(2)−Ir(2)−P(2)	92.62(4)
Cl(1)−Ir(1)−N(1)	88.05(9)	Cl(2)−Ir(2)−N(2)	88.48(9)
Cl(1)−Ir(1)−N(3)	89.20(9)	Cl(2)−Ir(2)−N(4)	90.86(9)
Cl(1)−Ir(1)−C(1)	96.42(13)	Cl(2)−Ir(2)−C(2)	89.24(14)
Cl(1)−Ir(1)−H(1)	175(2)	Cl(2)−Ir(2)−H(2)	175(2)
P(1)−Ir(1)−N(1)	94.25(9)	P(2)−Ir(2)−N(2)	177.04(9)
P(1)−Ir(1)−N(3)	178.45(9)	P(2)−Ir(2)−N(4)	90.98(9)
P(1)−Ir(1)−C(1)	87.63(13)	P(2)−Ir(2)−C(2)	90.48(13)
P(1)−Ir(1)−H(1)	88(2)	P(2)−Ir(2)−H(2)	91(2)
N(1)−Ir(1)−N(3)	86.92(12)	N(2)−Ir(2)−N(4)	86.26(12)
N(1)−Ir(1)−C(1)	175.17(15)	N(2)−Ir(2)−C(2)	92.28(16)
N(1)−Ir(1)−H(1)	87(2)	N(2)−Ir(2)−H(2)	88(2)
N(3)−Ir(1)−C(1)	91.29(15)	N(4)−Ir(2)−C(2)	178.53(15)
N(3)−Ir(1)−H(1)	93(2)	N(4)−Ir(2)−H(2)	93(2)
C(1)−Ir(1)−H(1)	88(2)	C(2)−Ir(2)−H(2)	87(2)

Table 3. Selected Spectroscopic Data for Triphenylphosphite (R) and Tri(*p*-tolyl)phosphine (R′) Derivatives

	complex	IR ν(CO)	^{31}P{^{1}H} NMR	Λ_M[e]
8	[{Ir(μ-Pz)(CO)(R)}$_2$]	1996[a]	87.1[b]	
9	[{Ir(μ-Pz)(H)(Cl)(CO)(R)}$_2$]	2079[c]	57.2[c]	0.8
10	[{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CO)(R)}$_2$]	2091[c]	54.9[d]	1.6
11	[(R)(CO)(Cl)Ir(μ-Pz)$_2$Ir(H)(CO)(R)]	2048, 2010[c]	69.9, 66.4[d]	0.9
12	[(R)(CO)Ir(μ-Pz)$_2$Ir(H)-(η^1-O$_2$CCF$_3$)(CO)(R)]	2089, 2000[c]	87.5, 55.4[d]	1.9
13	[{Ir(μ-Pz)(CO)(R′)}$_2$]	1963[a]	16.1[b]	
15	[{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CO)(R′)}$_2$]	2066[c]	−2.5[d]	3.6
14	[(R′)(CO)Ir(μ-Pz)$_2$Ir(H)-(η^1-O$_2$CCF$_3$)(CO)(R′)]	2062, 1969[a]	16.6, −1.2[d]	3.2

[a] Diethyl ether. [b] C_6D_6. [c] Dichloromethane. [d] HDA. [e] ~10^{-4} M in acetone in units of S cm^2 mol^{-1}.

nonbonding distance is 3.7701(3) Å, and the hydride−hydride separation is 1.95(6) Å.

In solution, complexes **9** and **10** were found to be single isomers of C_2 symmetry (Table 3, Scheme 3) showing the stereochemistry described for **9** in the solid state. Thus, the fine structure of the signal for the two equivalent H^4 protons of the pyrazolate rings in the ^{1}H NMR spectrum was an apparent quartet, due to the additional coupling with one P nucleus, which clearly indicates the mutually *trans* disposition of the pyrazolate bridges to the phosphite ligands. Moreover, the lack of nOe enhancements of the signal due to the H^{3,5} protons of the pyrazolate ligands upon irradiation of the hydride resonance accounted for the location of the hydride ligands inside the pocket of the complexes.

Table 4. Crystallographic Data for [{Ir(μ-Pz)(H)(η^1-O$_2$CCF$_3$)(CNBu^t)$_2$}$_2$] (**2**) and [{Ir(μ-Pz)(H)(Cl)(CO)(P{OPh}$_3$)}$_2$] (**9**)

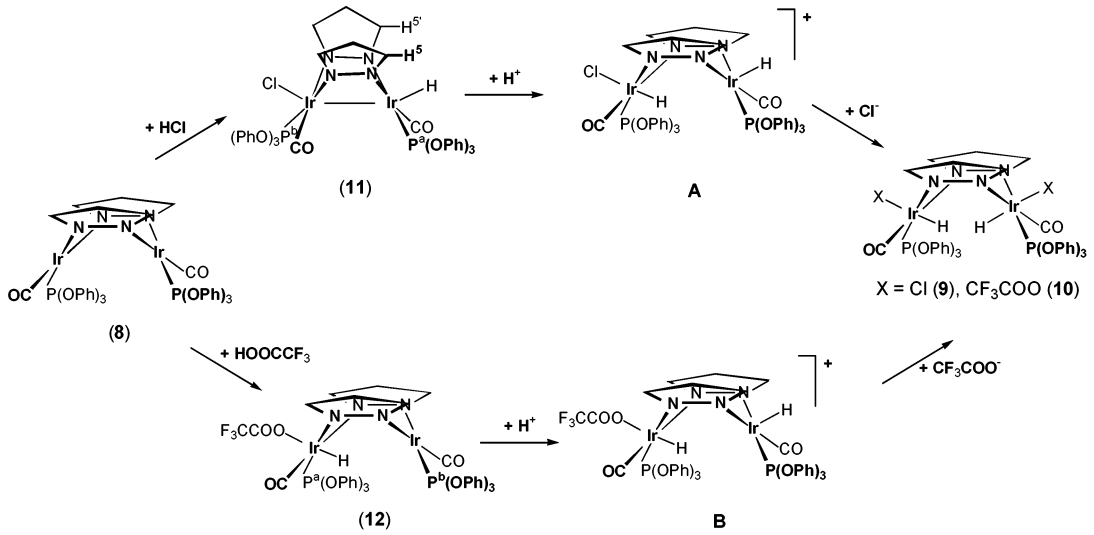
	2	**9**
formula	$C_{30}H_{44}F_6Ir_2N_8O_4$	$C_{44}H_{38}Cl_2Ir_2N_4O_8P_2$
fw	1079.13	1268.02
temp, K	100(2)	173(2)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	12.491(3)	9.5095(6)
b, Å	24.848(6)	13.8588(9)
c, Å	12.758(3)	17.6696(12)
α, deg	90	70.9120(10)
β, deg	101.202(5)	88.7760(10)
γ, deg	90	84.3340(10)
V, Å^3	3884.4(17)	2189.7(2)
Z	4	2
ρ(calcd), g cm^{-3}	1.845	1.923
μ(Mo Kα), mm^{-1}	6.917	6.324
$R(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.0469	0.0288
$R_w(F^2)$ [all data][b]	0.1058	0.0575

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, for 7117 and 8361 observed reflections for **2** and **9**, respectively. [b] $R_w(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

Both reactions were found to take place stepwise, allowing the isolation of intermediate products in each case, which were found to possess quite different nature. Thus, upon addition of 1 molar equiv of HCl to **8**, the orange complex [(P{OPh}$_3$)(CO)(Cl)Ir(μ-Pz)$_2$Ir(H)(CO)(P{OPh}$_3$)] (**11**) was isolated (Scheme 3). This complex was found to be a diamagnetic Ir(II)/Ir(II) compound with a formal iridium−iridium bond according to the spectroscopic data. Thus, two close ν(CO) bands in the IR spectrum and the two resonances with similar chemical shifts in the ^{31}P{^{1}H} NMR spectrum (Table 3) agreed with an identical oxidation state for both iridium centers in **11**. Moreover, the *transoid* disposition of the P-donor ligands found in the starting material was maintained in **11**, since the two inequivalent H^4 protons of the pyrazolate rings appeared as two quartets in the ^{1}H NMR spectrum. Furthermore, the location of the hydride ligand *trans* to the iridium−iridium bond (Scheme 3) was supported by the enhancement of the resonances corresponding to the H^5 and H$^{5'}$ pyrazolate protons and to the *ortho* protons of one of the phosphite ligands on irradiation of the hydride resonance in the ^{1}H NMR spectrum.

In contrast, the addition of 1 molar equiv of HO$_2$CCF$_3$ to **8** gave the mixed-valence Ir(I)/Ir(III) complex [(P{OPh}$_3$)-(CO)Ir(μ-Pz)$_2$Ir(H)(η^1-O$_2$CCF$_3$)(CO)(P{OPh}$_3$)] (**12**), which was isolated as a pale yellow solid. The shift to higher frequencies of one of the two ν(CO) bands in the IR spectrum relative to the starting material and the shift to high field of one of the two signals in the ^{31}P{^{1}H} NMR spectrum (Table 3) are indicative of rather different iridium centers, Ir(III) and Ir(I), in **12**. The *transoid* stereochemistry of the P{OPh}$_3$ ligands in **12** was again indicated by the fine structure of the signals due to the inequivalent H^4 protons of the pyrazolate rings in the ^{1}H NMR spectrum. In addition, the NOESY spectrum in CD_2Cl_2 showed the nOe cross-peaks between the hydride ligand and only the *ortho* protons of both phosphite ligands, which indicates their close proximity and agrees with the location of the hydride inside the pocket of the complex. The influence of the counteranion on the formation of intermediates **11** and **12** is not yet understood.

Scheme 3



However, we have previously reported the existence of tautomeric equilibria in solution between Ir(II)/Ir(II) and Ir(I)/Ir(III) dinuclear species that were found to be very sensitive to the ancillary anionic ligand (Cl or I).[8] It is likely that similar equilibria could be operative in these reactions, in such a way that the counteranion tips the balance to the metal−metal bonded or to the mixed-valence complexes. It is also noteworthy that Pfaltz and Crabtree have recently reported relevant counteranion effects on reactions involving mononuclear iridium species.[20]

While the addition of 1 molar equiv of HCl to dichloromethane or acetone solutions of **11** led to dihydride **9**, the outcome from the reaction of **12** with HO_2CCF_3 was found to be dependent on the solvent. Thus, the addition of 1 molar equiv of HO_2CCF_3 to **12** in dichloromethane caused the immediate formation of dihydride **10**, but no reaction was observed in acetone even in the presence of 10 molar equiv of HO_2CCF_3. In consequence, the preparation of **10** required the formation of the monohydride **12** in acetone followed by the addition of the second molar equivalent of HO_2CCF_3 in dichloromethane. The one-pot reaction to **10** from dichloromethane solutions of **8** was impracticable due to a faster and different reaction of the diiridium(I) complex **8** with the solvent.[21]

Most probably, the protonation of [(P{OPh}$_3$)(CO)(Cl)Ir(μ-Pz)$_2$Ir(H)(CO)(P{OPh}$_3$)] (**11**) with HCl occurs at the iridium−iridium bond, while the protonation of the mixed-valence [(P{OPh}$_3$)(CO)Ir(μ-Pz)$_2$Ir(H)(η^1-O_2CCF_3)(CO)(P{OPh}$_3$)] (**12**) with HO_2CCF_3 takes place at the external face of the iridium(I) center. In both cases, similar intermediates are formed (**A** and **B**, Scheme 3). The strong *trans* influence of the hydride ligand should favor the pentacoordination of one iridium center rather than the formation of the bridging hydride species with octahedral coordination of the metals. A Berry's pseudorotation in this pentacoordinated center would move the hydride to the internal position in the boat. Then, the coordination of the anion to the metal through the external face of the intermediates will give products **9** and **10**, respectively.

Finally, we have also investigated the protonation reactions of the related phosphine compound [{Ir(μ-Pz)(CO)(P{*p*-tolyl}$_3$)}$_2$] (**13**). Complex **13** was reacted with 1 molar equiv of HO_2CCF_3 in acetone to give the mixed-valence complex [(P{*p*-tolyl}$_3$)(CO)Ir(μ-Pz)$_2$Ir(H)(η^1-O_2CCF_3)(CO)(P{*p*-tolyl}$_3$)] (**14**). Further addition of 1 molar equiv of HO_2CCF_3 to **14** gave the neutral Ir(III) compound [{Ir(μ-Pz)(H)(η^1-O_2CCF_3)(CO)(P{*p*-tolyl}$_3$)}$_2$] (**15**). Both complexes were characterized according to their analytical and spectroscopic data (Table 3) and showed identical stereochemistry to that described for the triphenyl phosphite counterparts, respectively. Therefore, the outcome of the reactions of complexes [{Ir(μ-Pz)(CO)(PR$_3$)}$_2$] with HO_2CCF_3 does not seem to be influenced by the electronic and steric properties of the phosphine or phosphite ligands. However, while the reactions of the phosphite complex **8** with HCl were clean, a mixture of complexes resulted from the identical reaction with the phosphine complex **13**.

Concluding Remarks

The dinuclear bis(pyrazolate) iridium(I) complexes studied in this paper were protonated on both iridium centers to give neutral dihydride iridium(III)/iridium(III) complexes. The complexes [{Ir(μ-Pz)(H)(X)(CNBu^t)$_2$}$_2$] (X = η^1-O_2CCF_3 (**2**), Cl (**3**)) containing the hydride ligands inside the boat formed by the "Ir(N−N)$_2$Ir" dimetallacycle were found to be the isolated stereoisomers, but they establish an equilibrium with the corresponding cationic compounds [{Ir(μ-Pz)(H)(CNBu^t)$_2$}$_2$(μ-X)]X in solution. This transformation was found to be particularly clean and complete for complex **3**. On the other hand, the related complex [{Ir(μ-Pz)(H)(Cl)(CO)$_2$}$_2$] was found to be an unstable species evolving to the mononuclear [IrCl(HPz)(CO)$_2$] by a reductive elimination reaction above −50 °C. These results indicate that the iridium

(20) (a) Kovecevic A.; Grüdemann, S.; Miecznikowski, J. R.; Clot, E.; Eisenstein, O.; Crabtree, R. *Chem. Commun.* **2002**, 2580. (b) Pfaltz, A.; Blankenstein, J.; Hilgraf, R.; Hörmann, E.; McIntyre, S.; Menges, F.; Schönleber, M.; Smidt, S. P.; Wüstenberg, B.; Zimmermann, N. *Adv. Synth. Catal.* **2003**, *345*, 33.

(21) Tejel, C.; Ciriano, M. A.; Oro, L. A. Unpublished results.

centers in the isoelectronic complexes $[\{Ir(\mu\text{-}Pz)(L)_2\}_2]$ (L = $CNBu^t$ (**1**), CO (**6**)) are basic enough to react with H^+, but the carbonyl groups seem to be inappropriate to stabilize the Ir(III)−H bonds in this type of complex. Particularly interesting are the products obtained from the first protonation of $[\{Ir(\mu\text{-}Pz)(CO)(P\{OPh\}_3)\}_2]$ (**8**) with HCl and HO_2CCF_3, which were found to be the diamagnetic iridium(II)/iridium(II) complex $[(P\{OPh\}_3)(CO)(Cl)Ir(\mu\text{-}Pz)_2Ir(H)(CO)(P\{OPh\}_3)]$ (**11**) and the mixed-valence complex $[(P\{OPh\}_3)(CO)Ir(\mu\text{-}Pz)_2Ir(H)(\eta^1\text{-}O_2CCF_3)(CO)(P\{OPh\}_3)]$ (**12**), respectively. Since both complexes could be considered as derived from the cation $[(P\{OPh\}_3)(CO)Ir(\mu\text{-}Pz)_2Ir(H)(CO)(P\{OPh\}_3)]^+$, the nature of the entering anion seems to be the key to tip the balance toward either the metal-bonded species or the mixed-valence ones, supporting the existence of a delicate equilibrium between both types of complexes. However, both complexes produced dihydride compounds with identical stereochemistry on protonation of the iridium−iridium bond in **11** and the iridium(I) center in **12**.

Acknowledgment. The generous financial support from MCyT(DGI)/FEDER (Project BQU2002-00074) is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic data for complexes **2** and **9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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