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Iridium(I) Insertion into an Aromatic C–H Bond. Synthesis and Structure of $[Ir(H)(CO)(bq)(PPh_3)_2]PF_6$ (bq = 7,8-Benzoquinolinato)

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The organometallic species containing the five-membered $\overline{\mathrm{C(sp^2)\text{–}M\text{–}N(sp^2)}}$ ring are quite common products that form when ligands such as 2-phenylpyridine,[1] benzo[*h*]quinoline[1,2] (bqH, Figure 1), or 8-substituted quinolines[3] are reacted with group 8–10 transition metals. The main steps involved in this cyclometalation reaction[4] are thought to be (i) the N-coordination to the metal center and (ii) the formation of the M–C bond. Ultimately, this latter step is an example of C–H activation, a subject currently investigated for its synthetic implications.[5] Such an activation, when electron-rich, low-valent metal complexes are involved, is described as a simple intramolecular C–H oxidative-addition reaction, albeit few cyclometalated mononuclear compounds preserving the M–H group have been described in the literature for nitrogen-containing ligands.[6,7] Herein, we report on the hydrido complex that forms by reacting the iridium(I) cationic species $[Ir(CO)(MeCN)(PPh_3)_2]PF_6$[8] (**1**) with bqH. The cyclometalated product contains the complex cation $[Ir(H)(CO)(bq)(PPh_3)_2]^+$, obtained also by Crabtree under different reaction conditions.[9]

Discussion

The new organometallic compound $[Ir(H)(CO)(bq)(PPh_3)_2]PF_6$ (**2**) is obtained in good yield as a colorless microcrystalline solid from a benzene solution of **1** and bqH reacted under reflux for 16 h. In **2**, the coordination of a terminal CO ligand was confirmed by the observation in the IR spectrum of a single ν(CO) stretch at 2047 cm^{-1}, shifted by ca. 70 cm^{-1} to higher frequency with respect to ν(CO) of the parent complex **1** and thereby consistent with the higher formal oxidation state of the Ir center in **2**.[10] The hydrido ligand signals, in both the IR (ν 2220 cm^{-1}) and ^1H NMR (δ −15.04, a triplet with ^2J(PH) = 12.3 Hz) spectra, were found as expected for an Ir–H group trans to a N-donor ligand.[7,11,12] Furthermore, the ^2J(PH) value accounts for H cis to two magnetically equivalent PPh_3[13] groups, which in turn are mutually trans, as inferred from the $^{31}P\{^1H\}$ NMR spectrum. Finally, the $^{13}C\{^1H\}$ NMR spectrum, whose main feature is a triplet at δ 149.46 (^2J(PC) = 15.5 Hz) attributable to a metal-bonded carbon atom,[14] is in agreement with the occurrence of the $\overline{\mathrm{C(2)\text{–}Ir\text{–}N}}$ cyclometalated ring (Figure 2).

The structure of **2** was confirmed by an X-ray diffraction analysis, as shown in Figure 2. Important bond distances and angles are given in Tables I and II, respectively. The octahedral coordination around Ir involves two PPh_3 ligands in apical positions; one nitrogen and one carbon atom from the cyclometalated bq chelating ligand, one carbon atom from a terminal carbonyl group, and one hydride ligand complete the coordination in the equatorial sites. The correct assignment of the C and N atoms was confirmed by the unsatisfactory isotropic and anisotropic thermal parameters obtained with the reverse choice and by the difference, even if small, in the *R* value for the two situations after the anisotropic refinements (0.0439 against 0.0451). The hydride was clearly located in the final ΔF map, although the distance

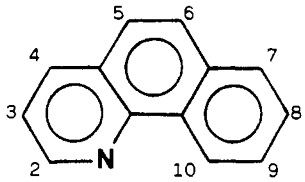

Figure 1. Benzo[*h*]quinoline (bqH) and proton-numbering scheme.

Table I. Bond Distances (Å)

Ir–P(1)	2.356 (3)	C(4)–C(5)	1.37 (3)
Ir–P(2)	2.349 (5)	C(5)–C(6)	1.38 (2)
Ir–N(1)	2.169 (9)	C(6)–C(7)	1.42 (2)
Ir–C(1)	1.939 (12)	C(6)–C(11)	1.43 (2)
Ir–C(2)	2.054 (10)	C(7)–C(8)	1.43 (2)
Ir–H(1)	1.49	C(8)–C(9)	1.40 (2)
N(1)–C(8)	1.37 (2)	C(9)–C(10)	1.47 (2)
N(1)–C(12)	1.33 (2)	C(9)–C(14)	1.37 (3)
C(2)–C(3)	1.39 (2)	C(10)–C(11)	1.34 (3)
C(2)–C(7)	1.39 (2)	C(12)–C(13)	1.37 (2)
C(3)–C(4)	1.44 (2)	C(13)–C(14)	1.37 (3)

Table II. Bond Angles (deg)

P(1)–Ir–P(2)	173.0 (1)	C(2)–C(3)–C(4)	118.9 (13)
P(1)–Ir–N(1)	91.0 (3)	C(3)–C(4)–C(5)	121.8 (14)
P(1)–Ir–C(1)	93.0 (4)	C(4)–C(5)–C(6)	119.7 (15)
P(1)–Ir–C(2)	85.1 (3)	C(5)–C(6)–C(7)	118.7 (14)
P(1)–Ir–H(1)	91.4	C(5)–C(6)–C(11)	123.5 (14)
P(2)–Ir–N(1)	90.6 (3)	C(7)–C(6)–C(11)	117.7 (13)
P(2)–Ir–C(1)	93.1 (4)	C(6)–C(7)–C(8)	119.2 (11)
P(2)–Ir–C(2)	88.6 (3)	C(2)–C(7)–C(8)	118.5 (11)
P(2)–Ir–H(1)	86.3	C(2)–C(7)–C(6)	122.3 (11)
N(1)–Ir–C(1)	105.6 (4)	N(1)–C(8)–C(7)	115.6 (10)
N(1)–Ir–C(2)	78.9 (4)	N(1)–C(8)–C(9)	121.3 (12)
C(1)–Ir–H(1)	80.2	C(7)–C(8)–C(9)	123.1 (12)
C(2)–Ir–H(1)	95.4	C(8)–C(9)–C(10)	115.4 (14)
Ir–N(1)–C(8)	112.7 (7)	C(8)–C(9)–C(14)	119.5 (14)
Ir–N(1)–C(12)	130.1 (8)	C(10)–C(9)–C(14)	125.1 (14)
C(8)–N(1)–C(12)	117.1 (9)	C(9)–C(10)–C(11)	122.0 (16)
Ir–C(1)–O(1)	173.6 (10)	C(6)–C(11)–C(10)	122.5 (17)
Ir–C(2)–C(3)	127.1 (9)	N(1)–C(12)–C(13)	123.6 (14)
Ir–C(2)–C(7)	114.3 (8)	C(12)–C(13)–C(14)	119.7 (15)
C(3)–C(2)–C(7)	118.6 (11)	C(9)–C(14)–C(13)	118.7 (15)

Table III. Crystallographic Data for $[Ir(H)(CO)(bq)(PPh_3)_2]PF_6$ (**2**)

chem formula $C_{50}H_{39}F_6IrNOP_3$	fw = 1069.00
a = 14.194 (3) Å	space group $P2_1/n$ (No. 14)
b = 14.106 (5) Å	T = 22 °C
c = 22.621 (4) Å	λ = 0.71073 Å
β = 103.28 (2)°	μ = 31.861 cm^{-1}
V = 4408 (2) $Å^3$	transmission coeff = 1.109–0.866
Z = 4	$R(F_o)$ = 0.0397
ρ_{calcd} = 1.611 g cm^{-3}	$R_w(F_o)$ = 0.0664

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Table IV. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms of **2**

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Ir	273 (1)	1904 (1)	2297 (1)	C(20)	535 (9)	3739 (8)	614 (6)
P(1)	−374 (2)	2535 (2)	1324 (1)	C(21)	−1159 (9)	1705 (8)	826 (7)
P(2)	727 (2)	1293 (2)	3288 (2)	C(22)	−800 (11)	1136 (10)	430 (7)
P(3)	1111 (3)	5338 (3)	3332 (2)	C(23)	−1452 (12)	483 (13)	57 (9)
F(1)	165 (7)	4694 (7)	3198 (5)	C(24)	−2332 (14)	384 (14)	114 (9)
F(2)	487 (7)	6090 (6)	2900 (5)	C(25)	−2733 (11)	942 (10)	484 (7)
F(3)	1997 (8)	5981 (10)	3396 (9)	C(26)	−2115 (9)	1604 (9)	853 (7)
F(4)	1690 (9)	4556 (11)	3734 (5)	C(27)	−1085 (7)	3621 (7)	1286 (5)
F(5)	1405 (7)	4848 (7)	2772 (4)	C(28)	−1869 (9)	3821 (9)	818 (6)
F(6)	840 (9)	5851 (10)	3882 (5)	C(29)	−2326 (10)	4690 (10)	770 (7)
C(1)	1551 (8)	2415 (8)	2326 (5)	C(30)	−1983 (10)	5370 (10)	1195 (7)
O(1)	2254 (7)	2791 (7)	2344 (5)	C(31)	−1152 (10)	5237 (10)	1648 (7)
N(1)	277 (6)	489 (6)	1922 (4)	C(32)	−717 (8)	4327 (8)	1698 (6)
C(2)	−1121 (7)	1478 (8)	2267 (5)	C(33)	233 (8)	1831 (8)	3893 (6)
C(3)	−1848 (9)	2005 (10)	2428 (6)	C(34)	−52 (9)	2776 (9)	3846 (7)
C(4)	−2797 (10)	1597 (14)	2346 (8)	C(35)	−354 (11)	3232 (11)	4320 (8)
C(5)	−2996 (10)	695 (14)	2127 (7)	C(36)	−388 (10)	2706 (11)	4836 (8)
C(6)	−2269 (9)	155 (11)	1980 (7)	C(37)	−101 (12)	1771 (11)	4884 (9)
C(7)	−1332 (8)	562 (9)	2050 (5)	C(38)	213 (9)	1318 (10)	4420 (6)
C(8)	−587 (9)	25 (8)	1876 (7)	C(39)	2039 (7)	1368 (7)	3596 (5)
C(9)	−726 (11)	−902 (10)	1647 (7)	C(40)	2651 (8)	954 (8)	3278 (6)
C(10)	−1697 (14)	−1299 (12)	1604 (8)	C(41)	3632 (9)	984 (9)	3480 (6)
C(11)	−2410 (13)	−792 (13)	1748 (8)	C(42)	4046 (10)	1429 (10)	4009 (7)
C(12)	990 (10)	5 (8)	1766 (6)	C(43)	3463 (11)	1881 (10)	4334 (8)
C(13)	900 (13)	−917 (10)	1565 (7)	C(44)	2435 (9)	1843 (8)	4133 (6)
C(14)	27 (14)	−1368 (11)	1486 (7)	C(45)	403 (6)	55 (7)	3340 (4)
C(15)	560 (8)	2866 (7)	917 (5)	C(46)	1047 (7)	−688 (7)	3356 (5)
C(16)	1289 (9)	2240 (9)	877 (6)	C(47)	770 (8)	−1635 (7)	3375 (5)
C(17)	1990 (10)	2458 (11)	574 (7)	C(48)	−178 (8)	−1840 (8)	3384 (6)
C(18)	1957 (11)	3326 (10)	300 (7)	C(49)	−845 (8)	−1127 (7)	3367 (5)
C(19)	1245 (9)	3971 (10)	329 (6)	C(50)	−562 (7)	−191 (7)	3353 (5)

from the metal is rather short, 1.49 Å. The very high trans influence of the hydride is indicated by the long Ir–N distance, 2.169 (9) Å, especially if compared to that involving carbon C(2), trans to the carbonyl, 2.054 (10) Å.

Complex **2**, which forms through an oxidative-addition reaction of the $[Ir(CO)(PPh_3)_2]^+$ moiety into an aromatic C–H bond, shows a structure comparable to that of the bqH derivative $[IrH(bq)(H_2O)(PPh_3)_2]SbF_6$,[15] previously synthesized by Crabtree in the reaction of $[Ir(COD)(PPh_3)_2]SbF_6$ with H_2, bqH, and H_2O. In this case, the Ir–N distance is 2.10 (2) Å and the Ir-C(2) distance, trans to a water molecule, is 1.99 (2) Å.

Moreover, the title compound contains a *cis*-hydrido–carbonyl array, so that it can be envisaged as a model for reactions that take place in processes wherein both hydrocarbons and carbon monoxide are involved.

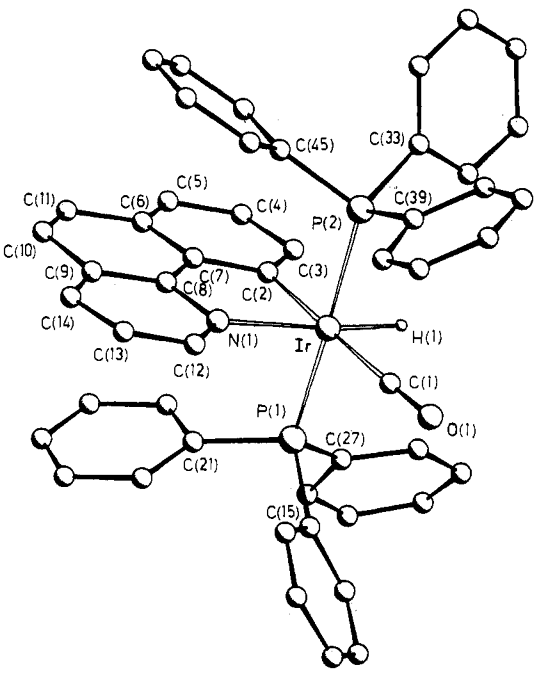

Figure 2. View of the structure of **2** with the atomic numbering scheme.

Experimental Section

General Procedures. All experiments were performed under a dinitrogen atmosphere. Anhydrous methylene chloride was purified by distillation from calcium hydride. Benzene and diethyl ether were distilled from sodium and benzophenone. NMR shifts are referenced to TMS for ^1H and ^{13}C and to external H_3PO_4 for ^{31}P. $[Ir(CO)(MeCN)(PPh_3)_2]PF_6$ was prepared according to the literature.[9] Benzo[*h*]quinoline was used as received (Fluka AG).

Preparation of $[Ir(H)(CO)(bq)(PPh_3)_2]PF_6$ (2). A solution of benzo[*h*]quinoline (72 mg, 0.40 mmol) in 5 mL of CH_2Cl_2 was added to a suspension of **1** (300 mg, 0.32 mmol) in 50 mL of benzene, and the resulting yellow solution was stirred under reflux for 16 h. The color became lighter. Partial evaporation of the solvent under reduced pressure caused a microcrystalline solid to precipitate, which was filtered off, washed with diethyl ether, and vacuum-dried. The product was recrystallized from CH_2Cl_2–Et_2O, affording **2** as single crystals: yield 240 mg (70%); mp 246–247 °C. Anal. Calcd for $C_{50}H_{39}F_6IrNOP_3$: C, 56.18; H, 3.68; N, 1.31. Found: C, 56.01; H, 3.71; N, 1.39. Λ_M (CH_2Cl_2 solution): 52.48 Ω^{-1} M^{-1} cm^2. IR (mineral oil mull): ν(IrH) 2220 cm^{-1} (w); ν(CO) 2047 cm^{-1} (s). ^1H NMR (300 MHz, CD_2Cl_2): δ 9.28 (d, 1 H, J = 5.0 Hz, H(2)), 7.96 (d, 1 H, J = 8.0 Hz, H(4)), 7.53 (dd, 1 H, J = 8.0 and 5.0 Hz, H(3)), 7.51 (d, 1 H, J = 9.0 Hz, H(5) or H(6)), 7.47 (dd, 1 H, J = 7.9 and 0.7 Hz, H(7) or H(9)), 7.38 (dd, 1 H, J = 7.1 and 0.9 Hz, H(9) or H(7)), 7.3–7.0 (m, PPh_3), −15.04 (t, 1 H, J(PH) = 12.3 Hz, Ir–H). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2): δ 174.86 (t, 1 C, J(PC) = 6–7 Hz, C≡O), 149.46 (t, 1 C, J(PC) = 11.5 Hz, metalated C(2)), 154.16, 152.12, 143.59, 141.00, 137.44, 135.92, 130.18, 128.20, 124.64, 123.47 and 123.13 (11 C, bq), 127.96 (J(PC) = 29.5 Hz), 128.60 (J(PC) = 5.2 Hz), 131.58 and 133.5 (J(PC) = 5.5 Hz, for C(1) to C(4) in PPh_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 7.00 (s;

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d, J(PH) ≈ 11 Hz, after selective decoupling of the nonhydridic protons).

X-ray Structure Determination. An Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator was used for data collection. The most important crystallographic data are reported in Table III; the detailed ones are given in Table SI (supplementary material). Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having $10 < \theta < 17°$. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[16] The structure amplitudes were obtained after usual Lorentz and polarization reduction.[17] A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.109 and 0.866, respectively).[18]

The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all the non-hydrogen atoms excepting the carbons of the phenyl groups. The hydride was clearly localized in the final ΔF map, but not refined; the other hydrogen atoms were placed at their geometrically calculated positions and introduced in the final structure factor calculation. The final cycles of refinement were carried out on the basis of 379 variables; after the last cycle, no parameters shifted by more than 0.5 esd. The biggest remaining peak in the final difference map was equivalent to about 0.6 e/Å^3. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 19. The final atomic coordinates for the non-hydrogen atoms are given in Table IV. The atomic coordinates of the hydrogen atoms are given in Table SII, and thermal parameters of the non-hydrogen atoms, in Table SIII (supplementary material).

Acknowledgment. This work was supported by the Italian CNR and Ministero della Pubblica Istruzione. We thank Johnson-Matthey, Ltd., for a generous loan of $IrCl_3 \cdot 3H_2O$.

Registry No. **1**, 51540-63-7; **2**, 121232-41-5; benzo[*h*]quinoline, 230-27-3.

Supplementary Material Available: Tables SI–S3, listing detailed crystal data and intensity collection parameters, coordinates and isotropic thermal parameters for the hydrogen atoms, and thermal parameters for the non-hydrogen atoms, and a complete list of interatomic distances and angles, least-squares planes, torsion angles, and possible hydrogen bonds (32 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

1988, Volume 27

Graeme Douglas, Michael C. Jennings, Kenneth W. Muir, Ljubica Manojlović-Muir,* and Richard J. Puddephatt*: Synthesis and Structure of the Cluster Cation $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$, Containing both PtAu and PtAg Bonds.

Pages 4516–4520. K. W. Muir was omitted from the list of authors. The following entries should be added to Table II: reflections used, 8006 [$I > 3\sigma(I)$, $2 \leq \theta$(Mo Kα) $\leq 22°$]; parameters refined, 673.—Richard J. Puddephatt