Table III. Selected Bond Distances (Å) and Angles (deg) for $[\mathrm{Ru(OEP\text{-}}N\mathrm{\text{-}C_6H_5)(C_6H_5)](BF_4)}$

	Distances		
Ru–N(21)	2.163 (3)	Ru–N(23)	1.993 (3)
Ru–N(22)	2.049 (3)	Ru–N(24)	2.035 (3)
Ru–C(1001)	1.999 (4)	Ru–H(2161)	2.52 (4)
N(23)–C(11)	1.374 (5)	N(23)–C(14)	1.382 (5)
N(21)–C(4)	1.467 (5)	N(21)–C(19)	1.453 (5)
N(21)–C(211)	1.501 (5)	C(216)–H(2161)	0.91 (5)
	Angles		
N(21)–Ru–N(22)	89.6 (1)	N(21)–Ru–N(23)	168.5 (1)
N(21)–Ru–N(24)	88.6 (1)	N(21)–Ru–C(1001)	91.9 (1)
N(21)–Ru–H(2161)	67 (1)	N(22)–Ru–N(23)	90.0 (1)
N(22)–Ru–N(24)	171.1 (1)	N(22)–Ru–C(1001)	97.1 (1)
N(22)–Ru–H(2161)	64 (1)	N(23)–Ru–N(24)	90.2 (1)
N(23)–Ru–C(1001)	99.5 (1)	N(23)–Ru–H(2161)	103 (1)
N(24)–Ru–C(1001)	91.1 (1)	N(24)–Ru–H(2161)	108 (1)
C(1001)–Ru–H(2161)	150 (1)	Ru–N(21)–C(211)	101.4 (2)
Ru–H(2161)–C(216)	110 (3)	C(211)–C(216)–H(2161)	119 (3)
		C(215)–C(216)–H(2161)	121 (3)

contact distance (ca. 2.9 Å[10]), reveals a bonding interaction between the two atoms. Such agostic hydrogens have been observed in many transition-metal complexes;[7] however, there is only one previous example[4f] of an *N*-aryl or *N*-alkyl porphyrin with a metal–H distance indicative of a metal–H bonding interaction. Second, the C skeleton of the pyrrole containing the N–$\mathrm{C_6H_5}$ group is tilted 38° from the plane of the other three pyrroles; N(21) of this pyrrole is out of the plane of the C skeleton by an additional 0.09 Å. This distortion, common with N-substituted porphyrins,[4,5] results in a Ru–N distance 0.14 Å greater than the average of the other three Ru–N distances (2.026 Å). Third, the Ru-bound $\mathrm{C_6H_5}$ is tilted 11.4° from normal to the porphyrin plane toward the *N*-$\mathrm{C_6H_5}$ group; the N(21)–Ru–C(1001) bond angle is 91.9°, which is not significantly changed from the (presumed) 90° of the $\mathrm{Ru(OEP)(C_6H_5)_2}$ precursor.

These cumulative distortions result in an unusual geometry about the Ru center. The Ru is 0.147 Å out of the porphyrin plane (three pyrroles) toward the "axial" $\mathrm{C_6H_5}$ ligand, while N(21) is 0.126 Å out of the porphyrin plane and slightly farther away from the Ru than the normal, bonding position. These, coupled with the 150° C(1001)–Ru–H(2161) bond angle, result in a severely distorted octahedral geometry about the Ru center.

Acknowledgment. We thank Prof. Ian P. Rothwell for many stimulating discussions and the Purdue Research Foundation for financial support.

Supplementary Material Available: A figure showing a complete ORTEP diagram and listings of crystal data collection parameters, hydrogen atom parameters, anisotropic thermal parameters, and full bond distances and angles (14 pages); a listing of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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(10) The van der Waals radius for Ru is not available; however, using analogous transition metals as a guide (Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441), we arrive at an estimate of 1.6–1.7 Å. The contact distance is thus ca. 2.9 Å.

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Synthesis and Structure of $[(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)]_2}$

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Transition-metal dimers of the type $[(\eta\mathrm{\text{-}C_5R_5)M(CO)]_2}$ (R = H, $\mathrm{CH_3}$; M = Co, Rh, Ir) have received a great deal of attention in recent years in the context of their interesting reactivity and novel electronic structures.[3] For R = H, the cobalt dimer is isolable,[4] but the Rh analogue is unstable above 200 K.[5] Thermolysis of $(\eta\mathrm{\text{-}C_5H_5)Ir(CO)H_2}$, which might have given the Ir analogue, instead affords the trimeric species $[(\eta\mathrm{\text{-}C_5H_5)Ir(CO)]_3}$.[6] In the pentamethylcyclopentadienyl series (R = $\mathrm{CH_3}$), the cobalt and rhodium complexes are easily prepared and have been extensively studied.[3] The iridium analogue $[(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)]_2}$ (**2**) was first reported as a byproduct of alkane activation reactions employing photolysis of $(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)_2}$ (**1**).[7] Subsequently, compound **2** was obtained as a minor byproduct in the thermolysis of $(\eta\mathrm{\text{-}C_5Me_5)}\overline{\mathrm{Ir[C(}p\mathrm{\text{-}ClC_6H_4)\!=\!NOC}}\mathrm{\!=\!O]CO}$.[8] It has also been reported that **2** can be obtained in 33% yield from the reaction of $[(\eta\mathrm{\text{-}C_5Me_5)Ir(}\mu\mathrm{\text{-}O)]_2}$ with carbon monoxide.[9] As part of a study of **2** and its derivatives,[10] we have established a convenient synthetic route to **2** and determined the solid-state structure of **2**. We also report improved procedures for the preparation of $[(\eta\mathrm{\text{-}C_5Me_5)IrCl_2]_2}$ and $(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)_2}$, which are the immediate precursors to **2**.

Experimental Section

All operations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Pentamethylcyclopentadiene was prepared by the method of Bercaw.[11] Solvents were reagent grade and were used as received.

Preparation of $[(\eta\mathrm{\text{-}C_5Me_5)IrCl_2]_2}$. To $\mathrm{IrCl_3{\cdot}3H_2O}$ (2.0 g, 5.4 mmol) in 50 mL of degassed methanol was added excess pentamethylcyclopentadiene (1.5 mL). The mixture was refluxed for 36 h. After the mixture was cooled to room temperature, the product was isolated by filtration and washed with cold methanol. The supernatant and washings were combined and cooled to 0 °C for 24 h. Total yield: 2.0 g (91%). ^{1}H NMR (δ, relative to residual solvent): 1.60 ($\mathrm{CDCl_3}$) (lit. δ 1.59).[12a]

Preparation of $(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)_2}$. $[(\eta\mathrm{\text{-}C_5Me_5)IrCl_2]_2}$ (1.0 g, 1.26 mmol) was dissolved in 50 mL of $\mathrm{CH_2Cl_2}$ in a pressure bottle. The bottle was flushed three times with 30 psi of CO and pressurized to 40 psi. After 3 h of stirring, 5 g of zinc (30 mesh) was added. The reactor was pressurized to 40 psi under CO and the mixture stirred for 12 h. Water (50 mL) was added. The mixture was stirred for 1 h and then filtered to remove the zinc. The $\mathrm{CH_2Cl_2}$ layer was separated, and the aqueous layer was extracted with 3 × 20 mL of $\mathrm{CH_2Cl_2}$. The $\mathrm{CH_2Cl_2}$ extracts were combined, dried over $\mathrm{MgSO_4}$, filtered, and evaporated to dryness. Sublimation (10^{-3} mmHg, 40 °C) affords $(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)_2}$, 0.76 g, 2.0 mmol, 80% yield. ^{1}H NMR (δ, relative to residual solvent): 2.15 ($\mathrm{CDCl_3}$) (lit. δ 2.19).[12a] IR (ν_{CO}, $\mathrm{cm^{-1}}$): 2005, 1930 ($\mathrm{CH_2Cl_2}$); 2020, 1953 (hexane) (lit. 2000, 1925 (solvent not specified)).[12a]

Preparation of $[(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)]_2}$ (2). $(\eta\mathrm{\text{-}C_5Me_5)Ir(CO)_2}$ (0.250 g, 0.652 mmol) and a boiling chip were placed in a 50-mL pear-shaped flask. Sufficient solvent (1-butanol) was added to give a solvent depth of 2 cm. The flask was outfitted with a reflux condenser and immersed 4.5 cm into an oil bath. The solution was refluxed for 1 week with the bath temperature maintained at 170 °C. After the solution was cooled to room temperature, volatiles were removed by pumping and the residue

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(3) Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101–162.

(4) Lee, W. S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 87–92.

(5) Anderson, F. R.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 112–114.

(6) Shapley, J. R.; Adair, P. C.; Lawson, R. J. *Inorg. Chem.* **1982**, *21*, 1701–1702.

(7) Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. Presented at the 23rd International Conference on Coordination Chemistry, Boulder, CO, July 1984; abstract THp 51-02.

(8) Chetcuti, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 943–945.

(9) Bergman, R. G.; Food, T.; McGhee, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8543–8545.

(10) Heinekey, D. M.; Michel, S. T.; Schulte, G. K. *Organometallics* **1989**, *8*, 1241–1246.

(11) (a) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5. (b) Threlkel, R. S.; Bercaw, J. E.; Seidler, P. F.; Stryker, J. M.; Bergman, R. G. *Org. Synth.* **1987**, *65*, 42–45.

(12) (a) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970–5977. (b) After submission of this manuscript we have learned that a similar preparative route to $[(\eta\mathrm{\text{-}C_5Me_5)IrCl_2]_2}$ has been developed by: White, C. W.; Yates, A.; Maitlis, P. M. *Inorganic Syntheses*, volume in preparation.

0020-1669/90/1329-2023$02.50/0

Table I. Crystallographic Data for $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (**2**)

$Ir_2C_{22}H_{30}O_2$	fw 710.88
$a = 8.0615\ (8)$ Å	space group $P2_1/n^a$
$b = 7.431\ (2)$ Å	$\lambda = 0.71073$ Å
$c = 17.941\ (3)$ Å	$\rho_{calcd} = 2.195$ g cm^{-3}
$\beta = 91.93\ (1)°$	$\mu = 123.26$ cm^{-1}
$V = 1074.21$ Å^3	transm coeff: 0.5557–0.2198
$Z = 2$	$R(F_o) = 0.053$
$T = 23$ °C	$R_w(F_o) = 0.081$

[a] An alternative setting of $P2_1/c$, which is No. 14.

extracted with CH_2Cl_2 (3 × 10 mL). The solution was filtered and the product crystallized by layering with heptane. Yield: 0.250 g, 2.0 mmol, 95%. In a larger scale procedure, 1 g of **1** was used along with 25 mL of solvent in a 100-mL pear-shaped flask. The yield varied from 90 to 95%. Large crystals of **2** appear black, while smaller crystals are deep red-orange. ^1H NMR (δ, relative to residual solvent): 1.57 (C_6D_6), 1.76 ($CDCl_3$), 1.72 (CD_2Cl_2). IR (ν_{CO}, cm^{-1}): 1670 (CH_2Cl_2), 1702 (hexane, sparingly soluble). UV/vis (toluene) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 375 (9.42 × 10^3), 444 (1.27 × 10^4). MS (14 eV, 140 °C): M^+, $(M - CO)^+$. Anal. Calcd for $C_{22}H_{30}Ir_2O_2$: C, 37.17; H, 4.25. Found: C, 37.14; H, 4.33.

Photochemical Synthesis of 2 in Methanol. $(\eta\text{-}C_5Me_5)Ir(CO)_2$ (0.200 g, 0.0522 mmol) was dissolved in methanol (50 mL) and freeze–thaw degassed under vacuum. This solution was photolyzed for 41 h a few centimeters from a water-cooled 450-W Hanovia medium-pressure mercury lamp in an annular Pyrex jacket. At this stage the solution was pale yellow, suggesting that an appreciable amount of **2** was not present. The solution was concentrated under vacuum to ca. 10 mL and left at room temperature for 3 days, during which the solution darkened and crystals of **2** formed, which were removed by filtration. The filtrate was further concentrated and cooled to −30 °C to recover additional product. Total yields of **2** by this method varied from 30 to 60%. Yields are drastically reduced if the photolysis is stopped and restarted or if solvent is completely removed in the concentration step. Crystals suitable for X-ray crystallography were obtained by a further crystallization from methanol at −20 °C.

Solid-State Structure of 2. A parallelepiped crystal of approximate dimensions 0.05 × 0.13 × 0.30 mm that had been crystallized at −20 °C was selected. The X-ray data were collected with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. Selected crystallographic data are given in Table I with further details included as supplementary material. Cell constants were obtained from a least-squares refinement of the setting angles of 23 reflections in the range $17 < 2\theta < 30°$. A total of 2127 reflections were measured for $2\theta < 50°$ of which 1448 reflections having $I > 3\sigma(I)$ were used in the final cycle of refinement. The structure was solved by using a three-dimensional Patterson synthesis, which gave the positional parameters of the Ir atom. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis. It was necessary to locate only half of the molecule in view of its position on a crystallographic center of symmetry. During refinement the C_5Me_5 group would not converge to a reasonable geometry, indicating possible disorder of this group. A difference Fourier over this region showed several peaks consistent with this interpretation. A detailed disorder model was deemed unjustified and further refinement was done with a rigid group constraint on this moiety (C–C = 1.42 Å, C–C–C = 108° for the ring carbons; C–C = 1.51 Å for methyl carbons; all atoms planar). The position and orientation of this group was refined, and then these atoms were fixed for the final cycles with only their isotropic thermal parameters allowed to vary. The central atoms of the molecule, Ir, C(1), and O, were refined anisotropically.

Final atomic coordinates for non-hydrogen atoms are listed in Table II. Selected bond distance and angles are given in Table III.

Results

The synthesis of $[(\eta\text{-}C_5Me_5)IrCl_2]_2$ from pentamethylcyclopentadiene and $IrCl_3{\cdot}nH_2O$ has been carried out in refluxing methanol. Carbonylation of $[(\eta\text{-}C_5Me_5)IrCl_2]_2$ affords $(\eta\text{-}C_5Me_5)Ir(CO)Cl_2$ (eq 1). This species was reduced with zinc

$$[(\eta\text{-}C_5Me_5)IrCl_2]_2 + CO \rightarrow (\eta\text{-}C_5Me_5)Ir(CO)Cl_2 \quad (1)$$

metal and further carbonylated in situ to afford the dicarbonyl complex $(\eta\text{-}C_5Me_5)Ir(CO)_2$ (**1**) in excellent yield (eq 2).

$$(\eta\text{-}C_5Me_5)Ir(CO)Cl_2 + Zn + CO \rightarrow (\eta\text{-}C_5Me_5)Ir(CO)_2 + ZnCl_2 \quad (2)$$

Thermolysis of **1** in 1-butanol affords the dimeric species $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (**2**) in excellent yield. The solid-state structure of **2** has been determined, the results of which are summarized in Tables I–III.

Table II. Atomic Coordinates and Isotropic Thermal Parameters

atom	x	y	z	U,[b] Å^2
Ir	434.79 (8)	78.54 (9)	55.13 (4)	3.33 (3)[c]
O	282 (2)	155 (2)	−93.3 (9)	6.8 (5)[c]
C(1)	377 (2)	86 (3)	−51 (1)	4.7 (6)[c]
C(2)	404	85	176	7.2 (7)
C(3)	465	255	153	9.8 (9)
C(4)	340	336	106	11 (1)
C(5)	202	217	102	7.4 (7)
C(6)	242	62	145	6.4 (6)
C(7)	496	−47	226	19 (2)
C(8)	633	334	173	25 (3)
C(9)	351	518	69	20 (2)
C(10)	41	250	58	13 (1)
C(11)	131	−99	155	15 (2)

[a] Coordinates × 10^3. Those coordinates lacking an estimated standard deviation were not refined in the last cycles. [b] Isotropic thermal parameter $U \times 10^2$ except as noted. [c] Equivalent isotropic thermal parameter $U_{(eq)} \times 10^2$.

Table III. Selected Bond Distances and Angles

(a) Distances (Å)			
Ir–Ir′	2.554 (1)	Ir-C(2)	2.196
Ir-C(1)	1.947 (14)	Ir-C(3)	2.190
Ir-C(1)′	1.954 (13)	Ir-C(4)	2.270
Ir-Cp	1.901	Ir-C(5)	2.322
C(1)-O	1.177 (15)	Ir-C(6)	2.278
(b) Angles (deg)			
Ir-C(1)-Ir′	81.8 (5)	Ir′-Ir-C(1)′	49.0 (4)
Ir-C(1)-O	140.6 (5)	Cp-Ir-C(1)	129.7
Ir′-C(1)-O	137.6 (5)	Cp-Ir-C(1)′	132.0
Ir′-Ir-C(1)	49.2 (4)		

[a] Cp represents the centroid of the $\eta\text{-}C_5Me_5$ ring. [b] Estimated standard deviations not specified when atom positions involved were not refined in final least-squares cycles.

Discussion

The report of cyclohexane activation by $(\eta\text{-}C_5Me_5)Ir(CO)_2$ drew attention to the fact that the product $(\eta\text{-}C_5Me_5)Ir(CO)(H)$(cyclohexyl), was stable only in dilute solution.[13] It was later shown that the principle decomposition product of this hydride in concentrated cyclohexane solution or as a neat oil at 50 °C was $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (**2**).[7] Yields were low, and the method was not well suited to larger scale reactions. In view of the stability and potential reactivity of the dimer, we sought alternative synthetic procedures.

Synthesis of Precursors. The preparation of $[(\eta\text{-}C_5Me_5)IrCl_2]_2$ reported here takes advantage of recent improvements in the preparationof pentamethylcyclopentadiene,[11] a compound which is also commercially available. It allows a much more convenient preparation than the original synthesis of this material from hydrated $IrCl_3$ and 1-(1-chloroethyl)pentamethylcyclopentadiene reported by Maitlis and co-workers.[12a,b] We have also explored the use of H_2IrCl_6 and $(NH_4)_2IrCl_6$ as alternative iridium starting materials in the reaction with pentamethylcyclopentadiene. While the desired product was obtained, the yields were unsatisfactory.

The conversion of $[(\eta\text{-}C_5Me_5)IrCl_2]_2$ to $(\eta\text{-}C_5Me_5)Ir(CO)_2$ (**1**) by reaction with $Fe_3(CO)_{12}$ was reported by Maitlis[12a] to afford the dicarbonyl complex in 89% yield. In our hands, we have found that this procedure gives good but variable yields of 60–80%, apparently due to variability in the quality of the $Fe_3(CO)_{12}$ employed; moreover, we have observed that the benzene filtrate from this procedure contains $Fe(CO)_5$. The alternative procedure reported here employs carbonylation of $[(\eta\text{-}C_5Me_5)IrCl_2]_2$ to the monomeric dichloride $(\eta\text{-}C_5Me_5)Ir(CO)Cl_2$, which was identified

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(13) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725.

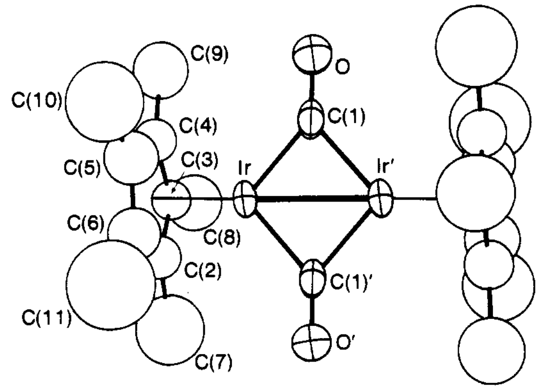

Figure 1. Molecular structure of **2**, showing the atom-numbering scheme. Primed atoms are related by a crystallographic center of symmetry.

by infrared spectroscopy[14] (eq 1). This species was reduced with zinc metal and further carbonylated in situ to afford **1** in excellent yield (eq 2). Workup of the reaction mixture was complicated by the apparent formation of the $ZnCl_2$ adduct of the product, which hinders sublimation of **1**. The product is easily freed of $ZnCl_2$ by a simple extraction of the dichloromethane solution with water. This procedure gives excellent (80%) and reproducible yields of **1**.

Synthesis of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (2). The iridium dimer **2** is less readily accessible from the monomer than its rhodium analogue. While $(\eta\text{-}C_5Me_5)Rh(CO)_2$ reacts readily with Me_3NO to afford $[(\eta\text{-}C_5Me_5)Rh(CO)]_2$,[15] we have found that **1** does not react with Me_3NO. The original route to the rhodium dimer[16] involved heating $(\eta\text{-}C_5Me_5)Rh(CO)_2$ at 80–85 °C, and we have found that this conversion will take place in the iridium case but only at substantially higher temperatures.[17] When a vessel containing **1** is placed in a bath at 170–180 °C, **2** is formed but much of the starting material sublimes unchanged.

We have found conditions for thermolysis of **1** that, if exactly followed, give excellent yields of **2**. A key aspect is the use of a refluxing solvent, 1-butanol (bp 117–118 °C), which returns sublimed starting material to the hot region of the thermolysis flask. Other key aspects are the bath temperature (170 °C) and the level of the bath surface, which must be higher than the solvent level in the flask (by 2.5 cm in the arrangement we describe). The product is relatively insoluble and forms as a dark crust above the solvent level. Isolation of **2** is straightforward, and a 95% yield of high-purity product is obtained after one crystallization.

The properties of **2** are similar to those of the Co and Rh analogues. The infrared spectrum exhibits a band at 1670 cm^{-1}, which is consistent with a doubly carbonyl-bridged structure. Complex **2** is highly colored, due to the intense absorption at 375 and 444 nm; large crystals appear black, while smaller crystal are deep red-orange to dark yellow-brown in color. In comparison, the dark blue Rh analogue has intense absorptions at 345 and 580 nm, while the emerald green Co analogue absorbs at 410 and 610 nm.[18] These observations are consistent with an increase in the HOMO–LUMO energy difference on descending the group. This is consistent with the results of a recent calculational and photoelectron spectroscopy study of these molecules.[19]

An interesting alternative synthesis of **2** arose from studies of the photolytic activation of methanol by $(\eta\text{-}C_5Me_5)Ir(CO)_2$. An important initial product of this reaction appears to be $(\eta\text{-}C_5Me_5)Ir(CO)(H)(CH_2OH)$,[20] and sufficiently concentrated methanol solutions on standing in the dark at room temperature afford **2** in yields of 30–60%. Useful quantities of 2 are available in this way, but the procedure at its present stage of development is inferior to the thermolysis route described above.

Structure of 2. The solid-state structure of **2** (Figure 1) reveals an Ir_2 moiety with two bridging carbonyl groups. Selected bond lengths and angles are tabulated in Table III. The crystallographic center of symmetry requires that the four-membered ring Ir–C(1)–Ir′–C(1)′ is planar. The centroid of the C_5Me_5 ring (designated Cp) is 0.063 Å below the plane, while O is 0.020 Å above it; Cp′ and O′ would necessarily be above and below the plane, respectively. The Cp–Ir–Ir′ angle is 177.9°, and the C_5Me_5 ring is tilted 4.0° with respect to the Cp–Ir vector. The *idealized* symmetry of the molecule is C_{2h}, with the pseudo-2-fold axis running through O–C(1)–C(1)′–O′. The center of inversion requires that the C_5Me_5 rings are in a mutually staggered conformation.

The rhodium dimer $[(\eta\text{-}C_5Me_5)Rh(CO)]_2$ also has the staggered arrangement and a Rh═Rh separation of 2.564 (1) Å,[21] very similar to the Ir═Ir value of 2.554 (1) Å found in this work. As expected, Co═Co in $[(\eta\text{-}C_5Me_5)Co(CO)]_2$ is much shorter, 2.338 (2)[22] and 2.327 (2) Å[23] in two determinations. In the Co analogue, the C_5Me_5 rings have an eclipsed arrangement, which was attributed[22] to a minimization of steric interactions with the bridging carbonyls. This is consistent with the staggered arrangement of **2**, where Cp–Ir is 0.20 Å longer than Cp–Co in the cobalt dimer.

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Supplementary Material Available: For **2**, lisitings of complete details of the structure determination, anisotropic thermal parameters, and bond distances and bond angles (3 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(14) Kang and Maitlis report ν_{CO} = 2035 cm^{-1} (KBr disk) for $(\eta\text{-}C_5Me_5)Ir(CO)Cl_2$: Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393–399. We have observed a band at 2048 cm^{-1} in dichloromethane, which we assign to $(\eta\text{-}C_5Me_5)Ir(CO)Cl_2$.

(15) Hermann, W. A.; Plank, J.; Bauer, Ch.; Ziegler, M. L.; Guggolz, E.; Alt, R. Z. *Anorg. Allg. Chem.* **1982**, *487*, 85–110.

(16) Nutton, A.; Maitlis, P. M. *J. Organomet. Chem.* **1979**, *166*, C21–C22.

(17) We have observed very small amounts of **2** in the residue after sublimation (60 °C, vacuum) of large batches of $(\eta\text{-}C_5Me_5)Ir(CO)_2$ prepared in refluxing benzene by the Maitlis procedure.[12]

(18) Anderson, F. R.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 112–114.

(19) Griewe, G. L.; Hall, M. B. *Organometallics* **1988**, *7*, 1923–1930.

(20) Hoyano, J. K. Unpublished results. The chloro derivative $(\eta\text{-}C_5Me_5)Ir(CO)(Cl)(CH_2OH)$ has been isolated after treatment of the irradiated methanol solution with CCl_4.

(21) Green, M.; Hankey, D. R.; Howard, J. A. K.; Louca, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 757–758.

(22) Cirjak, L. M.; Ginsburg, R. E.; Dahl, L. F. *Inorg. Chem.* **1982**, *21*, 940–957.

(23) Bailey, W. I.; Collins, D. M.; Cotton, F. A.; Baldwin, J. C.; Kaska, W. C. *J. Organomet. Chem.* **1979**, *165*, 373–381.

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Electrocatalytic Dehalogenation of α-Haloacetic Acids by Vitamin B_{12}

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Cob(I)alamin, the Co(I) form of vitamin B_{12}, is a powerful and versatile reductant.[1] Electrocatalytic reductions mediated by vitamin B_{12} involve reduction of the Co(II) form of the vitamin to cob(I)alamin, which then reduces a suitable substrate in solution. Cob(II)alamin (B_{12r}), regenerated in this homogeneous reaction in a thin layer of solution close to the surface of the electrode, can be continuously recycled to cob(I)alamin at the formal Co(II)/Co(I) potential.[2] Among alkyl halides, vicinal

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(1) Dolphin, D., Ed. *B_{12}*; Wiley: New York, 1982; Vol. I.