(2) (yield 20%). Anal. Calcd for $C_{18}H_{36}BrN_2P_2O_6Cu_2$: C, 33.50; H, 5.63; N, 4.34; P, 9.60; Br, 12.38; Cu, 19.66. Molecular weight determination: 594 (cryoscopic in benzene, concentration independent in the range 0.026–0.08 mol/L); calcd 645. Found: C, 32.71; H, 5.73; N, 3.96; P, 9.20; Br, 12.52; Cu, 18.87.

Reaction of $[Cu_4\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2Br_2]$ with Me_2SnBr_2. To a solution of $[Cu\{C_6H_3(CH_2NMe_2)\text{-}o,o'\}CuBr]$ (0.5 g, 1.25 mmol) in diethyl ether (15 mL) was added Me_2SnBr_2 (0.38 g, 0.5 mmol). The resulting suspension was stirred at room temperature for 1.5 h and filtered. The filtrate was evaporated to dryness to afford white $[\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}SnMe_2]^+Br^-$ which was characterized by comparing its ^1H NMR spectrum with that of an authentic sample. Yield: 0.42 g, 80%.

Crystal Structure Determination. Transparent yellow crystals of the title compound $Cu_4Br_2C_{24}H_{38}N_4$ are orthorhombic, space group *Pcab* with eight molecules in a unit cell of dimensions $a = 18.167$ (3) Å, $b = 19.462$ (3) Å, and $c = 17.036$ (2) Å. A total of 5655 independent intensities ($2\theta < 130°$) were measured on a Nonius CAD4 diffractometer, at 25 °C, using graphite-monochromated Cu Kα radiation (λ(Cu Kα) = 1.5418 Å. A total of 2587 reflections were below the $3\sigma(I)$ level and were treated as unobserved.

The Cu and Br positions were located by means of the symbolic addition program set SIMPEL.[25] The positions of the C and N atoms were obtained by standard difference Fourier techniques. After isotropic block–diagonal least-squares refinement an empirical absorption correction (DIFABS[26]) was applied (crystal dimensions 0.25 × 0.33 × 0.33 mm; $\mu = 64.3$ cm^{-1}).

Continued anisotropic refinement converged to $R = 0.066$ (H atoms were introduced at calculated positions). Continued refinement, anisotropic for Cu, Br, C, and N (the H atoms were kept at their idealized positions) converged to $R = 0.065$ ($R_w = 0.112$). An extinction correction was applied and a weighting scheme, $w = 1/(9.3 + F_o + 0.012F_o^2)$, was employed. The anomalous dispersion of Cu and Br were taken into account. The scattering factors were taken from ref 27 and were corrected for anomalous dispersion.[28]

Acknowledgment. Prof. K. Vrieze is kindly thanked for his interest in this research and Dr. D. M. Grove for the helpfull comments during the preparation of the manuscript.

Registry No. 1, 116926-17-1; 2, 116926-18-2; *o,o'*-$(Me_2NCH_2)_2C_6H_3Br$, 66479-06-9; CuBr, 7787-70-4; $CuBr\{P(OMe)_3\}$, 34836-54-9; Me_2SnBr_2, 2767-47-7; $[\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}SnMe_2]^+Br^-$, 66484-01-3.

Supplementary Material Available: Tables of fractional coordinates of the hydrogen atoms (Table 2), anisotropic thermal parameters (Table 3), bond distances of the non-hydrogen atoms (Table 4) and of the hydrogen atoms (Table 5), and bond angles of the non-hydrogen atoms (Table 6) and of the hydrogen atoms (Table 7) and an ORTEP view of 1 (9 pages); a listing of observed and calculated structure factors (Table 1) (24 pages). Ordering information is given on any current masthead page.

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[25] Overbeek, A. R.; Schenk H. In *Computing in Crystallography*: Schenk, H., Olthof, R., van Koningsveld, H., Bassi, C. G., Eds.; Delft University Press: Delft, The Netherlands, 1978.

[26] Walker N.; Stewart, D. *Acta Crystallogr.* Sect. A: *Found. Crystallogr.* **1983**, *A39*, 158.

[27] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

[28] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Aliphatic versus Aromatic C–H Activation and the X-ray Crystal Structure of $[IrH(H_2O)(7,8\text{-benzoquinolinato})(PPh_3)_2]SbF_6$

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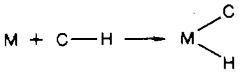
Received March 8, 1988

The crystal structure of $[(bq)IrH(H_2O)(PPh_3)_2]SbF_6$ (2, bq = 7,8-benzoquinolato) shows that benzoquinoline cyclometalates under conditions which give only a C–H···M bridged system with 8-methylquinoline. **2**, a rare example of an organometallic aqua hydride complex, crystallizes in space group $P2_1/c$ with $a = 13.330$ (4) Å, $b = 18.131$ (5) Å, $c = 21.777$ (7) Å, $\beta = 98.86$ (3)°, and $Z = 4$. The possible intermediacy of η^2-arene species is considered and rejected, and a transition state (7) for the C–H oxidative addition is proposed.

The question of aromatic versus aliphatic C–H bond activation has aroused considerable interest over the last few years.[1-3] It is generally agreed that examples of C–H bond oxidative addition (eq 1) are much more numerous for aromatic than for aliphatic or benzylic C–H groups.



$$M + C\text{—}H \longrightarrow M\begin{matrix} \diagup C \\ \diagdown H \end{matrix} \qquad (1)$$

Two types of explanations have been advanced to account for this observation. One suggestion, based on kinetic arguments, is that the arene group can bind to the metal, for example, in an η^2 fashion and that this binding leads to oxidative addition.[2] A second explanation is thermodynamic. On this idea, the deciding factor is the greater bond strength for an M–C(aryl) over an M–C(alkyl) or M–C(benzyl) bond in eq 1.[1,3] Part of our motivation for this study was an attempt to throw some light on this problem by using a ligand for which the first of these explanations would be unlikely to hold. We had already shown that 8-methylquinoline (mq) reacts with [Ir-

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[1] Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

[2] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240.

[3] Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

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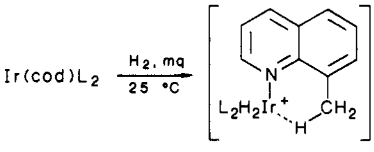
Table I. Crystal Data for $Ir(Ph_3P)_2(HOH)H(C_{13}H_8N)SbF_6$

formula	$IrSbF_6P_2C_{49}H_{41}NO$
mol wt	1149.8
a, Å	13.330 (4)
b, Å	18.131 (5)
c, Å	21.777 (7)
β, deg	98.86 (3)
V, Å^3	5200.3 (28)^3
$F(000)$	2248
μ(Mo Kα), cm^{-1}	31.82
λ(Mo Kα), Å	0.71069
D_{calcd}, g cm^{-3}	1.468
Z	4
obsd reflectns	5037
R	8.5%
space group	$P2_1/c$

$(cod)(PPh_3)_2]A$ (cod = 1,5-cyclooctadiene; A = SbF_6) in CH_2Cl_2 under H_2 to give complex 1, which contains a C–H···Ir bridge.[4] We therefore decided to look at an analogue of mq which contains an aromatic C–H bond in the place of the aliphatic C–H involved in the C–H···Ir bridge in 1: 7,8-benzoquinoline (bqH). This ligand, when it binds through the quinoline nitrogen presents an aromatic C–H bond to the metal in an end-on C–H···M fashion. Initial η^2 binding of a bqH aromatic ring is considered to be very unlikely. We will see that in spite of this, the cyclometalation of bqH occurs rapidly.[5]

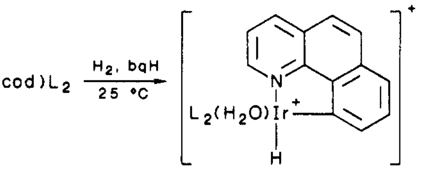
Results and Discussion

We find that the hydrogenation of $[Ir(cod)L_2]A$ (L = PPh_3; cod = 1,5-cyclooctadiene; A = SbF_6), under conditions which in the case of mq gave 1, with bqH (eq 2 and 3) lead instead to 2. Complex 2 is a rare example both of an organometallic aqua species and of an aqua hydride complex.[6,7] The presence of an H_2O ligand was unexpected and led to initial difficulties in characterization. The problem was finally solved by a combination of spectroscopic and crystallographic methods, described below.



(2)

1



(3)

2

mq = 8-methylquinoline; bqH = 7,8-benzoquinoline; L = PPh_3; cod = 1,5-cyclooctadiene

The ^1H NMR of 2 shows a triplet Ir–H resonance at δ – 16.0 with a coupling constant (^2J(P,H) = 15 Hz) corresponding to an Ir–H cis to the two PPh_3 groups. The protons of the coordinated H_2O appear at δ 2.54 as a broad singlet, much as they do in the related species $[IrH_2(H_2O)_2(PPh_3)_2]A$.[7] The IR spectrum shows a ν(OH) vibration at 3550 cm^{-1} and ν(Ir–H) at 2179 cm^{-1}.

Table II. Selected Angles (deg) and Distances (Å) for 2

Ir–P1	2.336 (7)	P1–Ir1–P2	173.0 (3)
Ir1–P2	2.319 (7)	P1–Ir1–O1	92.9 (6)
Ir1–O1	2.26 (2)	P1–Ir1–C2	88.4 (7)
Ir1–C2	1.99 (2)	P1–Ir1–N13	90.4 (6)
Ir1–N13	2.10 (2)	P1–Ir1–H99	110[a]
Ir1–H99	1.19[a]	P2–Ir1–O1	90.9 (6)
Sb–F	1.79–1.83 (4)[b]	P2–Ir1–C2	88.3 (7)
C1–C2	1.39 (4)	P2–Ir1–N13	95.1 (6)
C2–C3	1.39 (4)	P2–Ir1–H99	63[a]
C12–N13	1.34 (3)	O1–Ir1–C2	88.3 (7)
N13–C14	1.37 (3)	O1–Ir1–N13	95.2 (7)
		C1–Ir1–N13	80.2 (9)

[a] These values seem to be substantially different than expected, no doubt as a result of the difficulties of locating and refining H atoms in the presence of heavy atoms, and are only included for completeness. [b] The sixth Sb–F distance was unreasonably short (Sb1)–F6 = 1.53 (3) Å), for reasons we do not understand.

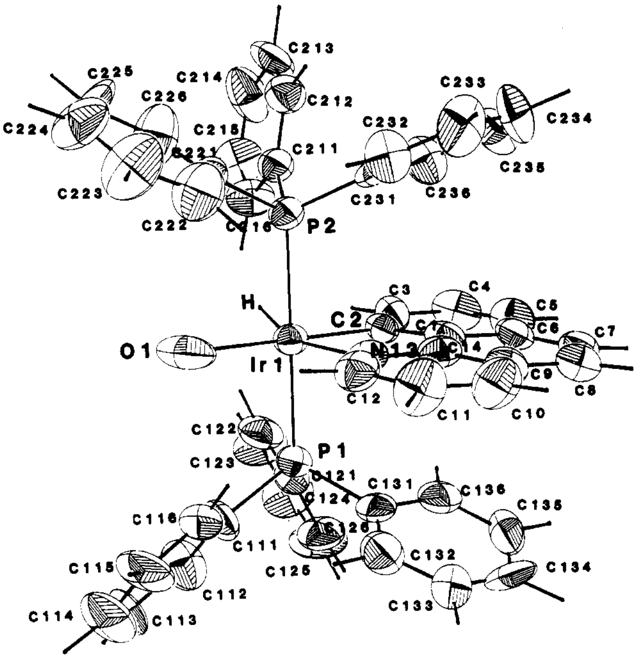


Figure 1. An ORTEP diagram of 2 showing the cyclometalated benzoquinoline ligand, the oxygen atom of the H_2O ligand, and the hydride ligand. The hydride may be an artefact, but its presence is confirmed by spectroscopic data (see text). The other H positions shown are calculated.

We wished to establish the atom connectivity of the structure. The X-ray analysis of a crystal of the complex grown from CH_2Cl_2-Et_2O shows the main structural feature: the bq group is clearly cyclometallated (Tables I–IV, Tables 1 and 2 {supplementary data}, and Figure 1). In addition, an electron density maximum was found in the difference Fourier that may be associated with the Ir–H hydride ligand. We do not rely on the crystallography, however, because the spectroscopic evidence demonstrates the presence of this hydride (see below). The oxygen atom of the coordinated H_2O was found trans to C-2 (rather than N-13) of the bq ligand. We examined the possibility that the C and N assignment was the reverse of this, but this choice did not lead to satisfactory anisotropic thermal parameters for these atoms. In confirmation of this assignment, the position of the ^1H NMR resonance for the Ir–H proton (δ – 16) is entirely consistent with its being trans to N but not C.[7] The covalent radius of N is 0.03

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(4) Crabtree, R. H.; Holt, E. M.; Lavin, M. E.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. Anklin, C. G.; Pregosin, P. S. *Magn. Reson. Chem.* **1985**, *23*, 671.

(5) A preliminary account of some of this work has appeared: Crabtree, R. H.; Lavin, M. *J. Chem. Soc. Chem. Commun.* **1985**, 794.

(6) Taube, H., *Coord. Chem. Rev.* **1978**, *26*, 33.

(7) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994 and references cited in this paper.

Table III. Positional Parameters for $IrSbF_6P_2C_{49}H_{41}NO$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ir1	0.7239 (1)	0.3940 (1)	0.2988 (0)	C233	0.8065 (28)	0.6675 (20)	0.3464 (19)
P1	0.7547 (5)	0.3377 (4)	0.2070 (3)	C234	0.8123 (30)	0.7033 (21)	0.4021 (20)
P2	0.7050 (5)	0.4620 (4)	0.3865 (3)	C235	0.7923 (28)	0.6653 (20)	0.4542 (15)
O1	0.5537 (15)	0.3875 (14)	0.2711 (9)	C236	0.7632 (23)	0.5926 (16)	0.4480 (13)
C1	0.9088 (18)	0.3307 (15)	0.3614 (11)	SB1	0.3450 (2)	0.1918 (2)	0.3519 (1)
C2	0.8731 (15)	0.3931 (15)	0.3281 (9)	F1	0.2502 (22)	0.1318 (18)	0.3157 (14)
C3	0.9475 (20)	0.4445 (15)	0.3208 (12)	F2	0.4118 (20)	0.1914 (20)	0.2843 (12)
C4	1.0525 (23)	0.4340 (20)	0.3440 (15)	F3	0.4179 (25)	0.1140 (21)	0.3851 (14)
C5	1.0814 (20)	0.3731 (20)	0.3734 (15)	F4	0.2826 (19)	0.1979 (25)	0.4208 (13)
C6	1.0151 (20)	0.3169 (18)	0.3844 (12)	F5	0.4464 (25)	0.2478 (24)	0.3920 (18)
C7	1.0390 (19)	0.2473 (17)	0.4152 (12)	F6	0.2945 (37)	0.2632 (15)	0.3250 (18)
C8	0.9707 (24)	0.1968 (18)	0.4237 (13)	H99	0.7233	0.41593	0.2932
C9	0.8638 (23)	0.2076 (17)	0.4023 (12)	H3	0.9270	0.4910	0.2977
C10	0.7841 (24)	0.1566 (16)	0.4096 (15)	H4	1.1034	0.4727	0.3388
C11	0.6895 (24)	0.1752 (17)	0.3844 (16)	H5	1.1548	0.3653	0.3878
C12	0.6670 (20)	0.2421 (16)	0.3553 (13)	H7	1.1117	0.2360	0.4291
N13	0.7376 (13)	0.2917 (12)	0.3448 (10)	H8	0.9952	0.1514	0.4486
C14	0.8354 (21)	0.2758 (15)	0.3712 (11)	H10	0.7993	0.1096	0.4344
C111	0.6417 (18)	0.3122 (17)	0.1514 (12)	H11	0.6326	0.1391	0.3856
C112	0.5628 (22)	0.2727 (16)	0.1726 (13)	H12	0.5948	0.2539	0.3403
C113	0.4801 (26)	0.2490 (21)	0.1327 (18)	H112	0.5687	0.2621	0.2181
C114	0.4679 (28)	0.2630 (25)	0.0717 (22)	H113	0.4250	0.2188	0.1490
C115	0.5426 (30)	0.3045 (24)	0.0488 (14)	H114	0.4073	0.2502	0.0417
C116	0.6304 (25)	0.3286 (20)	0.0884 (14)	H115	0.5385	0.3182	0.0026
C121	0.8295 (18)	0.3895 (16)	0.1585 (11)	H116	0.6867	0.3579	0.0737
C122	0.8292 (56)	0.4658 (18)	0.1603 (13)	H122	0.7881	0.4915	0.1882
C123	0.8878 (28)	0.5063 (19)	0.1224 (15)	H123	0.8859	0.5618	0.1236
C124	0.9446 (29)	0.4735 (23)	0.0884 (18)	H124	0.9855	0.5038	0.0628
C125	0.9474 (27)	0.3981 (25)	0.0847 (15)	H125	0.9914	0.3745	0.0579
C126	0.8896 (23)	0.3565 (19)	0.1202 (14)	H126	0.8895	0.3001	0.1176
C131	0.8215 (21)	0.2510 (15)	0.2213 (11)	H132	0.6999	0.1824	0.2024
C132	0.7742 (22)	0.1838 (18)	0.2176 (13)	H133	0.7886	0.0672	0.2334
C133	0.8260 (27)	0.1175 (20)	0.2342 (16)	H134	0.9688	0.0731	0.2609
C134	0.9257 (30)	0.1180 (17)	0.2509 (16)	H135	1.0532	0.1801	0.2704
C135	0.9781 (23)	0.1801 (24)	0.2560 (14)	H136	0.9692	0.2988	0.2429
C136	0.9293 (22)	0.2508 (18)	0.2408 (13)	H212	0.9039	0.4720	0.4527
C211	0.7696 (17)	0.4193 (13)	0.4583 (11)	H213	0.9982	0.4150	0.5430
C212	0.8691 (23)	0.4360 (18)	0.4765 (13)	H214	0.9194	0.3317	0.6015
C213	0.9243 (24)	0.4020 (19)	0.5304 (14)	H215	0.7443	0.3004	0.5684
C214	0.8807 (28)	0.3548 (20)	0.5636 (15)	H216	0.6500	0.3574	0.4797
C215	0.7784 (29)	0.3378 (19)	0.5451 (16)	H222	0.5368	0.3684	0.4013
C216	0.7226 (21)	0.3701 (17)	0.4922 (14)	H223	0.3636	0.3841	0.4114
C221	0.5720 (19)	0.4760 (15)	0.3974 (12)	H224	0.2958	0.5005	0.4066
C222	0.5079 (25)	0.4192 (20)	0.4024 (17)	H225	0.3928	0.6018	0.4008
C223	0.4068 (26)	0.4285 (22)	0.4057 (19)	H226	0.5741	0.5893	0.3871
C224	0.3693 (24)	0.4946 (20)	0.4051 (18)	H232	0.7686	0.5675	0.2998
C225	0.4246 (27)	0.5512 (23)	0.4006 (20)	H233	0.8229	0.6950	0.3088
C226	0.5304 (25)	0.5432 (21)	0.3938 (19)	H234	0.8345	0.7555	0.4056
C231	0.7552 (18)	0.5545 (16)	0.3935 (12)	H235	0.7953	0.6913	0.4952
C232	0.7766 (24)	0.5941 (17)	0.3415 (13)	H236	0.7487	0.5653	0.4861

[a] Estimated standard deviations are given in parentheses.

Å less than that of C^8 so at first sight the N should reveal itself by having the shorter distance to Ir. Unfortunately, the smaller N atom is trans to an unusually high trans influencing ligand (H) and the larger C atom to an unusually low trans influencing ligand (H_2O). Experimentally, the trans influence is the more important effect: Ir-C(2), 1.99 (2) Å; Ir-N(13), 2.10 (2) Å. The distances around the aromatic ring are not expected to be affected by the trans influence, and these are in agreement with the proposed identification. C(1)-C(2) (1.39 (4) Å) and C(2)-C(3) (1.39 (4) Å) are, as expected about 0.03 Å longer than C(12)-N(13) (1.34 (3) Å) and C(14)-N(13) (1.37 (3) Å). We do not have to rely on these small differences for this assignment, thanks to the spectroscopic evidence.

The identification of the coordinated H_2O as such rather than as a hydroxiide or oxo ligand is supported by the diamagnetism of the complex and the Ir–O distance of 2.26 (2) Å. This is rather long for an Ir–O coordinate link, but the high trans influencing C(2) carbon of the bq ligand probably helps lengthen the Ir–O bond. For comparison, Ir–O is 2.27 Å in the related complex $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$, in which a hydride, also a high trans influence ligand, is trans to the oxygen ligand.[9]

Otherwise, all distances and angles are normal (Table II) except that the bite of the bq ligand is only 80.2 (9)°, and there is one short Sb–F distance of the counterion, which we believe is an artefact. The observed Ir–H distance is clearly too short (1.19 Å), but the difficulties of detecting hydrogens in the presence of heavy atoms are well-known,[10] and we prefer to rely on the spectroscopic data which show the presence of a single H ligand (by ^1H NMR integration, adopting the usual precautions[11]). Given this single hydrogen, the logical location is the otherwise empty octahedral position trans to N(13). As

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(8) Pauling, L. *The Nature of the Chemical Bond*; Cornell University: Ithaca, NY, 1960.

(9) Crabtree, R. H.; Hlatky, G. G.; Parnell, C. P.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354.

(10) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(11) Crabtree, R. H.; Segmuller, B. E.; Uriarte, R. J., *Inorg. Chem.* **1985**, *24*, 1949.

Table IV. Anisotropic Thermal Parameters for $IrSbF_6P_2C_{49}H_{41}NO$[a]

atom	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Ir1	39 (0)	50 (0)	39 (0)	0 (0)	7 (0)	-9 (0)
P1	46 (4)	51 (4)	41 (4)	0 (3)	4 (3)	-8 (3)
P2	39 (3)	51 (4)	42 (4)	2 (3)	11 (2)	-3 (3)
O1	76 (13)	110 (18)	67 (13)	-27 (13)	27 (10)	-47 (14)
C1	35 (13)	72 (18)	38 (14)	-7 (12)	12 (10)	-17 (13)
C2	34 (11)	52 (14)	31 (12)	-2 (12)	4 (8)	-6 (12)
C3	55 (16)	58 (18)	52 (17)	1 (13)	-3 (12)	-2 (13)
C4	64 (20)	80 (24)	68 (22)	-34 (18)	22 (16)	-6 (18)
C5	34 (15)	98 (28)	78 (23)	-16 (15)	10 (14)	-15 (19)
C6	50 (16)	83 (23)	39 (16)	7 (16)	-2 (12)	-20 (15)
C7	43 (15)	72 (20)	49 (17)	2 (14)	-4 (12)	-23 (15)
C8	82 (22)	82 (23)	48 (18)	14 (18)	0 (15)	-14 (16)
C9	74 (20)	81 (22)	37 (16)	15 (16)	11 (13)	-1 (14)
C10	78 (22)	49 (19)	88 (24)	0 (16)	15 (18)	6 (16)
C11	73 (22)	55 (20)	105 (27)	-11 (16)	18 (19)	9 (18)
C12	49 (16)	64 (19)	57 (18)	1 (13)	19 (13)	-6 (14)
N13	12 (9)	63 (15)	76 (15)	-13 (9)	11 (9)	-34 (12)
C14	68 (18)	51 (16)	37 (15)	0 (13)	21 (12)	-5 (12)
C111	34 (14)	86 (21)	48 (16)	-7 (14)	-5 (11)	09 (15)
C112	70 (19)	53 (18)	59 (19)	1 (14)	-2 (14)	-16 (14)
C113	77 (23)	94 (27)	93 (28)	-38 (20)	-5 (20)	-46 (23)
C114	68 (24)	124 (36)	118 (36)	-39 (24)	-20 (23)	-45 (29)
C115	106 (29)	124 (33)	44 (19)	31 (26)	-44 (19)	-11 (20)
C116	84 (23)	104 (27)	47 (18)	-2 (20)	11 (16)	20 (17)
C121	48 (14)	55 (16)	53 (15)	-4 (14)	-3 (11)	-10 (15)
C122	105 (25)	77 (22)	37 (17)	0 (19)	8 (15)	-5 (15)
C123	124 (29)	80 (24)	69 (22)	-9 (21)	63 (21)	7 (18)
C124	101 (29)	93 (29)	104 (31)	-11 (24)	46 (23)	2 (24)
C125	103 (26)	128 (32)	69 (22)	-18 (27)	64 (19)	-33 (25)
C126	71 (20)	97 (24)	66 (21)	3 (18)	31 (16)	-28 (18)
C131	71 (18)	57 (17)	32 (15)	11 (14)	15 (12)	-10 (12)
C132	60 (18)	85 (23)	61 (21)	2 (17)	3 (15)	-9 (16)
C133	98 (26)	78 (25)	87 (24)	32 (21)	-25 (19)	-20 (20)
C134	151 (34)	51 (21)	81 (23)	34 (21)	9 (22)	-36 (18)
C135	62 (251)	171 (37)	42 (18)	65 (23)	4 (14)	-17 (21)
C136	70 (20)	82 (22)	42 (17)	6 (17)	15 (14)	-18 (15)
C211	38 (13)	41 (14)	45 (14)	6 (10)	16 (10)	-12 (10)
C212	67 (20)	80 (22)	55 (19)	-11 (17)	14 (14)	22 (16)
C213	81 (21)	76 (23)	57 (19)	-12 (19)	-15 (15)	0 (18)
C214	85 (25)	85 (25)	64 (22)	4 (20)	-18 (18)	34 (18)
C215	112 (29)	82 (25)	82 (24)	27 (21)	49 (22)	60 (20)
C216	58 (18)	72 (22)	71 (20)	-11 (15)	14 (14)	18 (16)
C221	46 (15)	57 (17)	45 (15)	7 (12)	11 (11)	2 (12)
C222	72 (22)	95 (29)	106 (28)	-2 (19)	25 (20)	7 (22)
C223	69 (23)	109 (31)	144 (36)	-13 (21)	55 (23)	8 (26)
C224	61 (20)	92 (26)	126 (31)	-6 (18)	47 (20)	-26 (22)
C225	86 (25)	115 (33)	148 (37)	62 (24)	45 (24)	-12 (28)
C226	67 (22)	98 (29)	128 (32)	9 (20)	30 (21)	35 (25)
C321	40 (14)	68 (19)	48 (16)	1 (13)	9 (11)	-10 (13)
C232	92 (22)	62 (22)	60 (19)	-12 (17)	30 (16)	-1 (15)
C233	92 (26)	71 (25)	106 (31)	-22 (20)	30 (22)	3 (22)
C234	105 (29)	74 (26)	102 (32)	-25 (22)	-36 (24)	12 (24)
C235	110 (28)	84 (25)	43 (19)	1 (21)	-22 (18)	-19 (17)
C236	79 (20)	54 (21)	57 (18)	4 (15)	5 (14)	-2 (14)
SB1	56 (1)	99 (2)	97 (1)	-1 (1)	9 (1)	-7 (1)
F1	150 (24)	206 (32)	187 (29)	-80 (23)	34 (21)	-18 (24)
F2	137 (22)	260 (37)	111 (20)	24 (23)	38 (17)	43 (22)
F3	223 (32)	274 (40)	161 (25)	165 (31)	79 (23)	48 (27)
F4	97 (18)	437 (58)	130 (23)	79 (27)	32 (16)	-27 (29)
F5	143 (27)	320 (51)	237 (39)	-77 (30)	64 (26)	102 (36)
F6	448 (62)	75 (18)	265 (41)	-69 (27)	242 (44)	-22 (22)

[a] Anisotropic thermal parameters of the form $\exp[-2\pi^2(U(11)h^2a^{*2} + U(22)k^2b^{*2} + U(33)l^2c^{*2} + 2U(12)hka^*b^* + 2U(13)hla^*c^* + 2U(23)klb^*c^*)] \times 10^3$.

mentioned above, this assignment is also consistent with the Ir–H resonance position.

The thermal parameters of the fluorine atoms of the SbF_6 group are large. This spherical anion is therefore probably poorly locked into position in the crystal. This may account for the relatively high R value of 8.5%. In spite of this, the important point, the connectivity of the heavy atoms of the complex itself is unequivocally established. In particular, the presence of the cyclometalated bq ligand would have been difficult to demonstrate in any other way.

The tricyclohexylphosphine analogue was synthesized by the method shown in eq 4. We used the acid $PhCH(SO_2CF_3)_2$[12] as the proton source and at 25 °C in the presence of bqH obtained the corresponding aqua complex **2a** (L = PCy_3). This was spectroscopically very similar to the PPh_3 analogue.

One striking feature of the reactions of eq 2–4 is the mildness of the conditions that lead in the benzylic case

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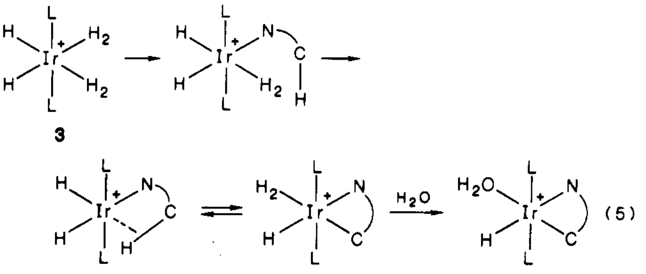
[12] Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 1510.

$$IrH_5(PCy_3)_2 + PhCH(SO_2CF_3)_2 + bqH + H_2O = \underset{\textbf{2a}}{[IrH(H_2O)(PCy_3)_2(bq)]}[PhC(SO_2CF_3)_2] + 3H_2 \quad (4)$$

(mq) to a C–H···Ir bridged species and in the other (bqH) to a cyclometalated form. The C–H activation is therefore kinetically very facile. The reason that different products are formed in the two cases is likely to be thermodynamic rather than kinetic. In particular, no η^2-arene intermediate is likely, as discussed below. This implies that the formation of an Ir–C(alkyl) and an Ir–H bond is insufficient to make up for the loss of the C–H bond, even a weak benzylic one. Halpern[3] has stressed the weakness of such M–C bonds for the late transition metals. In contrast an Ir–C(aryl) and an Ir–H bond so seem to be sufficient to outweigh the loss of the aryl C–H, even though this is a much stronger C–H bond. This is most likely to be a result of Ir–C π bonding, possibly only in the aryl case.

The formation of a C–H···Ir bridge can be seen as a way for the metal to attain an 18-electron configuration and so benefit from the presence of the C–H without having to supply the C–H bond dissociation energy.

A second feature of eq 3–4 is the tenacious binding of the aqua ligand. Even if the reagents used are dried, the aqua complex still tends to be formed from adventitious water. As we have previously shown,[13] if H_2 is bubbled through solutions of the aqua complex the H_2 molecule replaces the water to give the corresponding dihydrogen hydrides $[IrH(H_2)bqL_2]A$ (**4**). Dihydrogen complexes are still rather rare. These have been characterized by ^1H NMR of the H_2 and HD complexes including the determination of the T_1's, which are unusually short for dihydrogen complexes. For example, **3** (L = PCy_3) has been characterized in this way.[13] We can now suggest a reasonable course of events for the formation of the aqua complex **2** (eq 5). The dihydrogen complex **3** seems to be formed either by protonation of IrH_5L_2 or by hydrogenation of $Ir(cod)L_2^+$. In the presence of a quinoline, **3** would be expected to lose H_2 to form **1**. For the mq case, this species is the thermodynamically stable final product, although the equilibrium **1** ⇌ **4** has been invoked to explain certain H/D exchange properties of **1**.[13] For bqH, in contrast, the C–H cleavage probably occurs via the sequence **1** → **4** → **2**.



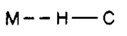
3 **1** **4** **2**

As we showed previously,[4] the 8-methyl group of the mq complex **1** is isotopically labeled over ca. 90 min at 25 °C by exposure of **1** to D_2. This, we argued, involves oxidative addition of the agostic C–H proton to the metal, so the agostic structure of **1** is not simply kinetically determined but must be the thermodynamically stable form.

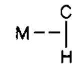
These results help confirm the importance of thermodynamic rather than kinetic factors in C–H activation. They also show the analogy between systems containing C–H···M bridges and dihydrogen complexes.

The Nature of the Transition State for C–H Activation

Since free arenes are not activated under these conditions, it is reasonable to imagine that the quinoline nitrogen of bqH binds before aryl C–H bond cleavage in the formation of **2** by eq 5. Examination of models shows that η^2-arene intermediates (which have been proposed in aryl C–H activation[2]) are unlikely because this would lead to unacceptable strain in the chelate ring. It might be argued that formation of the η^2-arene intermediate precedes binding of the quinoline N, but this is difficult to reconcile with the failure of $[IrH_2S_2L_2]A$ (S = H_2, acetone, pyridine) to react with simple arenes. As long as the arene remains planar, the C–H bond can only approach the metal end on as in **5** rather than side on as in **6**.

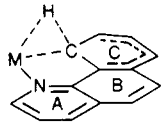


5



6

A study of a number of C–H···M agostic systems[4] led us to propose a kinetic trajectory for aliphatic C–H oxidative addition which involves a side-on transition state of type **6**, but this does not seem to be possible for bqH. A possible way out of this contradiction is to allow the ligand to twist, as shown in **7**. Here, the C ring is twisted out of the plane of the A ring, and the C–H bond to be broken is twisted further out of the plane by partial rehybridization of the C–H carbon toward sp^3 in the transition state. Such a rehybridization is believed to be important in electrophilic substitution of arenes and may not be unreasonable here. It is not yet clear to what extent these results may be generalized to arene C–H activation in general (i.e., where prior coordination of a ligating group to the metal does not occur). One possibility is that an η^2-arene intermediate could then be formed and that this species could undergo a ligand slip to give an transition state or intermediate like **7** but lacking the chelating interaction.



7

We are unfortunately unable to say anything about the relative rates of aryl and benzyl C–H activation in this system. The extent and origin of any kinetic advantage of aryl over alkyl or benzyl C–H oxidative addition is a general question of some interest, but which must be left for future work.

Conclusion

Thermodynamic factors seem to be at work in deciding the different outcomes of arene and benzylic C–H interaction with the metal. The benzylic C–H bond of mq binds in an agostic fashion, while the arene C–H of bqH, which must be stronger by ca. 25 kcal/mol,[14] is cleaved. The M–C bond strength in **2** must therefore be at least 25 kcal/mol stronger than the M–C bond in the hypothetical oxidative addition product (of type **2** or **4**) from mq. The Ir–Ph bond strength of 80.6 kcal/mol found by Bergman et al.[15] in the

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(13) Crabtree, R. H.; Lavin, M. J. *Chem. Soc., Chem. Commun.* **1985**, 794, 1661. Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(14) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 166.

(15) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. G. *J. Am. Chem. Soc.* **1987**, *109*, 3143.

Cp*Ir(PMe$_3$)HR system may be close to the value for the Ir–C bond in **2**. If so, the Ir–CH$_2$Ar bond in **2** or **4** (Ar = 8-quinolinyl) could be no stronger than ca. 50 kcal/mol.

Experimental Section

NMR spectra were obtained on a Bruker 250 MHz instrument, and IR spectra were recorded on a Nicolet 7000 instrument. Starting materials were prepared by published procedures,[7] and ligands were obtained from Aldrich Co.

(η^2-7,8-Benzoquinolinato)aquahydridobis(triphenylphosphine)iridium(III) Hexafluoroantimoniate. To [Ir(cod)(PPh$_3$)$_2$]SbF$_6$ (433 mg, 0.41 mmol) in distilled but not dried CH$_2$Cl$_2$ (20 mL) was added 7,8-benzoquinoline (73 mg, 0.41 mmol) and H$_2$ (1 atm) passed through the solution for 30 min at 0 °C. The light yellow solution was crystallized with Et$_2$O and the product recrystallized from CH$_2$Cl$_2$/Et$_2$O: yield 375 mg (85%). ^{1}H NMR: δ -16.1 (t (14), Ir–H), 2.54 (s, Ir(H$_2$O)), 7.2–7.9 (c, Ar). Anal. Calcd for C$_{49}$H$_{41}$NP$_2$OIrSbF$_6$: C, 51.20; H, 3.56. Found: C, 50.93; H, 3.40. The PCy$_3$ analogue was prepared similarly but using IrH$_5$(PCy$_3$)$_2$ and PhCH(SO$_2$CF$_3$)$_2$ (1 equiv) instead of [Ir(cod)(PPh$_3$)$_2$]SbF$_6$ and H$_2$. The acid was added at -80 °C for 10 min to the benzoquinoline. The mixture warmed slowly to 0 °C and was stirred at that temperature for 30 min, followed by isolation as above. ^{1}H NMR: δ 0.9–2.1 (c, PCy$_3$), 7.9 (c, Ar), 2.52 (s, H$_2$O).

Crystallography. A crystal of IrSbF$_6$P$_2$C$_{49}$H$_{41}$NO was sealed in a capillary and mounted on a Syntex P3 automated diffractometer. Unit-cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for fifteen independent reflections ($2\theta < 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.710 69 Å). Data (10 733 points) were collected at room temperature by using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below Kα_2 to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections, and as the intensities of these reflections showed less that 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. Since the calculated linear absorbtion correction is 31.82 cm^{-1}, absorbtion corrections were not applied. After removal of redundant and space group forbidden data, 5037 points were considered observed [$I > 3.0(I)$]. The structure was solved for heavy-atom positions by using Multan 80. Successive least squares/difference Fourier cycles allowed location of the remainder of the non-hydrogen atoms. Refinement of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The assignment of bonding carbon and nitrogen of the bidentate heteroaromatic ring system was established by observing isotropic thermal parameters for those atomic parameters, in turn the elemental identity of nitrogen and carbon. More suitable refinement was observed with the ring atom trans to water refined as carbon and the atom trans to the hydride position refined as nitrogen. An electron density maximum tentatively identified with the hydride coordinated to iridium was found in a difference Fourier synthesis which failed to reveal any of the remaining hydrogens. Those positions were all calculated, and all hydrogen positions with assigned isotropic thermal parameters were included in the final cycles of refinement but were held invariant. The final cycle of refinement minimized the function $(\sum|F_o| - |F_c|)^2$ and led to a final agreement factor, R = 8.5% [$R = 100(\sum(||F_o| - |F_c||)/|F_o|)$. No residual electron density maxima that might have been attributed to solvent molecules was detected. Anomalous dispersion corrections were made for Ir, Sb, and P. Scattering factors were taken from Cromer and Mann.[16] Unit weights were used throughout.

Acknowledgment. We thank NSF (M.L.) for funding and Dr. A. Siedle for a kind gift of PhCH(SO$_2$CF$_3$)$_2$.

Registry No. 2, 98938-36-4; bqH, 230-27-3; [Ir(cod)(PPh$_3$)$_2$]SbF$_6$, 91410-27-4; IrH$_5$(PCy$_3$)$_2$, 65231-12-1; PhCH(SO$_2$CF$_3$)$_2$, 40906-82-9.

Supplementary Material Available: A table of full angles and distances (3 pages); a listing of structure factors (57 pages). Ordering information is given on any masthead page.

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(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1961**, *A24*, 321.