electropositive substituent. Furthermore, the X-ray crystal structure of (η^5-C_5H_5)Re(NO)(PPh_3)(PPh_2) shows the phosphide phosphorus to be considerably closer to planarity (sum of bond angles 323°) than that of PPh_3 (sum of bond angles 309°).[5] Finally, there exist a number of ways to delocalize the phosphide lone pair in **1** and **2** to rhenium (η^5-C_5H_5 slippage, NO bending, direct interaction with an unoccupied orbital), any of which would contribute to a lowering of the inversion barrier. Further studies of (η^5-C_5H_5)Re(NO)(PPh_3) complexes of this interesting[4] and increasingly useful[10] ligand type are in progress.

Acknowledgment. We thank the National Science Foundation for support of this research. The 300-MHz NMR spectrometer utilized in this study was acquired via NSF and DOD instrumentation grants.

Supplementary Material Available: Table of microanalytical, IR, and NMR (^{1}H, ^{13}C, ^{31}P) data for the new compounds (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectroscopy, and Reactivity of Bis[(cyclooctadiene)(μ-hydroxypyridinato)iridium(I)]. A System Containing Two Interacting d^8 Metal Centers Capable of Formal Four-Electron Oxidations

Sir:

We have renewed our interest in the study of binuclear metal complexes with the weakly interacting d^8–d^8 electronic configuration,[1] because these systems may be capable of participating in multielectron photochemical processes. We now wish to report the synthesis, characterization, and reaction chemistry of a new series of binuclear, ligand-bridged, square-planar Ir(I) complexes that incorporate many of the factors we believe are needed to achieve excited-state multielectron transfers. The new complexes are of the general form [Ir(COD)(μ-L)]$_2$ where L is either of the well-documented bridging ligands[2] 2-hydroxypyridinate (hp) or 6-methyl-2-hydroxypyridinate (mhp). The [Ir(COD)(μ-L)]$_2$ compounds are synthesized in high chemical yields via the addition of stoichiometric amounts of NaL to THF solutions of [Ir(COD)Cl]$_2$.[3,4] The compounds are orange-red, slightly air-sensitive substances that are easily crystallized to yield X-ray quality crystals.

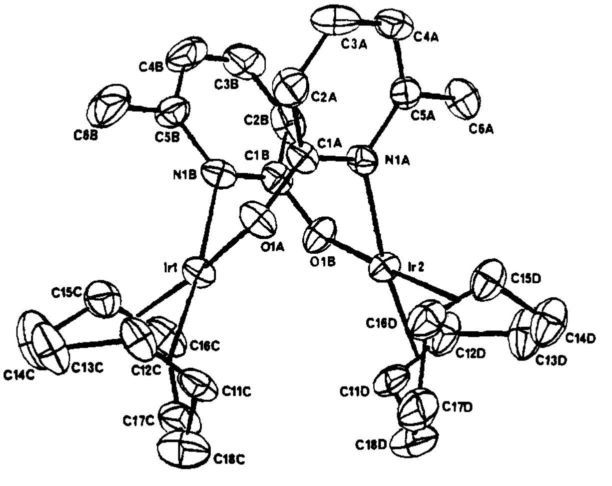

Figure 1. ORTEP drawing of [Ir(COD)(μ-mhp)]$_2$ showing the atomic numbering scheme. Thermal ellipsoids are at the 50% probability level.

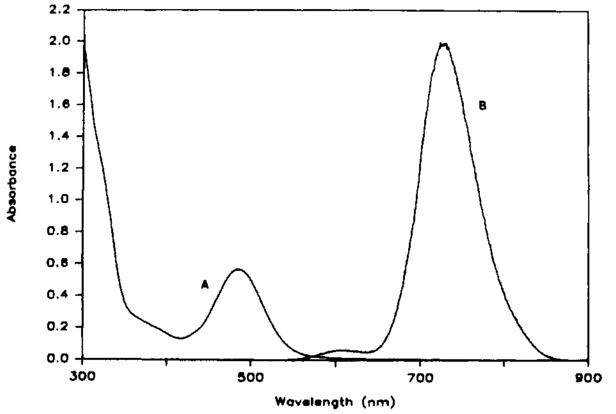

Figure 2. Room-temperature absorption spectrum (curve A) and 77 K emission spectrum (curve B) of [Ir(COD)(μ-mhp)]$_2$. The emission spectrum is uncorrected for photomultiplier tube response.

The X-ray structural determination of the L = mhp compound[5-7] verifies the binuclear nature of these compounds and illustrates several of their novel features. An ORTEP view is shown in Figure 1. The coordination sphere at each Ir(I) center is made up of a chelating η^4-COD ligand, a pyridine nitrogen from one and a pyridinolate oxygen from the other bridging mhp group. The eight-membered (IrNCO)$_2$ ring adopts a distorted "tub" conformation that gives an Ir(I)–Ir(I) distance of 3.242 (1) Å. This distance is indicative of a significant Ir(I)–Ir(I) interaction and is similar to that found in [Ir(COD)(μ-pz)]$_2$ (3.216 (1) Å), which contains a (IrNN)$_2$ six-membered ring in a "boat" conformation. The relative orientation of the two Ir(I) square planes in the mhp-bridged compound is significantly different from either the "face to face" geometry common for d^8–d^8 complexes containing four bridging ligands, i.e. $Rh_2L_4^{2+}$ (L = bridging diisocyanide ligand),[8] or the "open book" orientation found in the

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(2) (a) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. (b) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 584. (c) DeMarco, D.; Nimry, T.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 575. (d) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827.

(3) Characterization of [Ir(COD)(μ-mhp)]$_2$: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) mhp ring δ 7.022 (t, 1 H, *p*-H), 6.162 (t, 2 H, *m*-H), and 2.802 (s, 3 H, CH_3), COD olefinic δ 4.653 (m, 1 H), 4.255 (m, 1 H), 3.728 (m, 1 H), and 2.614 (m, 1 H), COD methylene δ 2.76 (m, 1 H), 2.48 (m, 2 H), 2.76 (m, 1 H, COD methylene), 2.10 (m, 1 H), 1.69 (m, 2 H), 1.41 (m, 1 H), and 1.26 (m, 1 H); λ_{max} = 484 nm, $\epsilon_{max} = 4.6 \times 10^3$ M^{-1} cm^{-1}. Anal. Calcd for $Ir_2C_{28}H_{36}N_2O_2$: C, 41.16; H, 4.44; N, 3.43. Found: C, 41.13; H, 4.70; N, 3.56.

(4) Characterization of [Ir(COD)(μ-hp)]$_2$: ^{1}H NMR (300 MHz, C_6D_6) hp ring δ 8.000 (m, 1 H, *o*-H), 6.595 (m, 1 H, *p*-H), 6.426 (m, 1 H, *m*-H), and 5.872 (m, 1 H, *m*-H); COD olefinic δ 5.162 (m, 1 H), 4.709 (m, 1 H), 3.910 (m, 1 H), and 3.012 (m, 1 H), COD methylene δ 2.908 (m, 1 H), 2.54 (m, 2 H), 2.02 (m, 1 H), 1.82 (m, 2 H), 1.39 (m, 1 H), and 1.26 (m, 1 H); λ_{max} = 490 nm, $\epsilon_{max} = 4.7 \times 10^3$ M^{-1} cm^{-1}. Anal. Calcd for $Ir_2C_{26}H_{32}N_2O_2$: C, 39.58; H, 4.09; N, 3.55. Found: C, 39.87; H, 4.38; N, 3.63.

(5) ^{1}H NMR spectra of the mhp and hp compounds are consistent with the X-ray crystal structure analysis of the mhp compound.

(6) Crystallographic data for [Ir(COD)(μ-mhp)]$_2$: M_r = 817.04; monoclinic; space group $P2_1/c$; a = 14.847 (5) Å, b = 11.991 (2) Å, c = 14.661 (11) Å; α = 90.04 (4)°, β = 104.99 (4)°, γ = 89.99 (2)°; V = 2521 Å^3; Z = 4; ρ(calcd) = 2.15 g cm^{-3}; crystal dimensions 0.15 × 0.2 × 0.2 mm; Mo Kα radiation, λ = 0.71073 Å; Enraf-Nonius SPD-CAD4 diffractometer; R = 0.0295, R_w = 0.0313 for 3335 observed reflections with $F_0^2 > \sigma(R_0^2)$. An empirical absorption correction was applied. All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs as described previously: Bohling, D. B.; Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1981**, *20*, 194.

(7) Positional parameters are available as supplementary material. The full details of the structures of [Ir(COD)(μ-mhp)]$_2$ and [Ir(COD)(hp)Cl_2] will be described elsewhere.

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

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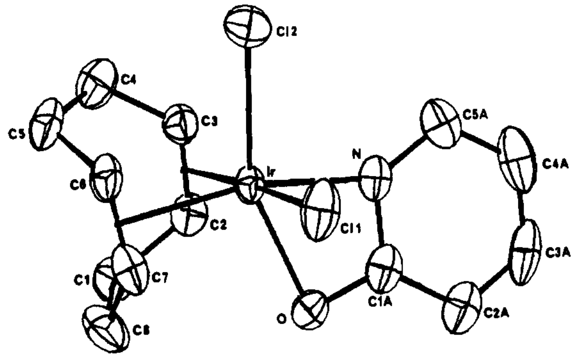

Figure 3. ORTEP drawing of [Ir(COD)(hp)Cl_2] showing the atomic numbering scheme. Thermal ellipsoids are at the 50% probability level.

[Ir(COD)(μ-pz)]$_2$ compound.[9] The Ir(I) square planes in [Ir(COD)(μ-mhp)]$_2$ are oriented so that the plane normals are misaligned and are directed toward an olefinic carbon atom coordinated to the opposing Ir(I).

The geometric constraints imposed on the d^8–d^8 interacting centers in these new complexes result in interesting electronic structural parameters and chemical reactivity. The electronic absorption spectrum of [Ir(COD)(μ-mhp)]$_2$ shown in Figure 2A exhibits the characteristically intense low-energy band attributed in other compounds containing the d^8–d^8 chromophore to the $d\sigma^* \rightarrow p\sigma$ electronic transition.[10] It is interesting that the [Ir(COD)(μ-mhp)]$_2$ spectrum is very similar to that of [Ir(COD)(μ-pz)]$_2$,[11] even though the interactions between the Ir(I) centers in the two compounds must be somewhat different due to the misalignment of the relatively diffuse $5d_{z^2}$ and $6p_z$ functions. The [Ir(COD)(μ-L)]$_2$ compounds also show the characteristic emissive behavior from the $p\sigma \rightarrow d\sigma^*$ transition, which is diagnostic of the d^8–d^8 interaction. The emission spectrum of [Ir(COD)(μ-mhp)]$_2$ at 77 K (Figure 2B) exhibits two emission bands. The emission band centered at 723 nm is significantly red shifted from the lowest absorption maximum, suggesting its tentative assignment to a formally spin-forbidden process.[10] The higher energy band at 598 nm overlaps the intense absorption feature, suggesting its assignment to a spin-allowed process. In fluid solutions at room temperature, the lower energy emission band at 723 nm is weak. At 77 K, the intensity of this emission band increases by a factor of 400. The increase in the intensity of this band with decreasing temperature is somewhat larger than that observed in previously studied d^8–d^8 binuclear compounds.[11]

The electrochemical, thermal, and photochemical behavior of the [Ir(COD)(μ-L)]$_2$ compounds has been investigated. The cyclic voltammogram of [Ir(COD)(μ-mhp)]$_2$ in CH_2Cl_2/TBAH (TBAH = tetra-*n*-butylammonium hexafluorophosphate) exhibits a quasi-reversible, one-electron wave at +0.332 V vs. aqueous Ag/AgCl.[12] This wave is shifted from a similar wave at +0.424 V observed in [Ir(COD)(μ-pz)]$_2$[13] under identical conditions and is indicative of the quasi-reversible electrode process:

$$e^- + [\mathrm{Ir(COD)}(\mu\text{-mhp})]_2^+ \rightleftharpoons [\mathrm{Ir(COD)}(\mu\text{-mhp})]_2$$

A second electrode process at more positive potentials is irreversible, but it is suggested that multielectron thermal chemistry and photochemistry might be profitably investigated in these compounds.

Thermal reaction of [Ir(COD)(μ-hp)]$_2$ with Cl_2 in CH_2Cl_2 at room temperature yields a yellow solid that is a 80:20 mixture of two products (^{1}H NMR). Similarly, photolysis (λ > 400 nm) of [Ir(COD)(μ-hp)]$_2$ in degassed CCl_4 gives a mixture of the same oxidation products. Low-temperature fractional crystallization of the yellow solid affords yellow crystals of the major product in pure form. Elemental analysis indicates this compound has the composition Ir(COD)(hp)Cl_2,[14] consistent with the presence of Ir(III) and the net, four-electron oxidation of [Ir(COD)(μ-hp)]$_2$. No band due to the $\sigma \rightarrow \sigma^*$ electronic transition of a binuclear Ir(II) compound is found above 300 nm in this complex.[15] An X-ray crystal structure analysis[7,16] (Figure 3) indicates this oxidized hp complex is a mononuclear complex of Ir(III) that contains a relatively rare chelating oxypyridine ligand. The complex adopts a distorted octahedral geometry, with cis chloride ligands. One Cl^- is trans to an Ir–olefin bond, while the other lies trans to the pyridinolate oxygen. The four membered IrNCO ring has an O–Ir–N bond angle of 63.3 (2)°, very similar to the O–Ru–N angle of 61.8 (2)° in Ru(mhp)$_2$(PPh$_3$)$_2$, the only other structurally characterized complex reported to contain a chelating hydroxypyridinate ligand.[17] The ^{1}H NMR spectrum[14] of Ir(COD)(hp)Cl_2 shows four distinct multiplets due to the COD olefinic protons, consistent with its solid state structure.

The net four-electron oxidation chemistry exhibited by [Ir(COD)(μ-hp)]$_2$ contrasts sharply with the thermal and photochemical two-center, two-electron oxidative addition reactions reported[9a,18] for the [Ir(COD)(μ-pz)]$_2$ complex. The differences between the hp- and pz-bridged systems are all the more surprising when the close similarities in the Ir(I)–Ir(I) distance, the absorption/emission properties, and the electrochemical response of the two series of compounds are considered. Further studies are currently in progress to elucidate the factors that control the course of the thermal and photochemical oxidative addition reactions in the [Ir(COD)(μ-hp)]$_2$ system.

Acknowledgment. We thank David Boyd for the electrochemical measurements, Professor D. D. Thomas for the use of the Spex Fluorolog II spectrofluorometer, Johnson-Matthey, Inc. for the loan of iridium trichloride, and Professor H. B. Gray for a helpful discussion. The Cary Model 17-D spectrophotometer was made available by funding received in part from the National Science Foundation (Grant CHE 78-23857).

Registry No. [Ir(COD)(μ-hp)]$_2$, 98330-72-4; [Ir(COD)(μ-mhp)]$_2$, 98330-73-5; Ir(COD)(hp)Cl_2, 98360-78-2; [Ir(COD)Cl]$_2$, 12112-67-3; Na(hp), 930-70-1; Na(mhp), 13472-90-7.

Supplementary Material Available: Atomic coordinates for [Ir(COD)(μ-mhp)]$_2$ and Ir(COD)(hp)Cl_2 (5 pages). Ordering information is given on any current masthead page.

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(10) Fordyce, W. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 985 and references therein.

(11) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027.

(12) $E^{0\prime}$ for $FeCp_2^+/FeCp_2$ was found to be +0.460 V under the experimental conditions employed.

(13) Boyd, D. C.; Rodman, G. S.; Mann, K. R., manuscript in preparation.

(14) Characterization of Ir(COD)(hp)Cl_2: ^{1}H NMR (300 MHz, $CDCl_3$) hp ring δ 8.026 (dd, 1 H, *o*-H), 7.596 (td, 1 H, *p*-H), 6.763 (t, 1 H, *m*-H); and 6.404 (d, 1 H, *m*-H), COD olefinic δ 6.086 (m, 1 H), 5.922 (m, 1 H), 5.526 (m, 1 H), and 5.136 (m, 1 H) COD methylene δ 2.93 (m, 1 H), ca. 2.7 (complex multiplets, 5 H), and 2.17 (m, 2 H); λ_{max} = 296 nm, $\epsilon_{max} = 3.0 \times 10^3$ M^{-1} cm^{-1}. Anal. Calcd for $IrC_{13}H_{16}Cl_2NO$: C, 33.55; H, 3.46; N, 3.01; Cl, 15.24. Found: C, 33.61; H, 3.81; N, 3.00; Cl, 14.99.

(15) (a) Mann, K. R.; Gray, H. B. "Inorganic Compounds With Unusual Properties"; American Chemical Society: Washington, DC, 1979; Adv. Chem. Ser. No. 173, p 225. (b) Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 920.

(16) Crystallographic data for Ir(COD)(hp)Cl_2: M_r = 465.40; monoclinic; space group $P2_1/n$; a = 10.259 (3) Å, b = 12.324 (1) Å, c = 10.824 (2) Å; α = 90.00 (1)°, β = 98.45 (2)°, γ = 90.00 (2)°; V = 1354 Å^3; Z = 4; ρ(calcd) = 2.28 g cm^{-3}; crystal dimensions 0.50 × 0.25 × 0.20 mm; Mo Kα radiation; λ = 0.71069 Å; Enraf-Nonius SPD-CAD4 diffractometer; R = 0.037, R_w = 0.044 for 2807 observed reflections with $F_0^2 > 2\sigma(F_0^2)$. An empirical absorption correction was applied.

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