Activation of a Vinyl Carbon–Hydrogen Bond in a Tris(pyrazolyl)boratoiridium Complex. The *X*-Ray Crystal Structure of [IrH{HB(pz)$_3$}(σ-C$_8$H$_{13}$)(η^2-C$_8$H$_{14}$)] †

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Reaction between [{Ir(μ-Cl)(C$_8$H$_{14}$)$_2$}$_2$] (C$_8$H$_{14}$ = cyclo-octene) and Na[HB(pz)$_3$] (pz = pyrazolyl) affords the vinyl hydrido complex [IrH{HB(pz)$_3$}(σ-C$_8$H$_{13}$)(η^2-C$_8$H$_{14}$)]. Protonation of this complex gives [IrH{HB(pz)$_3$}(η^2-C$_8$H$_{14}$)$_2$]BF$_4$. Treatment of [IrCl(C$_2$H$_4$)$_4$] with Na[HB(pz)$_3$] yields [Ir{HB(pz)$_3$}(η^2-C$_2$H$_4$)$_2$]. The molecular structure of [IrH{HB(pz)$_3$}(σ-C$_8$H$_{13}$)(η^2-C$_8$H$_{14}$)] (**1**) has been determined by *X*-ray analysis. Crystals of (**1**) are monoclinic, space group $P2_1/n$, with a = 20.284(2), b = 12.265(1), c = 20.554(2) Å, β = 97.103(7)°, and Z = 8. The co-ordination around the iridium atom is distorted octahedral involving the three N atoms from the tris(pyrazolyl)borato on one side, and a hydride, a π-bonded cyclo-octene, and a σ-bonded cyclo-octenyl group on the other; the last three ligands are mutually *cis*.

There is clear evidence that the chemistry of tris(pyrazolyl)-borato [HB(pz)$_3$] complexes of rhodium and iridium resembles in some aspects that of cyclopentadienyl (C$_5$H$_5$) [or pentamethylcyclopentadienyl (C$_5$Me$_5$)].[1–3] Although the area of carbon–hydrogen activation is well documented in the chemistry of C$_5$H$_5$ or C$_5$Me$_5$,[4] to the best of our knowledge only one report has appeared for HB(pz)$_3$ compounds, corresponding to the activation of alkanes by [Rh{HB-(dmpz)$_3$}(CO)$_2$] (dmpz = 3,5-dimethylpyrazolyl).[5] Here, we report the activation of a vinyl carbon–hydrogen bond in a tris(pyrazolyl)boratoiridium complex.

Results and Discussion

Reaction of [{Ir(μ-Cl)(C$_8$H$_{14}$)$_2$}$_2$] (C$_8$H$_{14}$ = cyclo-octene) with Na[HB(pz)$_3$] in dichloromethane gives [IrH{HB(pz)$_3$}(σ-C$_8$H$_{13}$)(η^2-C$_8$H$_{14}$)] (**1**) as the only product. The compound is obtained as white, air-stable crystals after concentration of the solution and addition of methanol. The formulation of the complex is supported by microanalysis, ^{1}H n.m.r. and i.r. spectroscopy; the molecular structure has been determined by single-crystal *X*-ray diffraction (see below). The ^{1}H n.m.r. spectrum of the complex shows, in addition to the aliphatic (C$_8$H$_{13}$, C$_8$H$_{14}$) and aromatic (pz) resonances, a singlet at δ −18.30 due to the hydride proton, two broad signals at 3.99 and 4.38 attributable to the vinyl protons of (η^2-C$_8$H$_{14}$), and a well resolved triplet at 5.24 (J_{HH} = 7.8 Hz) due to the vinyl proton of (σ-C$_8$H$_{13}$). The integration ratio for the three vinyl resonances is 1 : 1 : 1, in accord with co-ordination of a η^2-cyclo-octene and a vinyl σ-cyclo-octenyl. The i.r. spectrum in Nujol shows a band at 2 460 cm^{-1} corresponding to ν(B–H) and two bands at 2 215 and 2 270 cm^{-1} attributable to ν(Ir–H).

In order to establish the molecular parameters of complex (**1**) a single-crystal *X*-ray analysis was carried out. The crystal contains two independent (structurally analogous) molecules in the asymmetric unit. The Figure shows an ORTEP drawing of one of these molecules and Table 1 collects some selected bonding parameters (averages for the two independent molecules are used in the Discussion). The structure displays the expected pseudo-octahedral geometry around the metal with the tris(pyrazolyl)borate bonded through the N atoms and occupying three sites. The co-ordination sphere of the iridium is completed by a hydride, a π-bonded cyclo-octene molecule, and a σ-bonded cyclo-octenyl, the latter co-ordinated through a vinylic carbon.

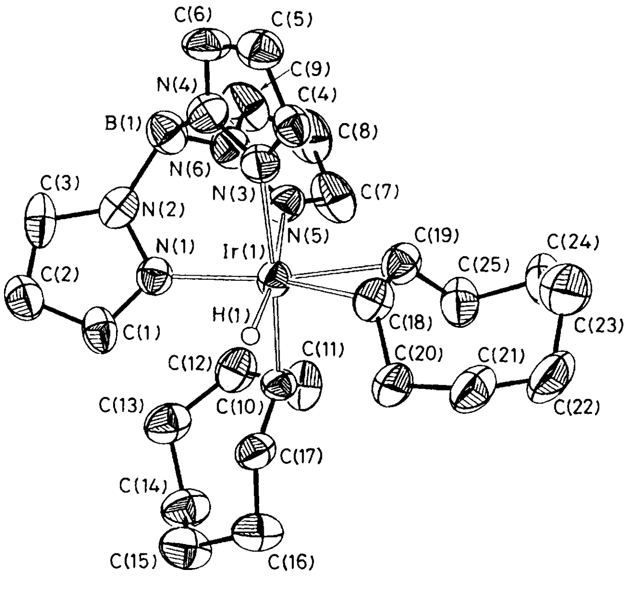

Figure. View of the molecular structure of [IrH{HB(pz)$_3$}(σ-C$_8$H$_{13}$)(η^2-C$_8$H$_{14}$)] (**1**) with the atomic numbering scheme

The Ir{HB(pz)$_3$} moiety has a normal geometry with the N–Ir–N angles in the range 81.3—87.4(3)°, distorted from 90° by the peculiar bite of the ligand. Interestingly, the Ir–N(1) bond distance, 2.079(7) Å, is markedly different from Ir–N(3) and

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† (η-Cyclo-octene)(σ-cyclo-octenyl)hydrido[tris(pyrazol-1-yl)borato]-iridium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Selected bond distances (Å) and angles (°) for $[IrH\{HB(pz)_3\}(\sigma\text{-}C_8H_{13})(\eta^2\text{-}C_8H_{14})]$ (**1**) with estimated standard deviations (e.s.d.s) in parentheses[a]

Ir(1)–N(1)	2.078(9)	2.080(9)	Ir(1)–C(18)	2.189(10)	2.195(11)
Ir(1)–N(3)	2.223(8)	2.226(8)	Ir(1)–C(19)	2.182(11)	2.196(10)
Ir(1)–N(5)	2.239(8)	2.209(9)	Ir(1)–C(10)	2.058(9)	2.051(11)
Ir(1)–CM(1)[b]	2.067(9)	2.075(8)	Ir(1)–H(1)[c]	1.51(–)	1.47(–)
C(10)–C(11)	1.523(13)	1.539(14)	C(13)–C(14)	1.539(16)	1.566(22)
C(10)–C(17)	1.334(13)	1.354(17)	C(14)–C(15)	1.567(16)	1.552(22)
C(11)–C(12)	1.580(15)	1.571(17)	C(15)–C(16)	1.557(18)	1.522(22)
C(12)–C(13)	1.527(17)	1.540(22)	C(16)–C(17)	1.555(15)	1.576(19)
C(18)–C(19)	1.422(14)	1.435(15)	C(21)–C(22)	1.605(20)	1.544(15)
C(18)–C(20)	1.517(15)	1.536(16)	C(22)–C(23)	1.548(21)	1.536(17)
C(19)–C(25)	1.527(14)	1.510(15)	C(23)–C(24)	1.529(18)	1.543(16)
C(20)–C(21)	1.554(15)	1.543(16)	C(24)–C(25)	1.563(18)	1.565(14)
N(1)–Ir(1)–N(3)	87.4(3)	84.9(3)	N(3)–Ir(1)–H(1)	100.5(–)	87.9(–)
N(1)–Ir(1)–N(5)	85.6(3)	87.0(3)	N(5)–Ir(1)–CM(1)	104.5(3)	104.8(3)
N(1)–Ir(1)–CM(1)	167.4(3)	167.6(4)	N(5)–Ir(1)–C(10)	98.3(3)	95.7(4)
N(1)–Ir(1)–C(10)	88.6(3)	90.0(4)	N(5)–Ir(1)–H(1)	170.6(–)	164.9(–)
N(1)–Ir(1)–H(1)	85.4(–)	81.6(–)	CM(1)–Ir(1)–C(10)	97.2(3)	85.0(4)
N(3)–Ir(1)–N(5)	81.8(3)	81.3(3)	CM(1)–Ir(1)–H(1)	84.9(–)	87.4(–)
N(3)–Ir(1)–CM(1)	86.6(3)	100.7(3)	C(10)–Ir(1)–H(1)	78.8(–)	94.2(–)
N(3)–Ir(1)–C(10)	176.0(3)	174.1(4)			
Ir(1)–C(10)–C(11)	118.4(7)	119.8(8)	Ir(1)–C(18)–C(19)	70.7(6)	71.0(6)
Ir(1)–C(10)–C(17)	122.9(7)	124.2(8)	Ir(1)–C(18)–C(20)	119.7(7)	117.9(7)
C(11)–C(10)–C(17)	118.5(9)	116.0(9)	C(19)–C(18)–C(20)	124.9(9)	121.8(9)
C(10)–C(17)–C(16)	127.6(9)	126.1(11)	Ir(1)–C(19)–C(18)	71.3(6)	70.9(6)
			Ir(1)–C(19)–C(25)	123.4(7)	118.5(7)
			C(18)–C(19)–C(25)	121.0(9)	123.2(10)

[a] The second value for each parameter corresponds to the second independent molecule. The atom numbering used for this molecule is related to the first one by adding 30 [*i.e.* C(11) and C(41)]. [b] CM(1) represents the midpoint of the olefinic bonds C(18)–C(19) or C(48)–C(49). [c] H(1) [and the corresponding H(31)] were tentatively located in a Fourier synthesis, but not refined.

Ir–N(5), average 2.224(5) Å, very likely due to the *trans* influence of the remaining ligands. The π-acceptor ability of the η^2-cyclo-octene *trans* to N(1) is probably forcing a stronger electronic release from this nitrogen towards the metal, compared with that of N(3) and N(5), giving rise to a shorter Ir–N(1) separation. A similar situation has been described for the related complex $[Rh\{B(pz)_4\}I_2(CO)]$,[6] where the shortest Rh–N distance was observed *trans* to the best π-acceptor ligand.

The σ-co-ordination of a vinylic carbon of cyclo-octene to a transition metal has been described only for two ruthenium(II) complexes $[Ru(\eta\text{-}C_5H_5)L_2(\sigma\text{-}C_8H_{13})]$ (L–L = $Me_2PCH_2CH_2PMe_2$ or $Ph_2PCH_2PPh_2$).[7] The metal–C(vinylic) bond distance is slightly shorter in our case [2.054(7) Å], than for the ruthenium complexes [average 2.115(4) Å]. However, the C=C distances are identical, [average 1.335(6) for the ruthenium compounds and 1.344(11) Å in (**1**)], indicating that no interaction is present between the olefinic bond and the metal. The C=C bond distance in free *trans*-cyclo-octene, as determined by gas-phase electron diffraction, is 1.332(17) Å.[8] Within iridium chemistry, only the molecular structure of two complexes containing a hydride ligand and a σ-co-ordinated vinylic carbon, $[IrH(\eta\text{-}C_5Me_5)(\sigma\text{-}CH{=}CH_2)(PMe_3)]$[9] and $[IrH\{N(CH_2CH_2PPh_2)_3\}]^+$[10] have been reported. Both complexes present Ir–C distances [2.054(4) and 2.09(1) Å, respectively] comparable to that observed in complex (**1**) [2.054(7) Å].

X-Ray studies of η^2-*cis*-cyclo-octene metal complexes are rather scarce. Only two rhodium(I) complexes $[\{Rh(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})[PMe(SiMe_3)_2]\}_2]$[11] and $[Rh(acac)(\eta^2\text{-}C_8H_{14})\{\eta^2\text{-}C_2(CF_3)_2\}]$ (acac = acetylacetonate),[12] and a gold compound $[AuCl(\eta^2\text{-}C_8H_{14})]$[13] have been characterized so far by *X*-ray analysis. As in these complexes, the co-ordination of *cis*-cyclo-octene in complex (**1**) causes a lengthening in the C=C bond distance compared with the value described for the free ligand.[8] The C=C distance in (**1**) [1.429(11) Å] is similar to that reported for the binuclear rhodium complex [1.413(4) Å],[11] but slightly longer than those of the mononuclear compounds [1.37(2)[12] and 1.38(2) Å[13]]. However the Ir–C(olefinic) bond distances are longer in complex (**1**) [2.190(10) Å] than in $[\{Rh(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})[PMe(SiMe_3)_2]\}_2]$[11] [2.098(3) and 2.110(3) Å].

In both independent molecules, the hydride ligand was located from a difference Fourier map at the appropriate positions to complete the octahedral environment around the metal. Potential-energy calculations[14] showed good agreement with the positions assigned to the hydrides. However the Ir–H distances seem not to be very reliable since previous determinations in related complexes gave markedly longer values of *ca.* 1.60 Å {*X*-ray studies: $[IrH(\eta\text{-}C_5Me_5)(\sigma\text{-}CH{=}CH_2)(PMe_3)]$, 1.61(5),[9] or $[IrH(\sigma\text{-}C_8H_{13})\{N(CH_2CH_2PPh_2)_3\}]^+$, 1.59(6) Å;[10] neutron studies: $[IrH_5(PPr^i_3)_2]$, 1.603(9) Å[15]}.

The reaction of $[\{Ir(\mu\text{-}Cl)(C_8H_{14})_2\}_2]$ with $Na[HB(pz)_3]$ involves an insertion into a cyclo-octene carbon (*sp*^{2}) hydrogen bond leading to the formation of the vinyl hydrido complex (**1**). Few mononuclear complexes are known to activate a vinyl–hydrogen bond, and these complexes contain $Ph_2PCH_2CH_2PPh_2$,[16] $N(CH_2CH_2PPh_2)_3$,[10] C_5H_5,[17] and C_5Me_5[9] as ancillary ligands, but, as far as we know, there are no precedents for this activation with tris(pyrazolyl)borato compounds.

We have tried to obtain the $[Ir\{HB(pz)_3\}(\eta^2\text{-}C_8H_{14})_2]$ species by thermolysis of complex (**1**) but on refluxing a solution of this complex in cyclohexane for 24 h, only the starting hydrido vinyl complex was isolated. Protonation of (**1**) with HBF_4 in diethyl ether gives $[IrH\{HB(pz)_3\}(\eta^2\text{-}C_8H_{14})_2]BF_4$ (**2**). This new complex has been fully characterized by elemental analysis, i.r. and ^1H n.m.r. spectroscopy.

Table 2. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for complex (**1**)[a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir(1)	1 488(1)	−501(1)	2 370(1)	Ir(31)	2 407(1)	2 716(1)	6 494(1)
H(1)[b]	1 840(−)	102(−)	2 953(−)	H(31)[b]	2 921(−)	3 467(−)	6 798(−)
N(1)	621(4)	102(6)	2 678(4)	N(31)	2 612(5)	3 517(6)	5 650(4)
N(2)	115(4)	484(6)	2 231(4)	N(32)	2 121(5)	3 980(6)	5 224(4)
N(3)	1 402(4)	817(6)	1 622(4)	N(33)	1 669(4)	4 042(6)	6 560(4)
N(4)	782(4)	1 071(7)	1 338(4)	N(34)	1 288(5)	4 326(6)	5 984(4)
N(5)	816(4)	−1 362(6)	1 588(4)	N(35)	1 550(5)	1 973(7)	5 885(4)
N(6)	284(4)	−786(7)	1 305(4)	N(36)	1 264(4)	2 586(7)	5 373(4)
C(1)	473(6)	335(8)	3 276(5)	C(31)	3 203(6)	3 792(8)	5 475(5)
C(2)	−164(6)	861(8)	3 224(6)	C(32)	3 082(7)	4 469(9)	4 908(5)
C(3)	−358(5)	937(8)	2 556(6)	C(33)	2 414(7)	4 571(8)	4 769(5)
C(4)	1 825(5)	1 475(8)	1 352(5)	C(34)	1 473(6)	4 681(8)	7 032(5)
C(5)	1 473(6)	2 155(8)	877(5)	C(35)	946(6)	5 348(9)	6 769(5)
C(6)	811(7)	1 876(9)	890(5)	C(36)	849(6)	5 116(9)	6 091(6)
C(7)	810(6)	−2 338(9)	1 292(6)	C(37)	1 261(6)	984(9)	5 859(6)
C(8)	260(7)	−2 367(10)	806(6)	C(38)	764(7)	956(11)	5 292(6)
C(9)	−57(6)	−1 387(10)	825(5)	C(39)	786(6)	1 964(11)	5 001(6)
C(10)	1 512(4)	−1 673(7)	3 089(4)	C(40)	3 072(6)	1 517(8)	6 331(5)
C(11)	1 241(5)	−2 802(8)	2 899(6)	C(41)	2 822(6)	454(8)	5 987(6)
C(12)	465(5)	−2 911(9)	2 899(5)	C(42)	2 717(7)	568(10)	5 220(6)
C(13)	207(6)	−2 626(9)	3 545(6)	C(43)	3 365(8)	859(13)	4 941(6)
C(14)	554(6)	−3 199(9)	4 160(5)	C(44)	3 979(8)	127(14)	5 184(8)
C(15)	1 075(6)	−2 459(10)	4 578(6)	C(45)	4 476(7)	668(13)	5 723(8)
C(16)	1 749(6)	−2 280(9)	4 304(5)	C(46)	4 265(7)	683(12)	6 408(7)
C(17)	1 710(5)	−1 467(8)	3 720(5)	C(47)	3 736(6)	1 589(9)	6 508(6)
C(18)	2 564(5)	−382(8)	2 363(5)	C(48)	2 129(5)	1 680(9)	7 287(5)
C(19)	2 300(5)	−1 152(8)	1 883(5)	C(49)	2 700(6)	2 316(8)	7 531(5)
C(20)	3 027(5)	−657(9)	2 978(6)	C(50)	1 448(6)	1 871(10)	7 521(5)
C(21)	3 766(5)	−674(10)	2 849(6)	C(51)	1 395(6)	1 273(10)	8 173(5)
C(22)	3 974(7)	−1 717(13)	2 449(8)	C(52)	1 766(6)	1 805(10)	8 794(5)
C(23)	3 717(7)	−1 678(12)	1 708(7)	C(53)	2 526(6)	1 694(9)	8 892(5)
C(24)	3 132(6)	−2 458(9)	1 544(6)	C(54)	2 915(6)	2 719(8)	8 729(5)
C(25)	2 516(6)	−2 345(8)	1 927(6)	C(55)	2 683(6)	3 208(9)	8 035(5)
B(1)	173(6)	407(10)	1 483(6)	B(31)	1 401(7)	3 802(11)	5 331(6)

[a] The atom numbering used for the second independent molecule is related to the first by adding 30 [*i.e.* C(11) and C(41)]. [b] These atoms were included in the last structure factor calculation, but not refined.

It has been reported that iridium complexes containing C_5Me_5[9] or C_5H_5[17] activate the carbon–hydrogen bond of ethylene. In this context, we have carried out the reaction of $[IrCl(C_2H_4)_4]$ with $Na[HB(pz)_3]$, under similar conditions to that used in the preparation of complex (**1**). The product of this reaction is the bis(η^2-ethylene) complex $[Ir\{HB(pz)_3\}(\eta^2\text{-}C_2H_4)_2]$ (**3**). Elemental analysis, i.r., and ^1H n.m.r. data are in concordance with the proposed formulation. The ^1H n.m.r. spectrum is very similar to that of $[Rh\{HB(pz)_3\}(\eta^2\text{-}C_2H_4)_2]$,[18] and shows at room temperature two doublets (δ 7.73 and 7.46) and a triplet (6.21) assignable to the pyrazolyl protons, as well as a broad resonance (2.09) due to eight equivalent ethylene protons.

Experimental

The reactions were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques. The compounds $[\{Ir(\mu\text{-}Cl)(C_8H_{14})_2\}_2]$[19] and $Na[HB(pz)_3]$[20] were prepared as previously reported. Proton n.m.r. spectra were recorded in $CDCl_3$ solution at room temperature on a Varian XL 200 spectrometer, i.r. spectra on a Perkin-Elmer 783 spectrophotometer. Elemental analyses were performed with a Perkin-Elmer 240 C elemental analyser.

Preparations.—$[IrH\{HB(pz)_3\}(\sigma\text{-}C_8H_{13})(\eta^2\text{-}C_8H_{14})]$ (**1**). The complex $[\{Ir(\mu\text{-}Cl)(C_8H_{14})_2\}_2]$ (400 mg, 0.44 mmol) was added to a dichloromethane (10 cm^3) solution of $Na[HB(pz)_3]$ (211 mg, 0.88 mmol). The solution immediately turned red, then rapidly changed to pale yellow. It was concentrated under reduced pressure and methanol (15 cm^3) was added. The mixture was set aside (−20 °C) for 24 h, after which time white crystals were formed. The crystals were separated by filtration, washed with methanol, and dried under vacuum. Yield 335 mg, 60% (Found: C, 47.8; H, 6.3; N, 13.4. Calc. for $C_{25}H_{38}BIrN_6$: C, 48.0; H, 6.1; N, 13.4%). ^1H N.m.r. ($CDCl_3$): −18.30 (s, 1 H, IrH), 0.7—2.6 (m, 24 H, CH$_2$), 3.99 (br, 1 H, =CH), 4.38 (t, 1 H, =CH), 5.24 (t, J_{HH} 7.8 Hz, 1 H, =CH), 6.04 (br, 1 H, pz), 6.10 (br, 1 H, pz), 6.35 (br, 1 H, pz), 7.5—7.6 (m, 3 H, pz), 7.75 (d, 1 H, pz), 8.04 (br, 1 H, pz), and 8.06 (d, 1 H, Pz).

$[IrH\{HB(pz)_3\}(C_8H_{14})_2]BF_4$ (**2**). Tetrafluoroboric acid in diethyl ether (22 µl, 0.16 mmol) was added to a solution of $[IrH\{HB(pz)_3\}(\sigma\text{-}C_8H_{13})(\eta^2\text{-}C_8H_{14})]$ (100 mg, 0.16 mmol) in diethyl ether (10 cm^3). Rapid precipitation of a white solid was observed. The mixture was allowed to react for 30 min and then the white precipitate was filtered off, washed with diethyl ether, and dried under vacuum. Yield 85 mg, 74% (Found: C, 41.6; H, 5.9; N, 11.7. Calc. for $C_{25}H_{39}B_2F_4IrN_6$: C, 42.1; H, 5.5; N, 11.8%). ^1H N.m.r. ($CDCl_3$): −15.24 (s, 1 H, IrH), 1.0—2.7 (m, 24 H, CH$_2$), 4.57 (br, 2 H, =CH), 5.08 (br, 2 H, =CH), 6.23 (br, 2 H, pz), 6.75 (br, 1 H, pz), 7.62 (br, 2 H, pz), 7.82 (br, 2 H, pz), 7.95 (br, 1 H, pz), and 8.62 (d, 1 H, pz). I.r. spectrum (Nujol): ν(Ir–H) 2 210 and ν(B–H) 2 500 cm^{-1}. Λ_M(acetone): 140 Ω^{-1} cm^2 mol^{-1}.

$[Ir\{HB(pz)_3\}(C_2H_4)_2]$ (**3**). The complex $[IrCl(C_2H_4)_4]$ was prepared *in situ* by the procedure of Onderdelinden and van der Ent,[21] *i.e.* bubbling ethylene through a solution of $[\{Ir(\mu\text{-}Cl)(C_8H_{14})_2\}_2]$ (431 mg, 0.48 mmol) in dichloromethane (5 cm^3) at 0 °C. To this solution $Na[HB(pz)_3]$ (227 mg, 0.96

mmol) was added, and the resulting pale yellow solution was left to react for 30 min. It was concentrated under reduced pressure and then methanol (10 cm^3) was added. The pale yellow precipitate formed was filtered off, washed with methanol, and dried under vacuum. Yield 255 mg, 57% (Found: C, 33.6; H, 4.1; N, 18.3. Calc. for $C_{13}H_{18}BIrN_6$: C, 33.8; H, 3.9; N, 18.2%). ^1H N.m.r. ($CDCl_3$): 2.09 (br, 8 H, C_2H_4), 6.21 (t, 3 H, pz), 7.46 (d, 3 H, pz), and 7.73 (d, 3 H, pz). I.r. spectrum (Nujol): ν(B–H) 2 475 cm^{-1}.

Crystal Structure Determination of $[IrH\{HB(pz)_3\}(\sigma\text{-}C_8H_{13})(\eta^2\text{-}C_8H_{14})]$.—*Crystal data.* $C_{25}H_{38}BIrN_6$, M = 625.65, monoclinic, space group $P2_1/n$ (no. 14), a = 20.284(2), b = 12.265(1), c = 20.554(2) Å, β = 97.103(7)°, U = 5 074.3(8) $Å^3$ (by least-squares refinement of the 2θ values of 46 accurately measured reflections in the range 20—35°), Z = 8, λ = 0.710 69 Å, D_c = 1.638 g cm^{-3}, $F(000)$ = 2 496, $\mu(Mo\text{-}K_\alpha)$ = 52.653 cm^{-1}, crystal dimensions 0.144 × 0.144 × 0.220 mm, An empirical method for the absorption correction was applied[22] (minimum and maximum values 0.868 and 1.085).

Data collection and processing. Four-circle Siemens AED diffractometer, ω—2θ mode, graphite-monochromated $Mo\text{-}K_\alpha$ radiation; 12 361 reflections measured. Of 6 431 independent reflections, 5 148 having $I \geqslant 3.0\sigma(I)$ were considered observed and used in the analysis.

Structure solution and refinement. Patterson and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms. No attempt was made to locate hydrogen atoms, except for the hydride ligands. Although it was not possible to locate unambiguously the hydride atoms H(1) and H(31), the co-ordination around the metals and potential-energy calculations[14] suggested the given positions as the most likely, among the maxima surrounding the metal atoms in a difference Fourier synthesis. These atoms were included for the last structure-factor calculations, but not refined. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, w, defined as $w = 2.1284/[\sigma^2(F) + 0.000\,162F^2]$. Final R and R' values were 0.039 and 0.041. The SHELX system of computer programs was used.[23] Atomic scattering factors, corrected for anomalous dispersion of iridium, were taken from ref. 24. Final atomic co-ordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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