Ru,[18] and Os[19] from readily available starting materials that possess oxygen donor or mixed oxygen–nitrogen donor ligand sets. We have now extended this chemistry to include reactions of dirhodium compounds; the specific reaction reported here, eq 1,

$$Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2 + 2Me_3SiCl + 2dmpm \xrightarrow[\Delta]{THF} Rh_2(dmpm)_2(PPh_2C_6H_4)_2Cl_2 + 2Me_3SiOOCH_3 \quad (1)$$

proceeds smoothly through a series of color changes from blue, which is the THF adduct $Rh_2(OCCH_3)_2(PPh_2C_6H_4)_2(THF)_2$, to deep green after addition of the Me_3SiCl, and finally to bright red upon addition of 2 equiv of dmpm. The red color persists even after prolonged reflux, and subsequent workup of the solution yields $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]Cl_2$ as a pale microcrystalline material in ~85% yield. The product was recrystallized from CH_2Cl_2–hexane to afford dark red crystals of $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2{\cdot}CH_2Cl_2$ which were used for vibrational and electronic spectroscopy, electrochemistry, and a single-crystal X-ray structural determination.

The IR spectrum of the title compound revealed the presence of both coordinated dmpm and ortho-metalated triphenylphosphine but no bands attributable to acetate ligands. The UV–visible spectrum of $Rh_2(dmpm)_2(PPh_2C_6H_4)Cl_2$, recorded in CH_2Cl_2 solution, exhibits several characteristic features at λ_{max}: (mn, ϵ) 550 (740); 520 sh; 368 (16400); 300 (9370). A cyclic voltammogram of the product in 0.2 M Bu_4NPF_6–CH_2Cl_2 shows the presence of one couple at $E_{1/2} = +0.85$ V vs. Ag/AgCl which corresponds to the one-electron oxidation $Rh^{II}Rh^{II} \overset{-e^-}{\rightleftharpoons} Rh^{II}Rh^{III}$. This redox behavior is typical of binuclear rhodium(II) complexes.[2]

The identity of $Rh_2(dmpm)[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ was confirmed by a crystallographic study following general procedures described elsewhere.[20–22] The molecule, shown in Figure 1, consists of two Rh atoms bridged by two $Me_2PCH_2PMe_2$ ligands in a cis disposition and two *o*-$(Ph_2P)C_6H_4^-$ ligands that are arranged in the same head-to-tail manner as in the parent compound $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2L_2$. The axial chloride ligands complete the coordination sphere for an overall distorted octahedral geometry around each Rh atom (angles are in the range 89–92°). The Rh(1)–Rh(2)–Cl(axial) angles (av = 171.9°) do not deviate significantly from linearity unlike the Rh–Rh–L(axial) angles observed for the adducts $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)(L)_2$ (L = CH_3COOH, C_5H_5N) (Rh–Rh–L(av) = 162.8°). In the new compound, the axial Rh–Cl bonds are relatively short (2.561 (6) Å) and this correlates with the length of the Rh–Rh bond, which is 2.770 (3) Å, the longest distance ever observed for a dirhodium(II) compound. The corresponding M–M distances in the diacetate starting material $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2(L)_2$ are 2.508 (1) Å for L = CH_3COOH and 2.556 (2) Å for L = C_5H_5N, which are also quite long compared to the Rh–Rh distances found in the tetracarboxylate dirhodium compounds.[2]

The Rh–P distances are in the expected range, with the Rh–P distances trans to another phosphorus atom being shorter than those trans to a carbon atom, in accord with the expected order of the trans influence of M–P and M–C bonds. The average Rh–C bond distance of 2.08 (1) Å is quite normal. Additional important interatomic dimensions are listed in the caption for Figure 1.

The isolation of the Rh(II) dimer reported here has important consequences. It documents the existence of a previously unknown chemistry for dirhodium compounds containing bridging carboxylate ligands. The method outlined in this paper can be used to prepare, from readily available starting materials, unusual mixed-ligand complexes that possess an Rh_2^{4+} dinuclear core. Work that is currently under way in our laboratories has confirmed the general nature of this synthetic approach. A complete report of these results will be submitted later.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Tables of crystallographic parameters, atomic positional parameters, and equivalent isotropic displacement parameters, bond distances and angles, and anisotropic thermal parameters (9 pages); table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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(22) Crystal data for $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2{\cdot}CH_2Cl_2$: monoclinic, $P2_1/c$; $a = 11.268$ (2) Å, $b = 24.834$ (3) Å, $c = 17.589$ (5) Å, $\alpha = \gamma = 90°$, $\beta = 99.14$ (2)°, $V = 4859$ (3) Å^3, $Z = 4$, $d_{calcd} = 1.581$ g/cm^3, μ(Mo Kα) = 11.181 cm^{-1}. An Enraf-Nonius CAD-4 was used to collect 5194 unique data at −106 °C using the ω–2θ scan technique. An empirical absorption correction was based on azimuthal scans of six reflections. The positions of two independent Rh atoms were derived from a three-dimensional Patterson map and refined by least squares. Refinement of 382 parameters gave residuals of $R = 0.064$ and $R_w = 0.074$ by using 2473 reflections with $F_o^2 > 3\sigma(F_o^2)$. The quality-of-fit index is 1.430 and the largest shift/esd = 0.17.

Heats of Reaction of $Cp^*(PMe_3)Ir(R)(H)$ (R = C_6H_5, C_6H_{11}, and H) with HCl, CCl_4, CBr_4, and CH_3I. A Solution Thermochemical Study of the C–H Insertion Reaction

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A number of coordinatively unsaturated transition-metal complexes have been found to insert into carbon–hydrogen bonds,[1] leading to stable hydrido alkyl metal complexes as shown in eq 1. In such reactions, the sum of the M–H and M–C bond

$$M + R\text{–}H \rightarrow R\text{–}M\text{–}H \quad (1)$$

dissociation energies in R–M–H must be comparable to, or larger than, the energy of the alkane C–H bond which is broken. This is the "driving force" for C–H activation and must be on the order of 110 kcal/mol for reaction to occur.[2] Values have been obtained for some first-row transition-metal–alkyl (=30 kcal/mol) and metal–hydride(=60 kcal/mol) bond strengths,[3] but less information has been available for the second- and third-row metals. We now wish to report thermochemical studies which provide a precise value of the difference between the metal–carbon and metal–hydrogen bond energies in $Cp^*(PMe_3)Ir(H)(R)$ complexes and reasonable estimates for the absolute values of these and several other Ir–X bonds (X = H, Cl, Br, I, C_6H_{11}, and C_6H_5).

Relative M–C bond strength estimates for a number of alkyl groups in this series were determined previously by one of our

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(1) For recent reviews, see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (c) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (d) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, Holland, 1984.

(2) In addition to breaking the C–H bond (on the order of 100 kcal/mol) the unfavorable entropy of reaction 1 can be estimated to contribute 10 kcal/mol opposing oxidative addition: Page, M. I. *Angew. Chem., Int. Ed. Engl.*, **1977**, *16*, 449.

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groups by study of exchange equilibria.[4] Kinetic measurements of the enthalpy of activation for reductive elimination of cyclohexane from the hydridocyclohexyliridium complex (note: in this and subsequent equations, L = PMe_3, Cp* = η^5-C_5Me_5, Cy = C_6H_{11}, Ph = C_6H_5, ΔH values are in kcal/mol) shown in eq 2

$$\mathrm{Cp^*(L)Ir(Cy)(H) + PhH \rightarrow Cp^*(L)Ir(Ph)(H) + CyH} \qquad \Delta H^{\ddagger} = 35.6 \pm 0.5 \quad (2)$$

led to the conclusion that the sum of the Ir–Cy and Ir–H bond strengths was 125–130 kcal/mol. With a reasonable estimate for the *sum* of the Ir–Cy and the Ir–H bond strengths, calorimetric studies were undertaken to determine the *difference* in these bond strengths which would allow calculation of *absolute* values for bond strengths in this system.

Reaction of $Cp^*(L)Ir(C_6H_{11})(H)$ or $Cp^*(L)IrH_2$ with anhydrous HCl in toluene at 25 °C is rapid and quantitative[5] and results in production of $Cp^*(L)IrCl_2$ as shown in eq 3 and 4.

$$\mathrm{Cp^*(L)Ir(Cy)(H) + 2HCl \rightarrow Cp^*(L)IrCl_2 + H_2 + CyH} \qquad \Delta H = -45.5 \pm 0.5 \quad (3)$$

$$\mathrm{Cp^*(L)IrH_2 + 2HCl \rightarrow Cp^*(L)IrCl_2 + 2H_2} \qquad \Delta H = -30.0 \pm 1.3 \quad (4)$$

Subtraction of these two equations leads directly to the heat of hydrogenation of the Ir–Cy bond as shown in eq 5.

$$\mathrm{Cp^*(L)Ir(Cy)(H) + H_2 \rightarrow Cp^*(L)IrH_2 + CyH} \qquad \Delta H = -15.5 \pm 1.8 \quad (5)$$

Using accepted bond strength values for H–H (104 kcal/mol) and Cy–H (96 kcal/mol),[6] we conclude that $D_{\mathrm{Ir-H}} - D_{\mathrm{Ir-Cy}} = 23.5$ kcal/mol. Accepting the lower limit for the sum $D_{\mathrm{Ir-H}} + D_{\mathrm{Ir-Cy}} = 125$ kcal/mol, absolute bond strengths for the Ir–Cy and Ir–H bonds are calculated to be 51 and 74 kcal/mol.

Because the estimate of the absolute value of $D_{\mathrm{Ir-H}}$ depends on the assumption of a low kinetic barrier to C–H insertion, we have confirmed this calculation by direct measurement using pulsed laser photoacoustic calorimetry.[7] Photolysis of di-*tert*-butyl peroxide in the presence of $Cp^*(L)IrH_2$ gives a mixture of products; however, irradiation of excess[8] *t*-BuOO-*t*-Bu in the presence of $Cp^*(L)IrD_2$ gives >90% *t*-BuO–D, thus the primary reaction of the *tert*-butoxy radicals involves abstraction of a hydrogen atom from the dihydride as shown in eq 6. From the

$$t\text{-BuO–O-}t\text{-Bu} \xrightarrow{h\nu} t\text{-BuO}^{\bullet} + \mathrm{Cp^*(L)IrH_2} \rightarrow t\text{-BuOH} + \mathrm{Cp^*(L)\dot{I}rH} \quad (6)$$

average of five determinations, the value of $D_{\mathrm{Ir-H}}$ measured in this experiment is 72.9 ± 4.3 kcal/mol, in excellent agreement with the value estimated from the thermochemical and kinetic experiments described above.

The heat of reaction of the phenyl hydride with HCl as shown in reaction 7 is remarkably close to the heat of reaction of the

$$\mathrm{Cp^*(L)Ir(Ph)(H) + 2HCl \rightarrow Cp^*(L)IrCl_2 + PhH + H_2} \qquad \Delta H = -30.6 \pm 2.7 \quad (7)$$

dihydride. This leads to the conclusion, by subtraction of eq 4 that hydrogenation of the phenyl hydride, as shown in eq 8, is

$$\mathrm{Cp^*(L)Ir(Ph)(H) + H_2 \rightarrow Cp^*(L)IrH_2 + PhH} \qquad \Delta H = -0.6 \pm 4.0 \quad (8)$$

virtually thermoneutral. Transferring the Ir–H bond strength value determined above (74.2 kcal/mol) leads to calculation of the Ir–Ph bond strength as 80.6 kcal/mol, some 6 kcal/mol stronger than the Ir–H bond, and 30 kcal/mol stronger than the Ir–Cy bond. The greater strength of the metal–phenyl vs. metal–alkyl bond has also been observed by Jones and Feher[9] for the analogous rhodium complexes $Cp^*Rh(PMe_3)(R)(H)$.

Table I. Bond Strength Estimates (kcal/mol) for $(PMe_3)Cp^*IrX_2$ and Related Systems

X	$(PMe_3)Cp^*IrX_2$[a]	Cp_2WX_2[b]	Cp_2ThX_2[c]	$L_2Cl(CO)IrX_2$[d]
H	74.2	72.9	97.5	60
Cl	90.3	82.9		71
Br	76.0	71.5		53
I	63.8	64.0		35
CH_3		50.2	82.4	35.4
C_6H_5	80.6[e]		90.6	
C_6H_{11}	50.8[e]		74.9	

[a] This work, average uncertainties in absolute bond strength values are on the order of ±5 kcal/mol. For experimental errors on specific measurements see text. [b] Calado, J. C. G.; Dias, A. R.; Salem, M. S.; Marthinho Simoes, J. A. *J. Chem. Soc., Dalton Trans* **1981**, 1174 and references therein. [c] Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824. [d] Yoneda, G.; Blake, D. M. *Inorg. Chem.* **1981**, *20*, 67 and references therein. [e] These bond strength estimates are based on the enthalpies of reaction of the $(PMe_3)Cp^*Ir(R)(H)$ complexes.

Table II. Enthalpies of Oxidative Addition Estimated for Selected Species in the Reaction

$$\mathrm{Cp^*(PMe_3)Ir + A{-}B \rightarrow Cp^*(PMe_3)Ir(A)(B)}$$

A–B	$-\Delta H$[a]	A–B	$-\Delta H$[a]	A–B	$-\Delta H$[a]
C_6H_{11}–C_6H_{11}	22	Cl_2	123	HCl	61
C_6H_{11}–H	30	Br_2	106	HBr	63
H–H	44	I_2	91	HI	67
C_6H_5–H	45				
C_6H_5–C_6H_5	49				

[a] All enthalpies of reaction are in kcal/mol and are calculated by using bond strength data taken from Table 1 and accepted bond strength values.[6] [b] Estimated bond based on the assumption that the lR–R bond strength is the same for both lr(R)(H) and $lr(R)_2$.

In order to generate additional Ir–X bond strength estimates, the heats of reaction of several hydrides with organic halides were measured as shown in eq 9–14.

$$\mathrm{Cp^*(L)IrH_2 + 2CCl_4 \rightarrow Cp^*(L)IrCl_2 + 2CHCl_3} \qquad \Delta H = -83.0 \pm 0.6 \quad (9)$$

$$\mathrm{Cp^*(L)Ir(H)(Cl) + CCl_4 \rightarrow Cp^*(L)IrCl_2 + CHCl_3} \qquad \Delta H = -41.8 \pm 0.7 \quad (10)$$

$$\mathrm{Cp^*(L)Ir(Ph)(H) + CCl_4 \rightarrow Cp^*(L)Ir(Ph)(Cl) + CHCl_3} \qquad \Delta H = -40.9 \pm 1.4 \quad (11)$$

$$\mathrm{Cp^*(L)Ir(Cy)(H) + CCl_4 \rightarrow Cp^*(L)Ir(Cy)(Cl) + CHCl_3} \qquad \Delta H = -43.1 \pm 1.5 \quad (12)$$

$$\mathrm{Cp^*(L)IrH_2 + 2CBr_4 \rightarrow Cp^*(L)IrBr_2 + 2CHBr_3} \qquad \Delta H = -82.9 \pm 0.3 \quad (13)$$

$$\mathrm{Cp^*(L)IrH_2 + 2CH_3I \rightarrow Cp^*(L)IrI_2 + 2CH_4} \qquad \Delta H = -74.6 \pm 2.5 \quad (14)$$

On a per-bond basis, the enthalpies of reaction with CCl_4 (reactions 9–12) were constant at −42.0 ± 0.9 kcal/mol and indicate that bond strengths are additive in this series. Bond strength estimates for this and several related systems are collected in Table I. The Ir–X bond strengths are some 20 kcal/mol stronger for $Cp^*(PMe_3)IrX_2$ than for $(PR_3)_2(CO)(Cl)IrX_2$. The large difference in bond strengths of the same metal and oxidation state [both are Ir(III)] highlights the difficulties in extrapolating results from one system to another. The strongest similarity to $Cp^*(PMe_3)IrX_2$ exists with Cp_2WX_2, another system known to undergo insertion into certain C–H bonds.[10]

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[8] Di-*tert*-butyl peroxide was present in excess sufficient to ensure that >95% of the light was absorbed by *t*-BuOO-*t*-Bu and not by $Cp^*Ir(PMe_3)(H)_2$.

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The data in Table I can be used to estimate the enthalpy of a number of interesting potential $Cp^*(PMe_3)Ir$ oxidative addition reactions; these are presented in Table II. The following conclusions can be drawn from the trends in this table: (1) C–C insertion into dicyclohexyl is mildly exothermic and into biphenyl is strongly exothermic; thus these reactions are inhibited by kinetic rather than thermodynamic barriers. (2) In spite of the fact that dihalogen bond energies decrease on moving down the periodic series, Ir–halogen bond energies decrease more (in contrast to the trend for M–C bonds)—thus the $M + X_2$ insertions become progressively less exothermic. (3) The almost identical exothermicities of the H–X insertions support Bercaw and Bryndza's correlation[11] of M–X with H–X bond energies, at least for electronegative X groups.

One of the most striking results of this work is the high strength of the Ir–phenyl bond. To our knowledge this is the first example of a solution-phase M–C bond stronger than an M–H bond in the same series. Further thermodynamic investigations are in progress aimed at determining the physical basis of this phenomenon.

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Origin of Rate Accelerations in an Enzyme Model: The *p*-Nitrophenyl Ester Syndrome

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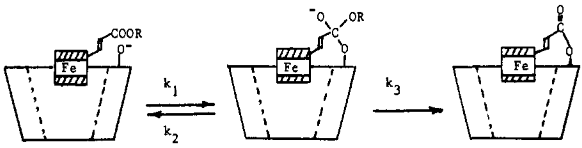
Laboratories the world over are designing, synthesizing, and examining organic systems that in some way "mimic" or "model" enzyme activity. For example, the digestive enzyme, chymotrypsin, has been modeled by groups in Strasbourg,[1] New York,[2] Los Angeles,[3] Evanston,[4] Fukuoka,[5,6] and Atlanta[7] to name a few. Impressive rate accelerations, even surpassing those of chymotrypsin, have been achieved. Yet these chymotrypsin models are deficient in at least one respect: they all use *p*-nitrophenyl esters as substrates.[8] Chymotrypsin "in real life" is, of course, *not* an esterase. Its primary function is to hydrolyze amides (substrates that are far less reactive than *p*-nitrophenyl esters). The question therefore arises as to why chemists persist in working with such artificial substrates. Favorable reaction time is ostensibly one explanation. But amides should, seemingly, present no serious rate problem when a mimic attains enzyme-like accelerations. A second explanation for the prevalence of *p*-nitrophenyl esters relates to convenience (their hydrolyses being easily followed spectrophotometrically). There appears, however, no reason why hydrolyses of "natural" substrates cannot be monitored by the same procedures commonly used with actual enzymes.[9] Is there perhaps a more fundamental reason for the popularity of *p*-nitrophenyl esters? In answering this question, we not only disclose the etiology of the "*p*-nitrophenyl ester syndrome", we uncover an important principle governing mimic behavior.

Table I. Rate Data for the Hydrolysis of Ferrocenylacrylate Esters ($FCH{=}CHCOOR$) as Complexes with β-Cyclodextrin ($k_{complex}$) and as Free Substrates (k_{un}).

R	pK_a of ROH	$10^8 k_{un}$, s^{-1}	$t_{1/2}$	$k_{complex}/k_{un}$
ethyl	15.9	0.5[c]	>2 year[a,b]	<2
benzyl	15.2	0.7	>1 year	<2
p-nitrobenzyl	14.6	0.9	>1 year	<2
phenyl	9.9	7.9	18 h	140
m-chlorophenyl	9.1	12	3.9 min	0.26×10^5
p-cyanophenyl	8.0	20	37 s	0.95×10^5
p-nitrophenyl[d]	7.2	28	7.4 s	3.3×10^5

[a] Half-lives for ester disappearance ($t_{1/2}$) were determined by using 6.4×10^{-2} M β-cyclodextrin in 60% (v/v) Me_2SO at 30.0 °C with a phosphate buffer of $pH_{app}10$. Quantitative isolation experiments along with the equation in ref 12 allowed the calculation of $t_{1/2}$ values. In addition, the $t_{1/2}$ for the *p*-cyano compound was measured spectrophotometrically and found to agree with that from the isolation method. [b] The ratio of β-cyclodextrin to ester always exceeded 100. Esters were >60% bound to β-cyclodextrin (as determined spectrophotometrically or by solubility measurements). [c] Observed rates for uncatalyzed hydrolyses (k_{un}) were calculated for reactions under the same conditions as mentioned above but without β-cyclodextrin (see ref 2 and 11). Buffer corrections were neglected. [d] Data from ref 2.

Our experiments were motivated by the remarkable 3.3×10^5 acceleration in hydrolysis rate, observed by Breslow et al.,[2,10] when *p*-nitrophenyl 3-ferrocenylacrylate binds fully to β-cyclodextrin (eq 1). Thus, the substrate–cyclodextrin complex in 60% (v/v) Me_2SO/H_2O at 30.0 °C and pH_{app} 10 has a half-life of only 7.4 s. In Table I, we compile rate data for complexes between β-cyclodextrin and several additional esters of 3-ferrocenylacrylic acid. Consider first the ethyl ester which is only 56 times less reactive than the *p*-nitrophenyl ester toward basic hydrolysis.[11] One might anticipate, therefore, that ethyl 3-ferrocenylacrylate should, when complexed with β-cyclodextrin, react with a half-life of a few minutes (i.e., 56 × 7.4 s). In actual fact, we found that the ethyl ester remains >99% unreacted after 10 days under the conditions of Breslow et al.[2,10] The half-life of bound ester is not a few minutes but at least 2 years.[12] Whatever the source of the 3.3×10^5 acceleration with the *p*-nitrophenyl ester, it vanishes totally with the ethyl ester. Little wonder that ethyl esters (not to mention amides) are seldom used to test the efficacy of chymotrypsin mimics.



(1)

Absence of significant rate accelerations with the ethyl ester could, possibly, be caused by insufficient binding. To investigate this point, we determined spectrophotometrically the association constant between the ethyl ester and β-cyclodextrin. It was found that $K_{assoc} = 24 \pm 7\ M^{-1}$ as compared to 133 M^{-1} reported for

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(12) Estimated from the quantitative recovery of ester, with an uncertainty <1%, and from ln [100/(% unreacted ester)] = *kt* where *t* = 10 days.

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