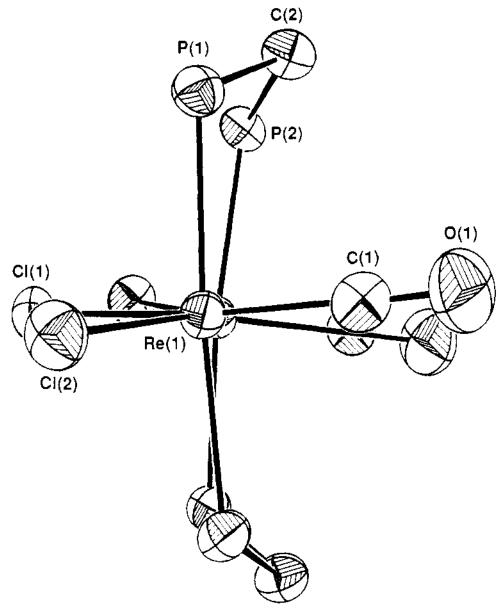

Figure 6. A side view of a molecule of **1**, emphasizing the syn orientation of the methylene bridgehead carbon atoms. The degree of twist from the perfectly eclipsed conformation is 8.5°.

by the ^1H NMR spectrum in the $-CH_2-$ regions of the dppm ligands (vide supra). As the side view of the molecule in Figure 6 clearly shows, the diphosphine ligands are twisted from an eclipsed conformation ($\chi = 8.5°$), resulting in a molecular symmetry of C_2 rather than C_{2v}.

The distances and angles in the molecule are within expected ranges (Table II). The metric parameters for **1** are very similar to those exhibited by other edge-sharing bioctahedral molecules such as $Re_2Cl_6(dppm)_2$[26] and $Re_2Cl_4(CO)_2(dppm)_2$[15] with the exception that the carbonyl ligands are not as swept back from the center of the molecule as is ordinarily the case with terminal ligands. In $Re_2Cl_4(CO)_2(dppm)_2$, the Re–Re–C_t angle is 125 (2)° and Re–Re–Cl_t = 141.3 (7)°.[15] In the present molecule, Re–Re′–C_t = 112.2 (3)° and Re–Re′–Cl_t = 146.23 (5)°. The unusually small angle that the CO ligands in **1** assume with respect to the metal–metal bond axis suggests that some attractive interaction may be occurring with the bridging hydride ligand. Attempts are underway to study the reactivity of the μ-H ligand with respect to CO activation.

The Re–Re bond length of 2.605 (1) Å is quite long for a complex formally derived from the Re_2^{4+} core. In fact this distance is close to those values found in Re_2^{6+} compounds such as $Re_2Cl_6(dppm)_2$ (Re–Re = 2.616 (1) Å).[26] The long metal–metal distance in $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ is even more surprising considering that it contains a μ-H group, which is known to have the effect of drawing metal atoms closer together. Clearly, more examples of these types of carbonyl–hydrido dimers are required to explain the structural parameters of this molecule.

Conclusion

The studies described herein were undertaken to gain a more complete understanding of the formation of an unusual hydrido–dirhenium complex. We have verified that the compound $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$ can be prepared by reactions of $Re_2Cl_4(dppm)_2$ with carbonyl clusters under an H_2 atmosphere and by the direct reaction of $Re_2Cl_4(dppm)_2$ with a CO/H_2 gas mixture at atmospheric pressure. The role of $H_2Os_3(CO)_{10}$ as a cluster precursor appears to be an important one in the high-yield synthesis of $Re_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(CO)_2(dppm)_2$. We have also noted the behavior of H_2 in assisting the reaction to form the title compound. Attempts to stabilize reactive intermediates that might provide an interesting mixed-metal complex are still under investigation.

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Supplementary Material Available: Tables of crystallographic parameters, atomic positional and thermal parameters, full bond distances and angles, and anisotropic thermal parameters (7 pages); a listing of structure factors (37 pages). Ordering information is given on any current masthead page.

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(28) (a) Anderson, L. B.; Barder, T. J.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3629. (b) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 4180. (c) Anderson, L. B.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Price, A. C.; Reid, A. H.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 2717.

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Synthesis and Characterization of $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2\cdot CH_3C_6H_5$

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The $^3(d\sigma^*p\sigma)$ excited state of $Ir_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) reacts with hydrogen atom donors to give $Ir_2(TMB)_4H_2^{2+}$ (Ir_2H_2). This d^7–d^7 dihydride has been isolated as a tetraphenylborate salt: ν(Ir–H) 1940 cm^{-1}, ν(Ir–Ir) 136 cm^{-1}. $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2\cdot CH_3C_6H_5$, $Ir_2C_{95}H_{114}N_8B_2$, crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14), with $a = 10.54$ (2) Å, $b = 31.02$ (4) Å, and $c = 27.05$ (4) Å, $\beta = 91.57$ (3)°, $V = 8841$ (3) $Å^3$, and $Z = 4$. The Ir–Ir separation is 2.920 (2) Å, approximately 0.3 Å shorter than Ir–Ir in the d^8 dimer (Ir_2) but ~0.1 Å longer than in the diiodide, $Ir_2(TMB)_4I_2^{2+}$. The reaction of Ir_2H_2 with styrene gives Ir_2 and ethylbenzene.

Triplet $d\sigma^*p\sigma$ excited states of binuclear d^8 complexes abstract hydrogen atoms from a variety of organic and organometallic molecules.[1-6] In the case of $Pt_2(P_2O_5H_2)_4^{4-}$ (Pt_2), the inorganic product is $Pt_2(P_2O_5H_2)_4H_2^{4-}$ (Pt_2H_2); this dihydride has been characterized spectroscopically, but it has not been isolated in crystalline form.[6]

We have found that irradiation of $Ir_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) in the presence of 1,4-

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† Oregon Graduate Center, Beaverton, OR 97006.

(1) Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55-61.
(2) Marshall, J. L.; Stiegman, A. E.; Gray, H. B. In *Excited States and Reactive Intermediates*; Lever, A. B. P., Ed.; ACS Symposium Series 307; American Chemical Society: Washington, DC, 1986; pp 166-176.
(3) Vlcek, A., Jr.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 286-287.
(4) Vlcek, A., Jr.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 1997-2001.

0020-1669/90/1329-0534$02.50/0

cyclohexadiene produces $Ir_2(TMB)_4H_2^{2+}$ (Ir_2H_2), which can be isolated as a crystalline tetraphenylborate salt. We report here the NMR, UV–vis, IR, and Raman spectra of Ir_2H_2, and a crystal structure analysis of $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2 \cdot CH_3C_6H_5$. The reaction of Ir_2H_2 with styrene also has been investigated.

Experimental Section

Standard Schlenk and high-vacuum techniques were used. Acetonitrile was used as received, freeze–pump–thaw-degassed, and stored under vacuum over activated alumina. 1,4-Cyclohexadiene was distilled under argon from $NaBH_4$, freeze–pump–thaw-degassed, and stored under vacuum. 9,10-Dihydroanthracene was recrystallized three times from absolute ethanol. Standard procedures were used to prepare $[Ir_2(TMB)_4][B(C_6H_5)_4]_2$.[7] The ^1H NMR spectra were obtained on a 400-MHz JNM-GX400 FT NMR spectrometer. The IR spectra were measured on a Beckman IR 4240 instrument. Absorption spectra were recorded with a Hewlett-Packard 8450A or a Shimadzu UV-260 spectrophotometer. Raman spectra were measured on a Dilor Z24 triple-grating scanning spectrophotometer by sampling methods described previously.[7] Elemental analyses were obtained from Galbraith Laboratories, Inc.

$[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2 \cdot CH_3C_6H_5$. A 20-fold excess of 1,4-cyclohexadiene was added to an acetonitrile solution of $[Ir_2(TMB)_4][B(C_6H_5)_4]_2$ under an inert atmosphere. The solution was freeze–pump–thaw-degassed three times and photolyzed for 2 h with a 1000-W high-pressure Hg/Xe lamp equipped with a Corning cutoff filter ($\lambda_{ex} > 550$ nm). The final solution was light orange. The solvent was removed under vacuum (care was taken to shield the material from light), yielding an off-white powder, which was recrystallized from acetonitrile/toluene. Anal. Calcd for $Ir_2C_{95}H_{114}N_8B_2$: C, 64.3; H, 6.5; N, 6.3. Found: C, 64.8; H, 6.8; N, 6.2. ^1H NMR (CD_3CN, 20 °C): δ −10.6 (singlet, 1 H, IrH), 1.4 (broad singlet, CH_3), 1.6 (broad singlet, CH_3), 1.8 (broad singlet, CH_2), 6.9 (triplet, 8 H), 7.04 (triplet, 16 H), 7.33 (multiplet, 16 H). IR (Nujol mull, NaCl plates): 1940 cm^{-1} (m), ν(Ir—H); 2160 cm^{-1} (s), $\nu(N{\equiv}C)$. UV–vis (CH_3CN, 25 °C): 320 nm (ϵ 17 000 M^{-1} cm^{-1}).

A procedure similar to the above was followed for the photolysis of $Ir(TMB)_4^{2+}$ in the presence of 9,10-dihydroanthracene. The material obtained after removal of solvent contained the desired iridium complex, anthracene, and 9,10-dihydroanthracene. This material was washed with dry, degassed benzene to remove the organics, and the remaining solid was dissolved in CH_3CN and filtered. The solvent was removed from the filtrate under vacuum, yielding a light blue-green powder.

Dihydride Reaction with Styrene. Acetonitrile and acetonitrile-d_3 were freeze–pump–thaw-degassed and stored under vacuum over activated alumina. A CH_3CN solution of Ir_2H_2 was prepared in a two-compartment cell. To this solution was added a large excess of styrene (styrene was freeze–pump–thaw-degassed and vacuum-transferred to a graduated cylinder; a known volume was vacuum-transferred to the reaction vessel). Slow growth of bands attributable to $Ir_2(TMB)_4^{2+}$ was observed in the UV–vis spectrum of the sample over a 24-h period. Two CD_3CN solutions of Ir_2H_2 were prepared in vacuum-adapted NMR tubes. To one of these solutions was added a 30-fold excess of styrene. Both tubes were stored in the dark at room temperature, and NMR spectra were recorded every 24 h over a 7-day period. No change was observed for the solution that did not contain styrene. For the sample with styrene, resonances of $Ir_2(TMB)_4^{2+}$ slowly appeared in the spectrum with loss of the $Ir_2(TMB)_4H_2^{2+}$ signals. The sample that contained styrene was clear, dark blue after 7 days. The NMR tube that contained the styrene solution was opened after 7 days, and the contents were transferred to a round-bottom flask. The volatiles were vacuum-transferred to a new NMR tube. This solution was clear and colorless, while a dark blue material remained in the round-bottom flask. The NMR spectrum of the solvent, in addition to strong styrene resonances, contained two weak signals attributable to the ethyl group of ethylbenzene (δ (ppm): 1.2 (triplet, 3 H, CH_3), 2.62 (quartet, 2 H, CH_2)). These resonances became visible in the NMR spectrum of the reaction mixture as the NMR spectrum of $Ir_2(TMB)_4^{2+}$ appeared.

Table I. Crystallographic Data for $[Ir_2(C_{10}H_{16}N_2)_4H_2][B(C_6H_5)_4]_2 \cdot CH_3C_6H_5$

formula: $Ir_2C_{95}H_{114}N_8B_2$	space group $P2_1/c$ (No. 14)
fw 1774.03	$T = 22$ °C
$a = 10.54$ (2) Å	$\lambda = 0.71073$ Å
$b = 31.02$ (4) Å	$\rho_{calcd} = 1.333$ (2) g cm^{-3}
$c = 27.05$ (4) Å	$\mu = 32.5$ cm^{-1}
$\beta = 91.57$ (3) Å	$R(F_o) = 0.118$
$V = 8841$ (13) $Å^3$	GOF = 1.16
$Z = 4$	

X-ray Data Collection and Reduction for $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2 \cdot CH_3C_6H_5$. Long, platelike crystals of the dihydride were grown by slow evaporation of a toluene/acetonitrile solution; they appeared dichroic under a microscope with large, colorless faces and narrow, light blue faces. A crystal was mounted in a capillary with a small amount of grease holding it in place; it was centered on a CAD-4 diffractometer equipped with graphite-monochromated Mo Kα radiation. Cell dimensions and an orientation matrix were obtained from the setting angles of 25 reflections with $15° < 2\theta < 25°$, and the intensities of reflections ($\pm h,\pm k,l$) were measured to $2\theta = 30°$. Absences of $0k0$ with k odd identified the space group as either $P2_1$ or $P2_1/m$; the coordinates of the iridium atoms, obtained from a Patterson map, suggested $P2_1/m$. The remaining non-hydrogen atoms were found by successive structure factor–Fourier calculations; however, the resulting structure appeared to be disordered in several regions.

Before we tried to derive an ordered model in space group $P2_1$, we took an oscillation photograph, the axis of rotation being the needle axis, $[20\bar{1}]$.[8] This photograph showed weak, intermediate layer lines that indicated a doubling of the c axis; none of these weak reflections had been noted by the CAD-4 diffractometer during the initial search. The crystal was then placed on a Nicolet $P2_1$ diffractometer, again equipped with Mo Kα radiation, and new cell dimensions were obtained. These were averaged with the cell dimensions determined on the CAD-4 diffractometer (with the c axis doubled) to give the final values listed in Table I. All reflections out to $2\theta = 30°$ were measured twice ($\pm h,\pm k,-l$ for 0–20°, $\pm h,\pm k,+l$ for 20–30°), and reflections from 30 to 40° were measured for $+h,+k,\pm l$, $h = 0$–2. The crystal by then showed severe decay. Absences in the data for $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, identified the space group as $P2_1/c$. The weakness of reflections with l odd is due to the fact that the iridium atoms lie very close to $y = 0.25$ and, hence, they (along with many of the lighter atoms) show a pseudotranslation of $^1/_2$ along c.

Backgrounds were measured at both ends of the scans; an average background as a function of 2θ was then calculated from the weak reflections and applied to all the data. Absorption corrections were made, first on the basis of the correct value of μ (38 cm^{-1}) and, later, on the basis of a revised value (32.5 cm^{-1}) that led to improved agreement between symmetry-related measurements. With this revised value, the goodness-of-fit for merging the 9434 measured intensities into 4692 independent reflections was 0.95; 3915 of these reflections had $F_o > 0$ and 2005 had $F_o^2 > 3\sigma(F_o^2)$. Variances $\sigma^2(F_o^2)$ for the individual reflections were assigned on the basis of counting statistics plus an additional term, $0.014I^2$. Variances for the merged reflections were determined by standard propagation of error plus another term, $0.014(I)^2$. Scattering factors were taken from standard references.[9]

After the earlier $P2_1/m$ model was converted to an ordered model in $P2_1/c$, several cycles of full-matrix least squares were run, minimizing $\sum w(F_o^2 - F_c^2)^2$. Hydrogen atoms were introduced at calculated positions (C–H = 0.95 Å); each hydrogen was given an isotropic thermal parameter 10% greater than that of the carbon to which it was bonded. The hydrogens bound to iridium appeared in difference maps and were placed in axial positions 1.6 Å from the iridium atoms. No hydrogen parameters were further adjusted. The toluene ring appeared as diffuse maxima in a late difference map. In the final refinement cycles, 411 parameters were adjusted: the coordinates of 100 atoms, the anisotropic thermal parameters of the Ir atoms, the isotropic thermal parameters for the 98 C, N, and B atoms (excluding the toluene), and a scale factor. The final goodness-of-fit, $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, was 1.16 for $n = 4692$ and $p = 411$; the R values were 0.118 for the 3915 reflections with $F_o^2 > 0$ and 0.045 for the 2005 reflections with $F_o^2 > 3\sigma(F_o^2)$. All calculations were done with programs of the CRYM crystallographic computing system. Final parameters for $Ir_2(TMB)_4H_2^{2+}$ are given in Table II, and selected bond lengths and angles in Table III. Anisotropic displacement coefficients for the Ir atoms, final anion parameters, hydrogen coordinates, and observed and calculated structure factors are provided as supplementary material.

Results and Discussion

Crystal Structure. $Ir_2(TMB)_4H_2^{2+}$ posesses a *trans*-dihydride (H–M–M–H) structure (Figure 1). The Ir–Ir separation is 2.920

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(5) Smith, D. C.; Gray, H. B. In *The Challenge of d and f Electrons*; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989; pp 356–365.

(6) Harvey, E. L.; Stiegman, A. E.; Vlcek, A., Jr.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 5233–5235.

(7) Miskowski, V. M.; Smith, T. P.; Loehr, T. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 7925–7934.

(8) Principal crystal faces {010} and $\{10\bar{2}\}$.

(9) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. Final Parameters for the Cation $Ir_2(TMB)_4H_2^{2+}$ (x, y, z, and $U_{eq} \times 10^4$)

atom	x	y	z	U_{eq}[a] or B,[b] Å^2
Ir1	45 (0.9)	2540 (0.5)	3276 (0.3)	298 (4)
Ir2	2126 (0.9)	2564 (0.4)	4010 (0.3)	321 (4)
C1	1041 (27)	2185 (8)	2832 (11)	4.4 (8)
N1	1679 (21)	1998 (6)	2560 (8)	4.2 (6)
C2	2426 (29)	1722 (8)	2212 (11)	3.9 (7)
C3	1959 (31)	1263 (9)	2278 (12)	7.0 (10)
C4	2201 (28)	1902 (8)	1703 (11)	6.5 (9)
C5	3767 (28)	1757 (8)	2425 (10)	5.5 (8)
C6	4372 (27)	2219 (8)	2360 (10)	5.5 (8)
C7	6060 (28)	2041 (8)	3037 (11)	5.6 (8)
C8	5748 (27)	2804 (8)	2728 (11)	5.8 (8)
C9	5154 (25)	2375 (9)	2835 (10)	5.3 (7)
N2	4177 (18)	2431 (7)	3211 (7)	4.0 (5)
C10	3395 (21)	2523 (10)	3504 (8)	4.3 (6)
C11	712 (25)	3059 (8)	2980 (10)	3.7 (7)
N3	1091 (20)	3358 (7)	2786 (8)	4.0 (6)
C12	1861 (28)	3716 (8)	2531 (11)	4.1 (7)
C13	2662 (31)	3498 (9)	2175 (12)	6.6 (9)
C14	943 (26)	4057 (8)	2320 (10)	5.1 (8)
C15	2691 (25)	3900 (8)	2975 (10)	4.5 (7)
C16	1964 (27)	4141 (8)	3348 (11)	5.4 (8)
C17	1451 (30)	4253 (8)	4248 (12)	7.3 (9)
C18	3752 (33)	4133 (9)	4056 (13)	7.2 (10)
C19	2270 (33)	4042 (9)	3897 (12)	6.2 (9)
N4	2179 (21)	3549 (7)	3958 (8)	3.9 (6)
C20	2108 (30)	3184 (9)	3990 (12)	4.3 (8)
C21	−1073 (30)	2858 (8)	3713 (11)	4.3 (8)
N5	−1749 (25)	3060 (7)	3938 (9)	5.9 (7)
C22	−2584 (33)	3295 (10)	4303 (13)	7.3 (9)
C23	−2512 (31)	3763 (9)	4129 (13)	7.2 (10)
C24	−3944 (35)	3099 (10)	4246 (13)	10.0 (11)
C25	−1953 (29)	3200 (9)	4790 (12)	6.8 (9)
C26	−1930 (31)	2755 (9)	5017 (12)	8.1 (10)
C27	−856 (33)	2120 (10)	5421 (13)	9.2 (11)
C28	−245 (34)	2862 (10)	5661 (14)	9.4 (12)
C29	−829 (28)	2572 (11)	5248 (11)	7.0 (8)
N6	212 (19)	2597 (7)	4867 (7)	5.0 (5)
C30	902 (21)	2569 (9)	4543 (8)	4.7 (7)
C31	−494 (24)	2024 (8)	3553 (9)	2.9 (7)
N7	−852 (18)	1684 (6)	3706 (7)	2.9 (5)
C32	−1280 (29)	1246 (8)	3887 (11)	4.8 (7)
C33	−2454 (38)	1349 (10)	4233 (15)	9.6 (12)
C34	−1691 (30)	986 (9)	3459 (12)	7.1 (9)
C35	−242 (31)	1079 (8)	4238 (12)	6.9 (9)
C36	896 (31)	939 (8)	3927 (11)	6.4 (9)
C37	2340 (30)	1006 (9)	4747 (13)	8.4 (10)
C38	3335 (35)	938 (9)	3933 (13)	7.0 (10)
C39	2178 (31)	1101 (9)	4172 (12)	6.2 (9)
N8	2215 (21)	1589 (7)	4132 (8)	3.7 (6)
C40	2193 (26)	1967 (8)	4075 (10)	2.4 (7)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$. [b] All entries except those for Ir1 and Ir2 are isotropic displacement parameters, B.

Table III. Bond Lengths and Angles Involving Iridium

	Bond Lengths, Å		
Ir1–Ir2	2.920 (2)	Ir2–C10	1.94 (3)
Ir1–C1	1.96 (3)	Ir2–C20	1.92 (3)
Ir1–C11	1.94 (3)	Ir2–C30	1.96 (3)
Ir1–C21	1.96 (3)	Ir2–C40	1.86 (3)
Ir1–C31	1.86 (3)		
	Bond Angles, deg		
C1–Ir1–C11	90.4 (11)	C10–Ir2–C20	92.9 (12)
C1–Ir1–C21	174.9 (11)	C10–Ir2–C30	175.9 (10)
C1–Ir1–C31	86.4 (11)	C10–Ir2–C40	88.7 (11)
C11–Ir1–C21	93.6 (11)	C20–Ir2–C30	90.4 (11)
C11–Ir1–C31	176.2 (11)	C20–Ir2–C40	175.9 (12)
C21–Ir1–C31	89.6 (11)	C30–Ir2–C40	87.8 (11)

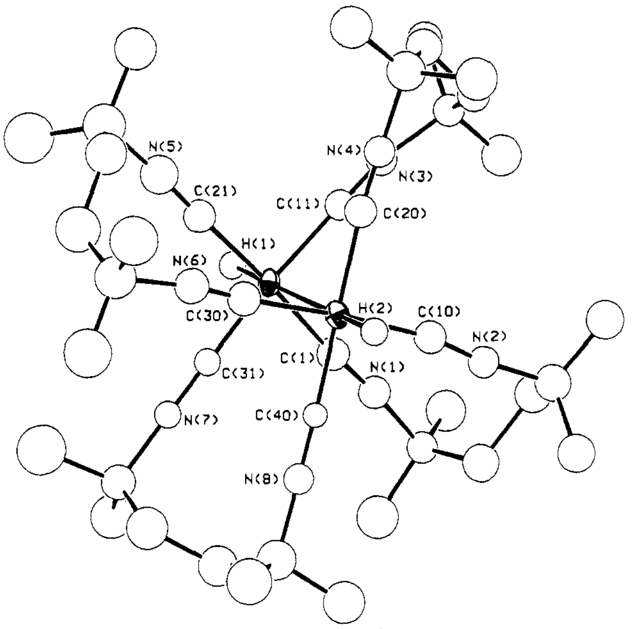

Figure 1. ORTEP drawing of $Ir_2(TMB)_4H_2^{2+}$ with 30% probability ellipsoids. Hydrogen atoms, except for the hydride atoms bonded to iridium, are omitted. The hydride atoms are shown with B = 3.0 Å^2.

Table IV. Comparison of Geometric Parameters for Ir_2H_2 with Those for Other Binuclear d^8 and d^7 Complexes

	Ir_2H_2	Ir_2I_2[a]	Ir_2[b]	Rh_2Cl_2[a]	Rh_2[c]
M–M, Å	2.920 (2)	2.803 (4)	3.199 (1)	2.773 (2)	3.262 (1)
M–X, Å	1.6	2.712 (7)		2.425 (6)	
M–C, Å	1.92 (1)	1.95 (1)	1.96 (1)	1.95 (1)	1.92–1.98
C–N, Å	1.16 (1)	1.16 (2)	1.12 (1)	1.15 (1)	1.16
ω, deg	28.2 (3)	31 (2)	28.1 (1)	33.1 (1)	31
C_β–C_γ–C_γ'–C_β', deg	136 (1)	130 (2)	141 (1)	137 (2)	
N···N′, Å	3.43 (1)		3.68 (1)		
M–M–C, deg	91.0 (3)	90.12 (5)	91.7 (2)	90.7 (4)	
M–C–N, deg	175.2 (1)	173 (1)	177.12 (6)	176 (1)	175
displacement of M from plane of the 4 N's (toward center of dimer), Å					
Ir1	0.05	0.15	0.08	0.15	
Ir2	0.11				

[a] Reference 11. [b] Reference 10. [c] Reference 12.

(2) Å, approximately 0.3 Å shorter than in the parent d^8 dimer (3.199 (1) Å),[10] indicating the formation of an Ir–Ir bond. This Ir–Ir separation is ~0.1 Å longer than in the diiodide, $Ir(TMB)_4I_2^{2+}$,[11] presumably a result of trans-hydride effects.

Some geometric parameters for $Ir_2(TMB)_4H_2^{2+}$ (Ir_2H_2), $Ir_2(TMB)_4^{2+}$ (Ir_2),[10] $Ir_2(TMB)_4I_2^{2+}$ (Ir_2I_2),[11] $Rh_2(TMB)_4Cl_2^{2+}$ (Rh_2Cl_2),[11] and $Rh_2(TMB)_4^{2+}$ (Rh_2)[12] are given in Table IV. The geometry of the $Ir(CN)_4$ unit in Ir_2H_2 deviates only slightly from the idealized geometry (M–M–C = 90°; M–C–N = 180°) and compares well with those of Ir_2 and Ir_2I_2. The two $Ir(CN)_4$ groups are twisted with respect to each other, the torsion angle N–M–M′–N′ of 28° being virtually the same as those observed for Ir_2 and Ir_2I_2. A best plane fit through the nitrogen atoms of $Ir(CN)_4$ units shows that each iridium is displaced slightly toward the center of the dimer (Ir1 by 0.05 Å; Ir2 by 0.11 Å).

With the different metal-metal separations observed for the Ir complexes, some variation of geometric parameters is expected. No variation within the $Ir(CN)_4$ units is found, but a compression of the $Ir(CN)_4$ units toward one another is exhibited (the N···N′ separation decreases 0.25 Å from Ir_2 to Ir_2H_2) in addition to a

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(10) Smith, D. C. Ph.D. Thesis, California Institute of Technology, 1989.

(11) Maverick, A. W.; Smith, T. P.; Maverick, E. F.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 4336–4341.

(12) Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462–2468.

Table V. Selected Vibrational and Structural Data for Ir_2H_2 and Related Complexes

	ν(M—H), cm^{-1}	ν(N≡C), cm^{-1} [a]
Ir_2H_2	1940	2160
Pt_2H_2 [b]	1840	
Ir_2		2140

	ν(M—M), cm^{-1} (Raman)	k, mdyn $Å^{-1}$	M—M, Å	
			X-ray	calcd [d]
Ir_2H_2	136	1.05 [c]	2.920 (2)	2.85
Ir_2I_2	116 [e]	2.09 [e]	2.803 (4) [f]	2.55
Ir_2Cl_2	140 [e]	1.56 [e]		2.69
Rh_2Cl_2	155 [e]	1.14 [e]	2.773 (2) [f]	2.75

[a] Free ligand: 2120 cm^{-1}. [b] Reference 6. [c] Reference 10. [d] Woodruff's relationship; ref 14. [e] Reference 7. [f] Reference 11.

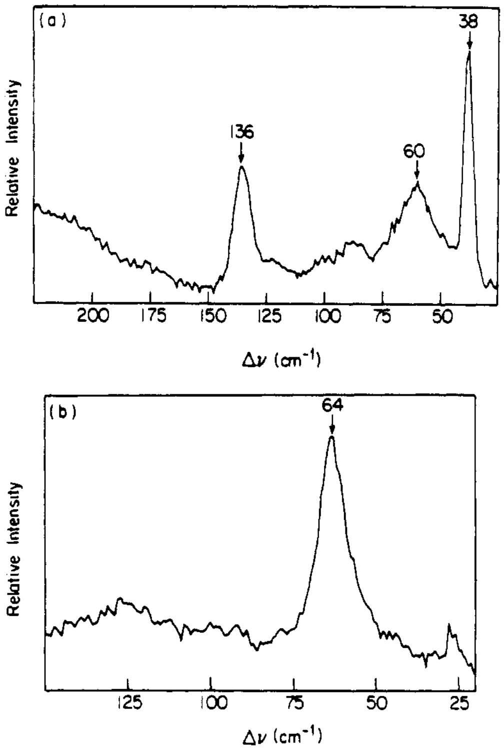

Figure 2. Raman spectra of $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2 \cdot CH_3C_6H_5$: (a) solid, 90 K, λ_{ex} = 488 nm; (b) solid, 90 K, λ_{ex} = 647.1 nm.

slightly increased pyramidal distortion of the $Ir(CN)_4$ moieties. With a compression of the $Ir(CN)_4$ units, an increase in the torsion angle (N-M-M′-N′; "ω" in Table IV) might be expected. This angle, however, is roughly the same (~31°) in all these complexes. Instead, there is a decrease in the torsion angle C_β-C_γ-C_γ'-C_β', probably because increased metal-metal bonding leads to a shorter metal-metal distance and thus a greater kinking of the carbon atom backbone of the TMB ligand. The other geometric parameters of the TMB ligand compare well through the series of complexes.

Spectroscopy. The vibrational spectroscopic data for $Ir_2(TMB)_4H_2^{2+}$ are summarized in Table V. An Ir—H absorption is observed at 1940 cm^{-1}, a feature characteristic of a complex possessing terminal metal hydrides. This absorption frequency is 100 cm^{-1} higher than that of the Pt—H band for Pt_2H_2,[6] indicating a stronger M—H bond for iridium. The N≡C frequency for Ir_2H_2 is 20 cm^{-1} higher than that observed for Ir_2 (a 40-cm^{-1} shift relative to the free ligand), probably owing to increased σ donation from the isocyanide to the Ir(II) center (which reduces the σ-antibonding contribution of the carbon lone pair to the C≡N bond).[13]

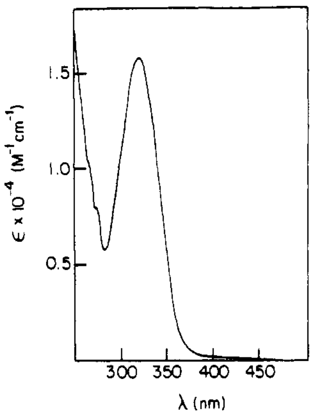

Figure 3. Electronic absorption spectrum of $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2$ in CH_3CN at 25 °C.

Raman spectra for Ir_2H_2 are shown in Figure 2. The 38-cm^{-1} spike is a plasma line. Excitation at 647.1 nm (on resonance for Ir_2) results in a large enhancement of the band at 60 cm^{-1}, identifying this feature as the Ir–Ir frequency of Ir_2. Thus, a small amount of Ir_2 is present in the Ir_2H_2 material (hence the light blue color of the crystals). The concentration ratio Ir_2/Ir_2H_2 (determined from optical absorption spectra) is 1/40, which is too small to be detected crystallographically. The band at 136 cm^{-1} represents the Ir–Ir stretching frequency of Ir_2H_2.

Although there are no crystal structure data for Ir_2Cl_2, a comparison of the Ir–Ir interactions in Ir_2Cl_2 and Ir_2H_2 can be made by using Raman parameters.[7] A significantly larger Ir–Ir force constant is found for Ir_2Cl_2, indicating a stronger Ir–Ir interaction and hence a smaller Ir–Ir separation (Table V).[14,15] The longer Ir–Ir distance for Ir_2H_2 is a consequence of trans-hydride effects.

The electronic absorption spectrum of $[Ir_2(TMB)_4H_2][B(C_6H_5)_4]_2$ is shown in Figure 3. By analogy to other binuclear d^7 complexes, the intense feature (λ_{max} 320 nm, ε 17000 M^{-1} cm^{-1}) is assigned to the dσ → dσ* singlet transition.[7] A weak absorption attributable to dπ → dσ* has not been identified in the spectrum. This feature is presumably obscured by the strong dσ → dσ* absorption. The large red shift of the dσ → dσ* band from Ir_2Cl_2 to Ir_2H_2 reflects the strong σ-donor character of the hydride ligand (the transition should have greater charge-transfer character in Ir_2H_2).

Reactions. Ir_2H_2 is thermally stable; no significant decomposition is observed at 80 °C in CH_3CN over 12 h.[10] Irradiation into the dσ → dσ* absorption of Ir_2H_2 produces H_2 and Ir_2,[10] but the reaction is not as clean as the analogous Pt_2H_2 photoprocess.[6]

Reaction of Ir_2H_2 with styrene results in a slow, clean conversion to Ir_2 and ethylbenzene. The reaction may be related to the step in the $Co(CN)_5^{3-}$-catalyzed hydrogenation of alkenes that involves hydrogen atom transfer from a coordinatively saturated metal hydride, $Co(CN)_5H^{3-}$.[16] A similar hydrogen atom transfer process most likely takes place in the photohydrogenation of cyclohexene or cyclopentene in the presence of Pt_2 and 2-propanol.[17] Since Ir_2H_2 can be formed from the reaction of $^3Ir_2^*$ with certain hydrogen atom donors, our finding that hydrogen acceptors such as styrene can be reduced by the dihydride indicates that Ir_2 also

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(13) An increase in the N≡C stretching frequency from the free ligand to Ir_2 would be counter to the expected shift if π-back-bonding were an important part of the metal-isocyanide interaction.

(14) Miskowski, V. M.; Dallinger, R. F.; Christoph, G. G.; Morris, D. E.; Spies, G. H.; Woodruff, W. H. *Inorg. Chem.* **1987**, *26*, 2127-2132. Conradson, S. D.; Sattelberger, A. P.; Woodruff, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 1309-1311.

(15) The agreement between the calculated and crystallographically determined Ir–Ir distances for Ir_2I_2 is poor. Mixing of metal-halide and metal-metal vibrations in Ir_2I_2 makes a force field analysis of this system quite difficult. For Ir_2Cl_2 and Ir_2Br_2, this mixing is much smaller, and force field analyses should yield more reliable estimates of the Ir–Ir force constants. Note that the calculated and crystallographically determined metal-metal distances for Rh_2Cl_2 accord fairly closely.

(16) Kwiatek, J. *Catal. Rev.* **1967**, *1*, 37-72.

(17) Che, C.-M.; Lee, W.-M. *J. Chem. Soc., Chem. Commun.* **1986**, 512-513.

could function as a photochemical hydrogen-transfer reagent.

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Supplementary Material Available: Tables of intensity collection data, anisotropic thermal parameters for iridium, final anion parameters, complete bond distances and angles, and assigned hydrogen parameters (8 pages); a complete listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Pyrazole Derivatives of 9-Borabicyclo[3.3.1]nonane[1]

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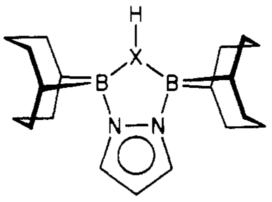
9-(Dimethylamino)-9-borabicyclo[3.3.1]nonane, $(C_8H_{14})BN(CH_3)_2$, reacts with 1 molar equiv of pyrazole (=Hpz) to form the complex $(C_8H_{14})B(pz)\cdot(CH_3)_2NH$ and with additional Hpz to yield $(C_8H_{14})B(pz)\cdot Hpz$. The latter complex is also obtained by the reaction of 9-borabicyclo[3.3.1]nonane dimer, $[(C_8H_{14})BH]_2$ (=9-BBN), with Hpz. The adduct can be deprotonated to form $[(C_8H_{14})B(pz)_2]^-$, which reacts with $PdCl_2$ to yield $Pd[(\mu\text{-pz})_2B(C_8H_{14})]_2$. This same Pd complex is obtained when $(C_8H_{14})B(pz)\cdot(CH_3)_2NH$ is reacted with NaH and then with $[ClPd(\pi\text{-}CH_2CHCH_2)]_2$ in boiling benzene, whereas at room temperature the latter reaction yields the complex $[(pz)Pd(\pi\text{-}CH_2CHCH_2)]_2$. Reaction of $[(C_8H_{14})B(pz)_2]^-$ with $[ClPd(\pi\text{-}CH_2CHCH_2)]_2$ yields the complex $(C_8H_{14})B(\mu\text{-pz})_2Pd(\pi\text{-}CH_2CHCH_2)$. The pyrazabole $(C_8H_{14})B(\mu\text{-pz})_2B(C_8H_{14})$ is obtained by the reaction of $(C_8H_{14})B(pz)\cdot Hpz$ with 9-BBN, the direct interaction of 9-BBN with Hpz, or the thermal decomposition of $(C_8H_{14})B(pz)\cdot(CH_3)_2NH$ in molten Hpz. A relative of this pyrazabole, i.e., $(C_8H_{14})B(\mu\text{-pz})(\mu\text{-NHCH}_3)B(C_8H_{14})$, is obtained by the reaction of $(C_8H_{14})B(pz)\cdot CH_3NH_2$ with 9-BBN.

Introduction

The first pyrazole derivatives of 9-borabicyclo[3.3.1]nonane, $[(C_8H_{14})BH]_2$ (=9-BBN), have recently been obtained from the reaction of $[(C_8H_{14})B]_2X$ (X = O, S, Se) with pyrazole (=Hpz).[2] The resultant species of type **1** are relatives of the pyrazaboles,



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$R_2B(\mu\text{-pz})_2BR_2$, but in which one of the bridging pz groups has been replaced by another moiety, i.e., XH. (Similar compounds of the type $R(pz)B(\mu\text{-pz})(\mu\text{-NHR}')BR(pz)$ were previously prepared by the reaction of borazines, $(RBNR')_3$, with Hpz.[3]) The reaction of **1** (X = O) with $[(C_8H_{14})BH]_2$ gave the pyrazabole $(C_8H_{14})B(\mu\text{-pz})_2B(C_8H_{14})$,[2] and the complex $Co[(pz)_2B(C_8H_{14})]_2$ has recently been described and was found to contain two agostic hydrogen bonds.[4] The present work is concerned with a general study of pyrazole derivatives of 9-BBN.

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 (high-resolution spectra), XL-200 (^{11}B), or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm, with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O\cdot BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, h = septet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants *J* are given in hertz. Unless otherwise noted, ^{13}C NMR spectra were recorded in the proton-decoupled mode. Electron impact (EI) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to *m/z* 30 for 5% or greater relative abundances (in parentheses) only. Field desorption (FD) mass spectra were recorded on a Finnigan MAT 250 instrument.

All nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. Pyrazole (=Hpz) was distilled over a small amount of metallic sodium and stored under anhydrous conditions. All syntheses were performed under argon cover.

$(C_8H_{14})BN(CH_3)_2$. A stirred solution of 9-borabicyclo[3.3.1]nonane (=9-BBN, 100 mL of 0.5 M solution in hexanes) was saturated with anhydrous dimethylamine. A milky mixture formed that was slowly heated to reflux while a slow flow of dimethylamine was maintained. Rapid gas evolution began at about 60 °C; after about 15 min, the solution was clear and gas evolution ceased. The mixture was refluxed for an additional 30 min, and the solvent was distilled off under atmospheric pressure. The residue was distilled under reduced pressure to give a 90% yield of the desired compound, bp 70 °C (1 Torr).

NMR data: $\delta(^1H)$ 2.78 (6 H, s), 1.9–1.3 (14 H, m); $\delta(^{11}B)$ 47.2 (s, $h_{1/2}$ = 125 Hz); $\delta(^{13}C)$ 38.4, 32.9, 23.2, 21*.

The compound has previously been prepared by the reaction of lithium dimethylamide with 9-OMe-9-BBN: bp 88 °C (2 Torr); $\delta(^1H)$ 2.74 (6 H, s), 2.0–1.3 (14 H, m).[5]

$(C_8H_{14})B(pz)\cdot(CH_3)_2NH$. A solution of 2.7 g (40 mmol) of Hpz in 30 mL of ether was added slowly with stirring to a solution of 6.4 g (39 mmol) of $(C_8H_{14})BN(CH_3)_2$ in 25 mL of ether. A precipitate formed immediately in a slightly exothermic reaction, and the mixture was stirred at ambient temperature for 15 min. The precipitate was collected, washed with ether, and dried under vacuum to give 8.5 g (93%) of (slightly hygroscopic) product. The colorless microcrystalline material decomposed with the release of dimethylamine on heating to 130–140 °C (with some sublimation) and finally melted at 230–240 °C. Anal. Calcd for $C_{13}H_{24}BN_3$ (M_r = 233.17): C, 66.97; H, 10.37; B, 4.64; N, 18.02. Found: C, 66.86; H, 10.41; N, 17.65.

NMR data: $\delta(^1H)$ 7.68 (1 H, d, *J* = 1.2), 7.58 (1 H, d, *J* = 2.2), 6.26 (1 H, unsym t = two overlapping d), 3.9* (1, H, s), 2.36 (6 H, d, *J* = 6), 2.0–1.2 (14 H, m); $\delta(^{11}B)$ 1.1 (s, $h_{1/2}$ = 150 Hz); $\delta(^{13}C)$ 139.7, 133.2, 103.5, 36.1 (CH_3), 30.9, 30.6, 23.8, 23.2, 20.6*. For mass spectral data, see text.

$(C_8H_{14})B(pz)\cdot Hpz$. A mixture of 1.0 g (4.3 mmol) of $(C_8H_{14})B(pz)\cdot(CH_3)_2NH$ (see above), 1.5 g (22 mmol) of Hpz, and 30 mL of toluene was refluxed with stirring for 2 h, and toluene was removed under

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(1) Boron-Nitrogen Compounds. 124 (K.N.). Part 123: Komorowska, M.; Niedenzu, K.; Weber, W. *Inorg. Chem.*, in press.

(2) Yalpani, M.; Köster, R.; Boese, R. *Chem. Ber.* **1989**, *122*, 19–24.

(3) Bielawski, J.; Das, M. K.; Hanecker, E.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* **1986**, *25*, 4623–4628.

(4) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 205–206; *Angew. Chem.* **1989**, *101*, 209–210.

(5) Nelsen, S. F.; Kessel, C. R.; Brien, D. J.; Weinhold, F. *J. Org. Chem.* **1980**, *45*, 2116–2119.

0020-1669/90/1329-0538$02.50/0