°C. The reaction mixture turned immediately from orange to dark brown. After the mixture was warmed to room temperature for 2 h, it became progressively yellow. Solvents were eliminated in vacuo, and the crude residue was recrystallized in pentane. The digermadioxetane **17** was the first to crystallize (0.56 g, 52%, white crystals, mp 125–126 °C). $^1$H NMR ($C_6D_6$): $\delta$ 1.47 (s, 12 H, *p*-Me), 1.98 (s, 24 H, *o*-Me), 6.53 (s, 8 H, arom Mes). Mass spectrum (EI, 70 eV, $^{74}$Ge; *m/e* (relative intensity)): 654 (M, 20), 535 (M − Mes, 30), 329 ($Mes_2Ge{=}O$ + H, 100). Yellow crystals of imine **9**[8] were also obtained, after **17**.

**Registry No.** **1**, 108946-03-8; **2**, 132774-99-3; **4**, 132775-01-0; **5**, 132775-02-1; **6**, 132775-03-2; **7**, 132775-04-3; **9**, 10183-82-1; **12**, 132775-00-9; **13**, 132775-05-4; **17**, 132775-06-5; PhCH=NEt, 6852-54-6; $Ph_2C{=}NH$, 1013-88-3; PhN=NPh, 103-33-3; PhNO, 586-96-9.

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# Aromatic and Benzylic C–H Activation. Synthesis and Structural Characterization of Iridium 2-Phenylpyridine and 8-Methylquinoline Complexes

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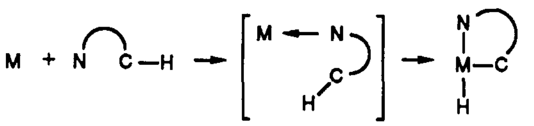
The reaction of 2-phenylpyridine (ppyH) or 8-methylquinoline (mqH) with [*trans*-Ir(CO)($CH_3CN$)($PPh_3$)$_2$]$PF_6$ (**1**) at 25 °C gives the four-coordinate complex [Ir(CO)(HL)($PPh_3$)$_2$]$PF_6$ (**2**, HL = ppyH; **3**, HL = mqH), wherein the ligand is N-coordinated. Cyclometalated hydrido complexes [Ir(H)(L)(CO)($PPh_3$)$_2$]$PF_6$ (**4**, L = ppy; **5**, L = mq) can be obtained in low yield by the same reaction at higher temperature. All complexes have been characterized by $^1$H, $^{31}$P, and $^{13}$C NMR spectroscopies. The molecular structure of **3** has been determined by X-ray analysis. The complex is monoclinic, space group $C2/c$, with $a$ = 36.973 (7) Å, $b$ = 10.782 (3) Å, $c$ = 27.145 (5) Å, $\beta$ = 119.682 (13)°, and $Z$ = 8. The iridium atom has a distorted square-planar coordination, with trans P atoms, one CO ligand, and the $\eta^1$-bonded mqH. The latter ligand is nearly planar and orthogonal to the coordination plane, with the methyl group in a pseudoaxial position (Ir–C(11) = 3.147 (13 Å).

## Introduction

Intramolecular C–H activation by transition metals has been widely investigated,[1-8] yet there is still considerable interest in the study of cyclometalated species,[9-13] particularly with regard to their electrochemical and photophysical properties.[9,11,13]

Many investigations involve platinum group metals (group 8–10) and aromatic N-donor ligands.[14] In all cases, initial N-coordination is believed to precede the cyclometalation (eq 1).



(1)

We have recently reported[15] that 7,8-benzoquinoline (bqH) reacts with [*trans*-Ir(CO)($CH_3CN$)($PPh_3$)$_2$]$PF_6$[16] (**1**)

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**Table I. $^1$H NMR Assignments[a] for ppyH, mqH, and Their Complexes 2–5**

| compd | $\delta(^1H)$, ppm | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | H(2) | H(3) | H(4) | H(5) | H(6) | H(7) | H(8) | H(9) | H(10) |
| ppyH | 8.70 (d) | 7.12 (m) | 7.60 (t) | 7.65 (d) | | | *b* | | |
| 2 | 7.78 (d) | 6.63 (m) | na | 7.12 (d) | | | *c* | | |
| 4 | 8.87 (d) | na | 7.52 (t) | na | 7.08 (d) | 6.61 (t) | 6.98 (m) | na | |
| mqH | 8.93 (d) | 7.31 (dd) | 8.04 (d) | 7.60 (d) | 7.38 (dd) | 7.52 (m) | 2.83 (br s)[d] | | |
| 3 | 8.94 (d) | 6.78 (dd) | 7.86 (d) | na | na | na | 3.47 (br s)[d] | | |
| 5 | 8.53 (d) | *e* | 7.94 (d) | *e* | *e* | *f* | 3.05 (t)[g] | | |

[a] In $CDCl_3$ (free ligands) or $CD_2Cl_2$ (complexes). Abbreviations: d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; s, singlet; na, not assigned. [b] The phenyl ring (AMM′XX′ spin system) shows resonances at 8.05 and 7.51–7.41 ppm. [c] Resonances centered at 7.64, 7.58, and 7.30 ppm. [d] $CH_3$ group. [e] H(3), H(5) (or H(7)), and H(6) protons give unresolved signals at 7.18–7.09 ppm. [f] A broad doublet at 6.97 ppm can be assigned to either H(7) or H(5) . [g] Metalated benzylic $CH_2$; $^3J(PH)$ = 11.4 Hz.

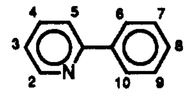
**Table II. $^{13}$C NMR Chemical Shifts[a] for ppyH, mqH, and Their Complexes 2–5[b]**

| compd | $\delta$(C), ppm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ppyH[c] | 157.4[d] | 150.0 | 139.7[d] | 136.9 | 129.2 | 129.0 | 127.1 | 122.4 | 120.5 | |
| 2 | 160.0 (w) | 151.4 (s) | 139.0 (s) | 137.6 (w) | 131.7 (s) | 128.7 (s) | 128.1 (s) | 127.9 (s) | 124.3 (s) | |
| 4 | 165.0 (w) | 153.5 (s) | 152.6 (w)[e] | 147.4 (w) | 143.2 (s) | 138.8 (s) | 131.1 (s) | 126.6 (s) | 124.8 (s) | 124.0 (s) (121.0 (s)) |
| mqH[f] | 148.3 | 146.6[d] | 136.4[d] | 135.3 | 128.8 | 127.5[d] | 125.5 | 125.1 | 120.0 | 17.6 (Me) |
| 3 | 152.9 (s) | 145.6 (2) | 140.8 (s) | 135.3 (s) | 131.9 (w) | 131.7 (w) | 128.9 (s) | 127.9 (s) | 120.8 (s) | 23.3 (Me) |
| 5 | 153.1 (s) | 151.1 (w) | 149.7 (w) | 138.6 (s) | 133.7 (s) | 128.7 (s) | 128.5 (w) | 125.0 (s) | 122.9 (s) | 13.0[g] |

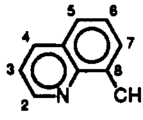
[a] In $CD_2Cl_2$ unless otherwise stated. Abbreviations: w, weak signal, nonprotonated carbons; s, strong signal, doublet in SFORD, protonated carbons; me, methyl carbons. [b] CO and triphenylphosphine signals reported in Experimental Section. [c] Values from ref 12e. [d] Nonprotonated C atoms according to author's assignments. [e] Triplet; $J(PC)$ = 10.4 Hz. [f] In $CDCl_3$.[25] [g] Triplet, metalated $CH_2$; $J(PC)$ = 7.0 Hz.

in refluxing benzene to give the cyclometalated complex $[Ir(H)(bq)(CO)(PPh_3)_2]PF_6$, which contains both new M–C and M–H bonds. The related aqua species $[Ir(H)(bq)(H_2O)(PPh_3)_2]SbF_6$ has been obtained by Crabtree under different conditions.[17]

In order to isolate N-coordinate intermediates (before the cyclometalation occurs), we decided to explore the reactivity of 1 with 2-phenylpyridine (ppyH) (I) and 8-methylquinoline (mqH) (II). In both cases, we expected for these ligands a lower ability to give cyclometalated species compared to bqH.



I



II

Although the bond strength of the M–C(aryl) bond is the same for orthometalated bqH and ppyH, the approach to the metal center of the C–H bond of the somewhat less rigid ppyH is more unlikely. A slight difference in the ligand's reactivity might allow the formation of a stable N($\sigma$)-coordinate intermediate.[18] On the other hand, the formation of an M–C(benzyl) bond would be more difficult for thermodynamic reasons.[19–21]

We herein report the formation and characterization of $[Ir(CO)(HL)(PPh_3)_2]PF_6$ (2, HL = ppyH; 3, HL = mqH) and their cyclometalated derivatives $[Ir(H)(L)(CO)(PPh_3)_2]PF_6$ (4, L = ppy; 5, L = mq). The solid-state structure of 3 is also reported and discussed.

## Results and Discussion

**A. N-Coordinated Iridium(I) Complexes.** We observed that an easy reaction occurs when 1 reacts with a slight excess of an N-ligand in $CH_2Cl_2$ at 25 °C. The displacement of an acetonitrile molecule from 1 affords the complexes shown in eq 2.

$$\underset{1}{[Ir(CO)(CH_3CN)(PPh_3)_2]PF_6} \xrightarrow[20\ ^\circ C]{HL} [Ir(CO)(HL)(PPh_3)_2]PF_6 \quad (2)$$

2, HL = ppyH
3, HL = mqH

Both species were obtained as yellow, air-stable solids in high yield. The complexes were characterized by elemental analysis and IR and NMR spectroscopies. Little or no shift was observed in $\nu$(CO) of 2 (1976 cm$^{-1}$) and 3 (1961 cm$^{-1}$) with respect to the value found for 1 (1975 cm$^{-1}$).

The $^{31}$P NMR data in $CD_2Cl_2$ solution are in agreement with the presence of two $PPh_3$ groups mutually trans, as observed in 1.[22]

The chemical shift values (2, $\delta$ 26.53; 3, $\delta$ 27.60) are also very similar to that observed for 1,[23] suggesting only minor changes at phosphorus.

Although some of the proton resonances in the aromatic region are masked by those due to the $PPh_3$ groups (and therefore they have not been assigned), the $^1$H NMR spectra of 2 and 3 show that the ligands ppyH and mqH are N-coordinated to the metal center. This coordination mode still enables free rotation about the bridge bond of ppyH. Consequently, the same pattern as in the free ligand (an AMM′XX′ spin system) was observed in the proton spectrum of 2 for the uncoordinated phenyl ring of ppyH (Table I). A downfield shift ($\Delta\delta$ 0.63 ppm) of the alkyl resonance of mqH on coordination is featured in 3. The same behavior has been reported for palladium[3]

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(18) The reaction of 1 and bqH at room temperature (monitored by $^{31}$P NMR spectroscopy) gave a mixture of 1, the cyclometalated product $[Ir(H)(bq)(CO)(PPh_3)_2]PF_6$, and a bqH·Ir(I) adduct. The latter showed a single phosphorus resonance at $\delta$ 26.06 (in $CD_2Cl_2$ at 121.5 MHz).

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(23) 1: $\delta$ 25.56 ($CD_2Cl_2$, 20 °C). A value of $\delta$ 23.2 (in $C_6H_6$ at 40 °C) has been previously reported: Williams, A. F.; Bhaduri, S.; Maddock, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1958.

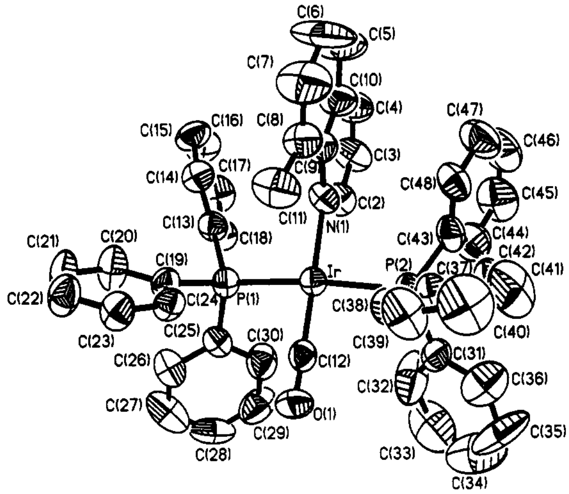

**Figure 1.** ORTEP view of the cation of $[Ir(CO)(mqH)(PPh_3)_2]PF_6$ (**3**) with hydrogen atoms omitted for clarity.

and platinum[11a,c] complexes of 8-alkylquinolines. This suggests that only a weak interaction is present between the C–H bond of the methyl group of mqH and the metal ion. On the other hand, a strong M--H–C "agostic" interaction is said to cause a high-field shift of the proton resonance.[24]

The $^{13}$C NMR spectrum of **2** features nine aromatic resonances (except for the carbonyl and $PPh_3$ resonances) (Table II). The single-frequency off-resonance decoupling (SFORD) spectrum shows that no superposition of resonances is present. This means that, due to unhindered rotation, both the carbon atoms ortho, as well as meta, to the bridge bond in the phenyl ring of ppyH are equivalent. The SFORD spectrum also indicates that signals at $\delta$ 160.0 and 137.6 arise from two nonprotonated carbon atoms.

All 10 carbon resonances of mqH are present in the $^{13}$C NMR spectrum of **3** (Table II). The aliphatic resonance at $\delta$ 23.3 has been assigned to the methyl carbon resonance. No other assignments were attempted. As seen from Table II, the $^{13}$C chemical shift of the methyl group of mqh moves to lower field on complexation by ca. 5 ppm. Moreover, $^1J(^{13}C^1H)$ at 125 Hz is normal[26] and similar to that observed in mqH.[27] Although inconclusive, this observation supports the belief that the C–H bond is still methylic in nature and no rehybridization at the C atom had occurred upon coordination.

**B. Molecular Structure of $[Ir(CO)(mqH)(PPh_3)_2]PF_6$.** In $[Ir(CO)(mqH)(PPh_3)_2]PF_6$ (**3**) a mqH molecule has replaced the acetonitrile ligand of **1**. A view of the cation is shown in Figure 1. Relevant structural data are reported in Tables III and IV. The iridium is distorted square planar with mutually trans P atoms. The P(1) and P(2) atoms show the largest displacement (0.19 and 0.22 Å, respectively) from the mean coordination plane (defined by Ir and the four ligand atoms). As a consequence, the P(1)–Ir–P(2) angle is slightly bent (168.3 (1)°). The Ir–N(1) distance of 2.131 (9) Å is similar to those reported by Crabtree for iridium complexes of N-coordinate 8-fluoroquinoline[28] and 8-methylquinoline[28] (2.130 (9) and 2.168 (8) Å, respectively). mqH is nearly planar and roughly perpendicular to the mean coordination plane. It also appears slightly asymmetrically coordinated, being tilted away by ca. 10° (Ir–N–C angles of 111.1 (7) and 131.4 (8)°). The same feature has been previously observed in square-planar complexes of quinoline-8-carbaldehyde[11a]

**Table III. Crystal Data for $[Ir(CO)(mqH)(PPh_3)_2]PF_6$ (3)**

| | |
|---|---|
| formula | $C_{47}H_{39}F_6IrNOP_3$ |
| fw | 1032.9 |
| color | yellow |
| cryst system | monoclinic |
| space group | $C2/c$ |
| $a$, Å | 36.973 (7) |
| $b$, Å | 10.782 (3) |
| $c$, Å | 27.175 (5) |
| $\beta$, deg | 119.682 (13) |
| $V$, Å$^3$ | 9412 (3) |
| $Z$ | 8 |
| $d_{calc}$, g cm$^{-3}$ | 1.458 |
| cryst size, mm | 0.14 × 0.15 × 0.18 |
| $F(000)$ | 4096 |
| diffractometer | Siemens R3m/v, graphite monochromator |
| radiation (λ, Å) | Mo K$\alpha$ (0.710 73) |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 28.82 |
| $T$, K | 298 |
| $2\theta$ range, deg | 3.5–54.0 |
| scan method | $\omega$ |
| scan speed, deg min$^{-1}$ | 2.0–15.0 |
| no. of data | 11136 |
| no. of unique data | 9279 |
| no. of data obsd [$I \geq 3\sigma(I)$] | 6511 |
| no. of params refined | 532 |
| transm factors | 1.054–0.898 |
| $R$[a] | 0.0590 |
| $R_w$[b] | 0.0610 |
| goodness of fit[c] | 1.79 |

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

**Table IV. Selected Distances (Å), Angles deg), and Torsion Angles (deg) for 3**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Ir–P(1) | 2.323 (2) | Ir–P(2) | 2.335 (3) |
| Ir–C(12) | 1.814 (12) | Ir–N(1) | 2.131 (9) |
| C(9)–N(1) | 1.39 (1) | C(2)–N(1) | 1.32 (2) |
| C(3)–C(4) | 1.33 (2) | C(2)–C(3) | 1.40 (2) |
| C(9)–C(10) | 1.40 (2) | C(4)–C(10) | 1.42 (2) |
| C(8)–C(9) | 1.44 (2) | C(5)–C(10) | 1.40 (2) |
| C(6)–C(7) | 1.37 (3) | C(5)–C(6) | 1.38 (3) |
| C(8)–C(11) | 1.47 (2) | C(7)–C(8) | 1.40 (2) |
| Ir–H(11a) | 2.25 (1) | C(12)–O(1) | 1.16 (2) |
| | Bond Angles | | |
| P(1)–Ir–P(2) | 168.3 (1) | P(2)–Ir–C(12) | 89.7 (3) |
| P(1)–Ir–N(1) | 90.8 (2) | P(2)–Ir–N(1) | 91.3 (2) |
| P(1)–Ir–C(12) | 87.9 (3) | C(12)–Ir–N(1) | 178.4 (4) |
| Ir–C(12)–O(1) | 177.4 (1) | Ir–N(1)–C(9) | 131.4 (8) |
| Ir–N(1)–C(2) | 111.1 (7) | N(1)–C(2)–C(3) | 125.3 (11) |
| C(2)–N(1)–C(9) | 117.3 (10) | C(3)–C(4)–C(10) | 120.7 (14) |
| C(4)–C(10)–C(9) | 118.7 (11) | C(4)–C(10)–C(5) | 119.5 (15) |
| C(5)–C(10)–C(9) | 121.8 (15) | N(1)–C(9)–C(10) | 120.4 (11) |
| N(1)–C(9)–C(8) | 121.3 (12) | C(8)–C(9)–C(10) | 118.3 (11) |
| C(6)–C(5)–C(10) | 119.7 (17) | C(5)–C(6)–C(7) | 119.4 (15) |
| C(6)–C(7)–C(8) | 123.3 (17) | C(7)–C(8)–C(9) | 117.3 (14) |
| C(9)–C(8)–C(11) | 125.1 (11) | C(7)–C(8)–C(11) | 117.5 (14) |
| | Torsion Angles | | |
| N(1)–C(9)–C(8)–C(11) | –6.2 (20) | P(1)–Ir–N(1)–C(2) | –83.8 (7) |
| N(1)–C(9)–C(8)–C(7) | 176.7 (13) | P(2)–Ir–N(1)–C(2) | 84.8 (7) |
| N(1)–C(9)–C(10)–C(5) | –176.1 (14) | P(1)–Ir–N(1)–C(9) | 101.9 (9) |
| C(2)–N(1)–C(9)–C(8) | 178.2 (11) | P(2)–Ir–N(1)–C(9) | –89.6 (9) |
| C(4)–C(10)–C(9)–C(8) | –177.6 (13) | | |

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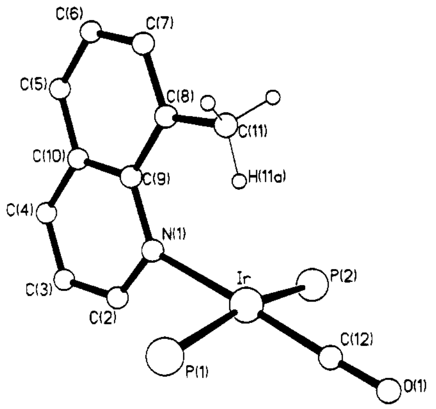
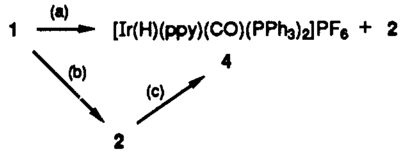


**Figure 2.** PLUTO drawing of the inner-coordination sphere of the cation of 3.

**Scheme I**[a]



[a] Conditions: (a) ppyH, $CH_2Cl_2$/2-methoxyethanol, reflux, 24 h; (b) ppyH, $CH_2Cl_2$, 25 °C; (c) $CH_2Cl_2$/2-methoxyethanol, reflux, 24 h.

and 7,8-benzoquinoline.[11a,30]. The methyl group of mqH is located above the the coordination plane in a pseudoaxial position (Figure 2), leading to an M–C distance of 3.147 (13) Å.

Although shorter than a noninteracting Ir–$CH_3$ group (ca. 3.5 Å), this separation is longer than that observed in $[Ir(H)_2(mqH)(PPh_3)_2]BF_4$[29] (Ir–C = 2.69 (1) Å), in which the methyl group is believed to be bridging. A difference Fourier synthesis failed to locate any of the hydrogen atoms. Therefore, except for the methyl hydrogens, all hydrogen atoms were included in the structural model in calculated positions and refined. After refinement, it became apparent that one C–H vector points toward the metal atom. The C–H and Ir–H distances, obtained in refinement, are 0.97 (1) and 2.25 (1) Å, respectively. The latter distance is well within the range observed for a weak M–H interaction.[31] Moreover, the C(11)–H(11a)–Ir angle of ca. 154° is actually wider than any reported C–H···M angle for agostic structures.[31] Crabtree et al.[29] argued that the most favorable orientation of a C–H bond approaching a metal leads to a M–H–C angle of ca. 130°, which maximizes both M–H and M–C interactions.

All other angles and distances in the molecule are not unusual. Only the $PF_6^-$ ion shows a certain degree of disorder.

**C. Cyclometalated Iridium Complexes. (a) 2-Phenylpyridine.** In order to obtain cyclometalated species of ppyH and mqH, the reaction with 1 was carried out at higher temperature. Whereas 2 was the only product of the reaction of 1 and ppyH in $CH_2Cl_2$/toluene (1:7, v/v) under reflux (see Experimental Section), a mixture of 2 and the iridium compound 4 (in the approximate ratio of 2:1) was obtained in $CH_2Cl_2$/2-methoxyethanol solution (1:3, v/v) heated under reflux (Scheme I).

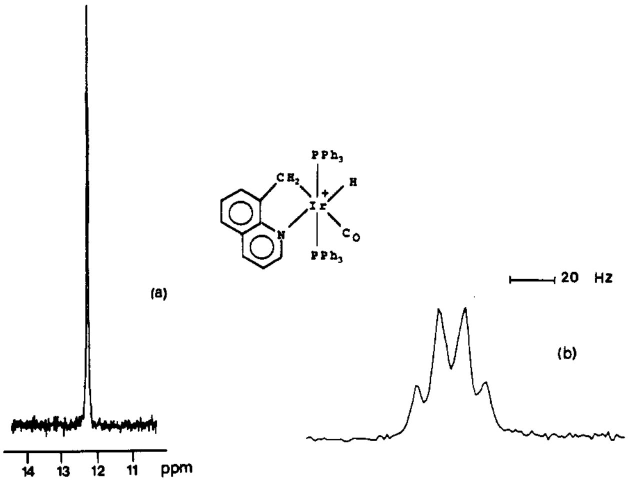
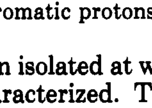


**Figure 3.** $^{31}P$ NMR spectra of $[Ir(H)(mq)(CO)(PPh_3)_2]PF_6$ (5) at 121.5 MHz: (a) $^1H$-decoupled spectrum; (b) selectively decoupled spectrum of aromatic protons only.

Complex 4 has been isolated at white microcrystals and spectroscopically characterized. The IR spectrum shows two absorptions at 2222 and 2044 $cm^{-1}$, assigned to $\nu$(IrH) and $\nu$(CO) stretching modes, respectively.

The presence of a hydride group bonded to the iridium center has been confirmed by $^1H$ NMR spectroscopy. A triplet at $\delta$ −15.26 ($^2J$(PH) = 12.6 Hz) is indicative of a hydride cis to two $PPh_3$ groups. A comparison of NMR data of 4 and related complexes[15,17] led us to suggest that in 4 the hydride ligand is trans to the aromatic N atom. The $^{13}C$ NMR spectrum clearly shows that 4 is a cyclometalated species. A triplet at $\delta$ 152.6 ($^2J$(PC) = 10.4 Hz) has been interpreted as the resonance arising from the metalated carbon atom (Table II).

In light of this spectroscopic evidence and the crystallographic data for $[Ir(H)(bq)(CO)(PPh_3)_2]PF_6$,[15] an octahedral coordination geometry has been proposed for 4, wherein $PPh_3$ molecules (L) occupy apical positions (III). The observation of a single resonance in the $^{31}P$ NMR spectrum of 4 confirms that proposal.



III

Although in lower yield, the formation of 4 has been also achieved through thermolitic rearrangement of 2 (pathway c in Scheme I). Again the choice of the solvent was critical and only the dichloromethane/2-methoxyethanol mixture has proven satisfactory. The use of other solvents gave no reaction or extended decomposition.

**(b) 8-Methylquinoline.** The previous considerations about experimental conditions apply also to the formation of cyclometalated hydrido species of mqH. A species formulated as $[Ir(H)(mq)(CO)(PPh_3)_2]PF_6$ (5) has been obtained either from a high-temperature reaction between 1 and mqH or by thermolitic rearrangement of 3. In both cases the new species is obtained as one component of a mixture (the other one being 3). The separation of the two compounds can be achieved only by repeated crystallization. The spectroscopic characterization of 5 clearly shows that the complex is the result of metal insertion into the benzylic C–H bond of mqH.

The $^1H$ NMR spectrum shows a triplet at $\delta$ −15.46 with a coupling constant ($^2J$(PH) = 12.5 Hz) accounting for a hydride cis to two $PPh_3$ groups. As for 4 the hydride

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resonance was assigned to a hydrogen atom trans to an N-donor ligand. Furthermore, a triplet at $\delta$ 3.05 ($^2J$(PH) = 11.4 Hz) can be assigned to a metalated benzylic $CH_2$ group. The $^{31}P$ NMR spectrum (Figure 3a) shows a single resonance according to structure III. Moreover, a broad quartet was observed in the $^{31}P$ NMR spectrum obtained by selective decoupling of the aromatic protons (Figure 3b). Two different coupling constants can be measured: a $^2J$(PH) coupling of$\cong$12 Hz, which results from coupling to the hydridic proton (vide supra), and a $^3J$(PH) coupling of $\cong$11 Hz, corresponding to coupling to the benzylic protons of metalated 8-methylquinoline. The apparent quartet is actually a doublet of triplets, wherein the similar magnitude of the coupling constants causes line superposition.

All the nine resonances due to the aromatic skeleton of mqH were observed in the $^{13}C$ NMR spectrum of **5** between 120.0 and 160.0 ppm.

Observation of the SFORD spectrum allowed the identification of three nonprotonated C atoms. The high-field triplet at 13.0 ppm ($^2J$(PC) = 7.0 Hz) was assigned to the metalated benzylic $CH_2$ group. No other assignments were made.

## Conclusion

The present study indicates that cyclometalation of ppyH and mqH can be achieved by means of **1**. It also shows that the formation of an N-coordinate adduct is clearly the first step in the activation of the C–H bond, the following step being oxidative addition to the metal and hydride formation.

In the case of an aliphatic and benzylic C–H bond being activated by a metal ion, a strong "agostic" interaction could be a good model for the transition state of the reaction. This is more likely true in the case of nucleophilic activation.[8] What is not clear is whether the $M \leftarrow H–C$ bonding interactions observed are essential in the overall process of activation. The occurrence of such an interaction may well be due to the necessity to minimize steric repulsions elsewhere in the complex. This seems to be particularly true with $d^8$ square-planar metal complexes.

As in many other cases, it is not demonstrated that in **3** (long M–C distance, normal $^1J(^{13}C^1H)$ value, low-field $^1H$ shift, etc.) the $M \leftarrow H–C$ interaction has some bonding character. We prefer to think of this as an "opportunistic" interaction, in which geometric constraints play a major role.

## Experimental Section

All reactions were carried out under a nitrogen atmosphere in dried solvents. The $^1H$ (300.13 MHz), $^{13}C$ (75.469 MHz), and $^{31}P$ (121.5 MHz) NMR spectra were recorded with a Bruker WH 300 spectrometer. Chemical shifts are referenced to internal TMS ($^1H$ and $^{13}C$) and to external 85% $H_3PO_4$ ($^{31}P$). Single-frequency off-resonance decoupled (SFORD) $^{13}C$ spectra were obtained in order to assign the nonprotonated carbon atoms. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer for KBr pellets or mineral oil mulls.

Analyses were performed by the Microanalysis Laboratory of our department.

The ligands 2-phenylpyridine (Aldrich) and 8-methylquinoline (Fluka AG) were used as received without further purification.

**Formation of $[Ir(CO)(ppyH)(PPh_3)_2]PF_6$ (2). (a) In $CH_2Cl_2$.** 2-Phenylpyridine (40 $\mu$L, 0.279 mmol) was added to a stirring solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]PF_6$[16] (1) (0.200 g, 0.215 mmol) in $CH_2Cl_2$ (10 mL) whereupon the yellow solution immediately lightened. After the mixture was stirred for 1 h, addition of diethyl ether gave a pale yellow microcrystalline product. The solid was removed by filtration, washed with diethyl ether, and dried in vacuo: yield 0.194 g (86%); mp 217–218 °C. Anal. Calcd for $C_{48}H_{39}F_6IrNOP_3$: C, 55.17; H, 3.76; 1.34. Found: C, 54.82; H, 3.69; N, 1.31. IR (KBr): $\nu$(CO) 1976 (vs) $cm^{-1}$. $\Lambda_M$ ($10^{-3}$ M $CH_2Cl_2$ solution) = 52.60 $\Omega^{-1}$ $M^{-1}$ $cm^2$. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 26.53 (s). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 173.5 (t, $J$(PC) = 12.2 Hz, Ir–CO), [134.3 (t, $J$(PC) = 6.0 Hz), 131.9 (s), 130.1 (t, $J$(PC) = 27.4 Hz), 129.3 (t, $J$(PC) = 5.4 Hz) ($PPh_3$)].

**(b) In $CH_2Cl_2$/Toluene.** 2-Phenylpyridine (40 $\mu$L, 0.279 mmol) was added to a solution of 1 (0.200 g, 0.215 mmol) in $CH_2Cl_2$/toluene (40 $\mu$L, 1:7 v/v). The stirred mixture was refluxed, and then within a few minutes a yellow solid began to precipitate. After 5 h 0.175 g of product **2** was collected by filtration (yield 78%).

**Formation of $[Ir(CO)(mqH)(PPh_3)_2]PF_6$ (3).** A slight excess of 8-methylquinoline (25 $\mu$L, 0.182 mmol) was added to a stirred solution of 1 (0.100 g, 0.107 mmol) in $CH_2Cl_2$ (4 mL). After 2 h of stirring, addition of diethyl ether afforded a yellow precipitate, which was collected by filtration, washed with diethyl ether, and dried in vacuo. Recrystallization from $CH_2Cl_2$/diethyl ether gave 0.096 g (83% based on 1 $CH_2Cl_2$ of crystallization) of yellow crystals, mp 204–205 °C. Anal. Calcd for $C_{47}H_{39}F_6IrNOP_3{\cdot}CH_2Cl_2$: C, 51.62; H, 3.70; N, 1.25. Found: C, 51.79; H, 3.93; N, 1.22. IR (KBr): $\nu$(CO) 1961 (vs) $cm^{-1}$. $\Lambda_M$ ($10^{-3}$ M $CH_2Cl_2$ solution) = 54.20 $\Omega^{-1}$ $M^{-1}$ $cm^2$. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 27.60 (s). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 173.0 (t, $J$(PC) = 11.8 Hz, Ir–CO), [134.2 (t, $J$(PC) = 6.0 Hz), 131.8 (s), 129.8 (t, $J$(PC) = 27.4 Hz), 129.2 (t, $J$(PC) = 5.1 Hz) ($PPh_3$)].

**Formation of $[Ir(H)(ppy)(CO)(PPh_3)_2]PF_6$ (4). (a) Reaction of 1 with ppyH.** 2-Phenylpyridine (40 $\mu$L, 0.280 mmol) was added to a solution of 1 (0.200 g, 0.215 mmol) in $CH_2Cl_2$/2-methoxyethanol (40 mL, 1:3 v/v). The resulting yellow solution was stirred under reflux for 24 h. The solution was then concentrated (to ca. 20 mL) in vacuo and diethyl ether dropwise added until yellow microcrystals of **3** began to form. The solid was collected by filtration and dried in vacuo. Yield: 0.117 g (52%). The yellow mother liquor was concentrated under reduced pressure. Addition of diethyl ether afforded a pale yellow powder. Recrystallization of this powder from $CH_2Cl_2$/diethyl ether gave, after cooling at −20 °C, analytically pure **4** as white microcrystals (0.050 g, 22%). Anal. Calcd for $C_{48}H_{39}F_6IrNOP_3$: C, 55.17; H, 3.76; N, 1.34. Found: C, 54.52; H, 4.13; N, 1.32. IR (mineral oil mull): $\nu$(IrH) 2222 (w), $\nu$(CO) 2044 (s), $\nu$(PF) 840–830 (s, br) $cm^{-1}$. $\Lambda_M$ ($10^{-3}$ M $CH_2Cl_2$ solution) = 55.96 $\Omega^{-1}$ $M^{-1}$ $cm^2$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ −15.26 (t, $J$(PH) = 12.6 Hz, Ir–H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 6.70 (s, doublet after selective decoupling of nonhydridic protons, $PPh_3$), −142.1 (septet, $^1J$(PF) = 711 Hz, $PF_6^-$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 174.9 (t, $J$(PC) = 6.0 Hz, Ir–CO), [133.9 (t, $J$(PC) = 5.4 Hz), 131.8 (s), 129.1 (t, $J$(PC) = 5.5 Hz), 128.4 (t, $J$(PC) = 29.0 Hz) ($PPh_3$)].

**(b) Thermal Rearrangement of 2.** A solution of **2** (0.200 g, 0.191 mmol) in $CH_2Cl_2$/2-methoxyethanol (20 mL, 1:3 v/v) was stirred under reflux for 24 h. The yellow solution was then filtered on a glass frit to remove a small amount of black insoluble solid. The volume of the solution was reduced to ca. 10 mL by evaporation under vacuum. Addition of diethyl ether induced precipitation of a yellow-green solid (0.112 g), identified as the starting complex **2** by IR and NMR spectroscopies. Overnight cooling (−20 °C) of the brown mother liquor gave white microcrystals of **4** (0.033 g, 15%).

**Formation of $[Ir(H)(mq)(CO)(PPh_3)_2]PF_6$ (5). (a) Reaction of 1 with mqH.** A slight excess of 8-methylquinoline (25 $\mu$L, 0.182 mmol) was added to a stirred solution of 1 (0.130 g, 0.140 mmol) in $CH_2Cl_2$/benzene (25 mL, 1:4 v/v) and the reaction mixture heated under reflux for 24 h. The solution was then concentrated (to ca. 10 mL) in vacuo. Slow addition of diethyl ether induced precipitation of a yellow powder of **3** (0.040 g, 28%). The solid was removed by filtration, and the yellow filtrate was taken to dryness. The resulting viscous yellow oil was redissolved in $CH_2Cl_2$, and pentane was added to the solution to induce precipitation of a pale yellow solid (0.060 g). The solid was shown to be formed from a mixture (ca. 1:2) of **3** and the new cyclometalated product **5** by $^1H$ NMR analysis. The products were separated by repeated fractional crystallization from $CH_2Cl_2$/diethyl ether at −20 °C. Complex **5** (white grayish solid): mp 198–199 °C. Anal. Calcd for $C_{47}H_{39}F_6IrNOP_3$: C, 54.65; H, 3.80; N, 1.36. Found: C, 53.86; H, 3.75; N, 1.50. IR (mineral oil mull): $\nu$(IrH) 2200 (br w), $\nu$(CO) 2041 (s) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ −15.46 (t, $J$(PH) = 12.5 Hz, Ir–H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 12.27

(s, doublet of triplets after selective decoupling of aromatic protons, $^2J$(PH) = 12 Hz, ($^3J$(PH) = 10 Hz, PPh$_3$). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): δ 173.5 (t, *J*(PC) = 7.0 Hz, Ir–CO), [133.4 (t, *J*(PC) = 5.6 Hz), 131.6 (s), 129.3 (t, *J*(PC) = 30 Hz), 128.9 (t, *J*(PC) = 5.3 Hz) (PPh$_3$)].

**(b) Thermal Rearrangement of 3.** A pale yellow solution of **3** (0.150 g, 0.145 mmol) in CH$_2$Cl$_2$/benzene (15 mL, 1:2 v/v) was stirred under reflux for 22 h. The resulting yellow-brown solution was taken to dryness, the solid residue dissolved in CH$_2$Cl$_2$ (5 mL), and diethyl ether added to afford a pale yellow powder (0.110 g). The IR (mineral oil mull) spectrum of the solid showed the residual ν(CO) absorption band of **3**, together with new bands at ca. 2200 (br w) and 2040 (s) cm$^{-1}$, assigned to complex **5**. $^1$H and $^{31}$P NMR analyses showed the presence of **3** and **5** in almost equimolar amounts.

**X-ray Structure Study.** Diffraction data for compound **3** were collected on a Siemens R3m/v four-circle diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation and an ω-scan technique. Accurate unit cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 25 strong reflections in the 15 < 2θ < 30 range. Lorentz and polarization corrections were applied to the intensity data. An absorption correction was applied (DIFABS[32]). The structure was solved by using standard Patterson methods and subsequently by using Fourier maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms of the methyl group (from a Δ*F* map) and other hydrogen atoms (from calculated positions) were included with a common thermal parameter ($U$ = 0.08 Å$^2$). Of 11 136 reflections there were 9279 unique and 6511 with $I > 3\sigma(I)$. These data were used in the final refinement of the structural parameters to arrive at residuals of $R$ = 0.059 and $R_w$ = 0.061. The weighting scheme used in the last refinement cycle was $w = 1.0000/\sigma(F_o)^2 + 0.001(F_o)^2$. All calculations were performed by using the SHELTX PLUS (version 3.43)[33] and PARST[34] computer programs.

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**Supplementary Material Available:** Complete listings of bond distances, angles, atomic coordinates, and anisotropic thermal parameters (6 pages); a listing of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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# Small Heteroborane Cluster Systems. 1.[1] Theoretical Study of Bridged and Cage-Inserted Phosphaborane Cluster Compounds with Semiempirical Molecular Orbital Calculations

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The structural, thermodynamic, and electronic properties of 91 phosphaborane cluster compounds have been calculated by using the MNDO–SCF semiempirical molecular orbital calculational method. The geometry-optimized minimum energy structures for all the known, structurally characterized phosphaborane systems have been calculated, and exceptionally good agreement between experimentally determined and calculated structural parameters has been observed. Calculations for five classes of small phosphaborane clusters, with fewer than nine vertex atoms, have been completed and have been related to experimentally and spectroscopically proposed structural types. The relationship between bridged and inserted phosphaborane structures has been related to the variation in molecular orbital energies as a function of the (phosphorus-bridged boron atom plane)–(basal boron plane) dihedral angle. Complete MO correlation diagrams that relate the orbitals for bridged phosphaborane systems to inserted systems have been constructed. Linear relationships have been observed between the calculated charge on the phosphorus atom and both the phosphorus–apical boron bond distance and the bridgehead basal boron bond distance. The hydrogen atoms bridging basal boron atoms in the phosphorus-inserted clusters were found to be deflected toward the boron atoms bonded to the phosphorus. The boron atoms bonded to the phosphorus atom, therefore, more closely resemble BH$_2$ units with two terminal protons rather than BH units that contain only one terminal proton each. Predictions concerning structural and chemical reactivities for unknown phosphaborane compounds have been made on the basis of these MO calculations.

## Introduction

It has become clearly evident that borane and heteroborane clusters and their transition-metal complexes bear close electronic and structural relationships with other main-group and organometallic clusters and that experimental and theoretical insights gained from the study of these boron caged systems can be profitably extended to other classes of molecular polyhedra.[2,3] The theoretical study of heteroborane cluster species by semiempirical

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