Advantage was now taken of the erythro-selective course of BF_3-catalyzed allylstannane–aldehyde condensations.[15] Treatment of a mixture of **8** and **9** with this Lewis acid gave, after heating with a catalytic quantity of CSA to effect lactonization, a difficulty separable mixture of **10** and its diastereomer in a 7.5:1 ratio (78%). The major constituent was assigned the indicated stereochemistry on the basis of extensive precedent set by less substituted congeners and X-ray crystallographic analysis of a lower homologue.[16]

Expediency and brevity were best served by concurrent chemoselective oxidation of the γ-lactone ring and (phenylthio)methyl side chain. For this purpose, the dianion of **10** was generated with 2 equiv of potassium hexamethyldisilazide. This dianion smoothly underwent 2-fold phenylselenenylation, thereby allowing for subsequent controlled hydrolysis with aqueous silver perchlorate to unmask the aldehyde, and periodate oxidation to produce the butenolide unit. The efficiency of this three-step sequence for acquiring **11** was 63% (Scheme II). Although selenoacetals are well-established intermediates,[17] little use has been made previously of selenothioacetals in synthesis. The feasibility of effecting selenoxide generation and elimination in the presence of a very reactive aldehyde carbonyl group is also noteworthy.

Once **11** had been converted into bromide **12** (99%), introduction of the remaining framework carbons was addressed. Cuprate-based displacement reactions were unsatisfactory for this purpose because of competing rapid conjugate addition to the butenolide ring. In the event, appendage of various side chains to **12** by means of Pd(0)-catalyzed vinylstannane coupling[18] proved especially general and serviceable. The pivotal macrocyclization step was probed in turn with all of these[19] and proved nonworkable in every example save one. Interconnective bonding between **12** and **13**[20] as duly promoted by Pd(0) furnished **14** (56%), a colorless oil. Reliable replacement of a tetrahydropyranyloxy substituent by bromide rested on the unique properties of 1,2-bis(diphenylphosphino)ethane tetrabromide.[21] In CH_2Cl_2, rapid interchange occurs without perturbation of the other structural elements in yields routinely in excess of 75%. This satisfying result made possible deprotection of the primary hydroxyl (62%) and its oxidation to the aldehyde level as in **15** (52%).

The transition-state model for chromous chloride induced cyclization[22] of **15** contemplated intramolecular π-facially selective attack at the aldehyde carbonyl by the flanking π-bond such that both large groups are equatorially disposed on the oxachromium six-membered ring (see **16**). Indeed, it seems that this trajectory is favored, since cyclization product **3** does form stereoselectively in 20–25% yield when admixed with 10 equiv of $CrCl_2$ and 4-Å molecular sieves in deoxygenated THF (25 °C, 5.5 h). Since two threo-selective processes are available to **15** and only one operates, the stereogenicity of the newly formed chiral centers in **3** is interlinked in a significant way with the configuration of those already present in the bromo aldehyde. The overall stereochemistry of **3** was firmly established by 2-D $^1H/^{13}C$ correlation studies.[23] Still and Mobilio's approach to asperdiol was the first to utilize the Heathcock–Hiyama allylchromium process for the stereoselective closure of a macrocycle.[24] The tolerance of yet additional functional groups to these organometallic conditions is herein demonstrated.

This method of assembling furanocembranolide systems, as demonstrated by the present direct total synthesis of **3**, should be amenable to the preparation of other members of this class. Such investigations are currently underway in this laboratory.[25]

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[16] The X-ray work was performed on the crystalline triol obtained by $LiAlH_4$ reduction of the des(*tert*-butyldimethylsiloxy)ethyl system. We emphasize that ^1H NMR correlations are especially useful and diagnostic in delineating specific diastereomers in this series.

[17] Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986.

[18] (a) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833. (b) Milstein, D.; Stille, J. K. *Ibid.* **1979**, *101*, 4992. (c) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

[19] Included in this group are various modifications of the ene reaction, allylsilane–carboxaldehyde condensations, and Cr(II)-promoted cyclization of the *Z* isomer of **15**.

[20] Prepared from the known 1,1,3-tribromo-2-methyl-1-propene (Fischetti, W.; Mak, K. T.; Stakem, F. G.; Kim, J.-L.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 948) via the following sequence of steps: (a) K_2CO_3, H_2O, Δ; (b) DHP, (TsOH); (c) CH_3Li, LiBr, Et_2O, pentane, −100 °C, then CH_3OH; (d) *t*-BuLi, DME, then Me_3SnCl.

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[23] The significant signals in **3** determined in $CDCl_3$ at 500 MHz compare very closely to those of **1** (see ref 2 for numbering):

	δ		ppm
β-H-2	2.67 (dd, J = 2.9, 15.1 Hz)	C-1	30.4
α-H-2	3.65 (dd, J = 13.2, 15.0 Hz)	C-2	47.7
H-1	2.87 (dd, J = 2.6, 13.2 Hz)	C-3	69.3
H-12	3.01 (br m)	C-4	35.3
α,β-H-11	2.55 (d, J = 7.4 Hz)	C-6	150.5
H-9	7.23 (s)	C-7	80.7
H-8	5.39 (s)	C-8	49.4
H-7	3.75 (s)	C-9	111.4
H-5	6.42 (s)		

The mass spectrum of **3** was scanned to m/z 800 to guard against the substance actually being a dimer of the structure shown.

[24] Still, W. C.; Mobilio, D. *J. Org. Chem.* **1983**, *48*, 4785.

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A Stable η^2-Silene Complex of Iridium: $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(\eta^2\text{-}CH_2{=}SiPh_2)$

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The ability of transition metals to stabilize reactive species by ligation has recently allowed isolation of silylene,[1] silene,[2] and disilene[3] coordination complexes. Such complexes have often been invoked in mechanistic proposals,[4] and recently Berry and Procopio have obtained good evidence for the participation of an osmium silene complex in a catalytic cycle.[5] We recently isolated the first stable silene complexes, $Cp^*(PR_3)Ru(H)(\eta^2\text{-}CH_2{=}SiPh_2)$ (Cp^* = $\eta^5\text{-}C_5Me_5$; **1**, R = ^iPr; **2**, R = Cy), which are apparently stabilized by the electron-rich ruthenium center.[2] Reactivity studies with **1** and **2** so far indicate only processes involving migration of hydride to the silene ligand to produce reactive 16-electron alkyl or silyl derivatives.[2] Here we report the synthesis of a second type of η^2-silene complex, $Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2{=}SiPh_2)$ (**3**), its X-ray structure, and preliminary reactivity studies that demonstrate direct interaction of reactants with the coordinated silene ligand.

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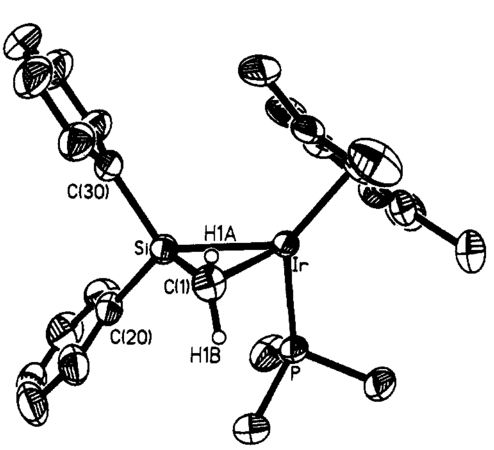
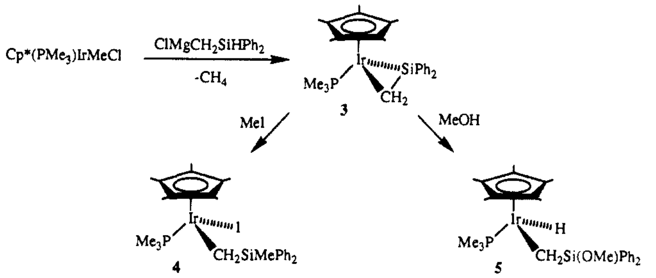


Figure 1. ORTEP view of **3**. Important bond distances (Å) and angles (deg): Ir–P 2.238 (2), Ir–Si 2.317 (2), Ir–C(1) 2.189 (8), Si–C(1) 1.810 (6), C(1)–H(1A) 0.75 (1), C(1)–H(1B) 1.00 (1), Si–C(20) 1.904 (6), Si–C(30) 1.887 (7); Si–Ir–C(1) 47.3 (2), Si–C(1)–Ir 70.1 (2), C(1)–Si–Ir 62.7 (3), C(20)–Si–Ir 127.4 (2), C(30)–Si–Ir 121.2 (2), C(20)–Si–C(1) 120.2 (3), C(30)–Si–C(1) 116.6 (3), C(20)–Si–C(30) 104.2 (3), H(1A)–C(1)–H(1B) 111 (1), H(1A)–C(1)–Ir 106 (1), H(1A)–C(1)–Si 115 (1), H(1B)–C(1)–Ir 114 (1), H(1B)–C(1)–Si 130 (1).

Scheme I



Complex **3** is synthesized by reaction of Cp*(PMe$_3$)IrMeCl[6] with ClMgCH$_2$SiHPh$_2$ in cold (−78 °C) diethyl ether (see Scheme I) and is obtained as yellow prisms from pentane.[7] Intermediates were not observed when this reaction was monitored by low-temperature ^{31}P NMR spectroscopy (−60 °C, toluene-d_8). The rate of formation of **3** ($t_{1/2}$ = ca. 1 h at −15 °C) is surprisingly fast, considering the nonlabile nature of Cp*(PMe$_3$)IrXY complexes.[8,9] The analogous reaction with ClMgCH$_2$SiDPh$_2$ in benzene-d_6 (sealed NMR tube) produced CDH$_3$ and no observable CH$_4$. Further experiments are needed to distinguish between various mechanistic possibilities for the formation of **3**.

As expected, inequivalent methylene protons and phenyl groups are observed for **3** by ^{1}H NMR spectroscopy. The ^{13}C NMR chemical shift for the silene carbon of **3** (δ −33.37) occurs at considerably higher field than the shift for analogous ethylene carbons in Cp*(PMe$_3$)Ir(η^2-CH$_2$=CH$_2$) (δ 10.55).[9] However, the $^1J_{CH}$ coupling constants for the coordinated =CH$_2$ groups in **3** (142.3 Hz) and Cp*(PMe$_3$)Ir(η^2-CH$_2$=CH$_2$) (150.6 Hz) are comparable and suggest substantial sp^2 character.[10] The mass spectrum of **3** contains a molecular ion at m/e 600 and a peak at m/e 404 resulting from loss of the silene ligand.

The crystal structure of **3** contains both enantiomers, which are related by an inversion center.[11] Bonding parameters that describe the silene ligation in **3** (Figure 1) resemble corresponding values observed for **1**.[2a] For example, the Si–C(1) bond length of 1.810 (6) Å is close to the analogous distance of 1.79 (2) Å in **1** and shorter than normal Si–C single bonds (1.87–1.91 Å). π-Bonding between iridium and the silene ligand results in a relatively short Ir–Si bond[12] (2.317 (2) Å) and concomitantly an Ir–C(1) bond that is somewhat elongated (2.189 (8) Å). For comparison, the Ir–C(sp^3) distance in Cp*(PMe$_3$)Ir(Cy)H is 2.13 Å (average),[6] the Ir–C(sp^2) distance in Cp*(PMe$_3$)Ir(CH=CH$_2$)H is 2.054 (4) Å,[9] and the Ir–Si distance in Cp*IrH$_2$(SiEt$_3$)$_2$ is 2.390 (1) Å.[12a]

The methylene protons in **3** were located and refined, allowing comparisons with the related ethylene complex Cp*(PPh$_3$)Rh(η^2-CH$_2$=CH$_2$).[13] Whereas in the latter compound there is considerable twisting of the CH$_2$ groups relative to one another about the C=C bond, no such torsional strain is found in **3**. Thus the H(1A)–C(1)–Si–C(20) and H(1B)–C(1)–Si–C(30) torsion angles are equivalent (142°). The nonplanarity of the diphenylsilene ligand may be described by angles between the Si–C(1) bond and the Si,C(20),C(30) and C(1),H(1A),H(1B) planes.[14] In **3** these angles are 17.3° for the CH$_2$ group and 39.2° for the SiPh$_2$ group, which can be compared to analogous angles of 19° and 29° for the CH$_2$ groups of Cp*(PPh$_3$)Rh(η^2-CH$_2$=CH$_2$). In **1** the SiPh$_2$ group is tilted by 36.2° (average) away from the ruthenium atom. The sum of the C–Si–C angles in **3** (341°) suggests some sp^2 character at silicon, but slightly less than was observed in **1** (343°). Overall the spectroscopic and structural data are consistent with a high degree of metal-to-silene π-back-bonding, but C=Si double-bond character is also evident.

Complex **3** is quite robust, exhibiting no decomposition when heated at 140 °C for several days in the presence of excess PMe$_3$. Also, no sign of reaction was observed when the complex was exposed to UV irradiation for 8 h (in benzene-d_6) or when pressurized with hydrogen (100 psi, benzene solution, 24 h). Reactions with MeI and MeOH result in clean rupture of the Ir–Si bond to afford the isolable complexes **4** and **5**[7] (see Scheme I). For comparison, Werner has shown that Cp(P^{i}Pr$_3$)Ir(η^2-CH$_2$=CH$_2$) loses ethylene upon reaction with MeI to give Cp(P^{i}Pr$_3$)IrMeI.[15]

Following the synthetic procedure for **3**, we have also prepared the silene complexes Cp*(PMe$_3$)Ir(η^2-CH$_2$=SiMe$_2$) (**6**) and Cp*(PMe$_3$)Rh(η^2-CH$_2$=SiPh$_2$) (**7**). These species have so far not been isolated in pure form, but were characterized by ^{13}C and ^{31}P NMR spectroscopy and by high-resolution mass spectroscopy.[7] A byproduct in the formation of **6** is Cp*(PMe$_3$)Ir(Me)H,[6] which may result from β-hydrogen elimination by Cp*(PMe$_3$)Ir(Me)CH$_2$SiHMe$_2$.[12e] In reactions between Cp*(PCy$_3$)IrMeCl and the Grignards ClMgCH$_2$SiHR$_2$ (R = Me or Ph), the latter process is more pronounced, with the hydrido methyl complex Cp*(PCy$_3$)Ir(Me)H (**8**) being formed in high yields (>80%).[7]

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[7] Characterization data for new compounds is contained in the supplementary material.

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[11] C$_{26}$H$_{36}$SiPIr, triclinic, $P\bar{1}$, a = 10.380 (3) Å, b = 10.523 (3) Å, c = 12.562 (5) Å, α = 75.52 (3)°, β = 82.11 (3)°, γ = 77.08 (2)°, V = 1290 (1) Å^3, Z = 2, R_F = 3.74%, R_{wF} = 4.76%.

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Supplementary Material Available: Characterization data for 3–8 and tables of crystal, data collection, and refinement parameters, atomic coordinates and isotropic displacement parameters, bond distances and angles, and hydrogen atom coordinates for 3 (12 pages); listings of observed and calculated structure factors for 3 (27 pages). Ordering information is given on any current masthead page.

Modulation of Interprotein Electron Transfer Energetics by Heme-Ligand Variation

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The coordination environment of the metal ion in electron-transfer (ET) metalloproteins usually is fixed. In contrast, mixed-metal hemoglobin hybrids, [MP,Fe(L)P],[1] are ideal for studying the specific role of the metal ligands in interprotein long-range ET[2-4] because the exogenous ligand L coordinated to FeP is easily varied (neutral L ≡ L^0 = H_2O, ImH; anionic L ≡ X^- = CN^-, F^-, N_3^-) with minimal structural perturbation.[5,6] We report here a dramatic dependence on ligand of both photoinitiated and thermally activated ET (eqs 1 and 2, respectively),

$$\underset{A^*}{[^3(\mathrm{MP}),\mathrm{Fe}^{3+}(\mathrm{L})\mathrm{P}]} \xrightarrow{k_t} \underset{I}{[(\mathrm{MP})^+,\mathrm{Fe}^{2+}(\mathrm{L})\mathrm{P}]} \tag{1}$$

$$\underset{I}{[(\mathrm{MP})^+,\mathrm{Fe}^{2+}(\mathrm{L})\mathrm{P}]} \xrightarrow{k_b} \underset{A}{[(\mathrm{MP}),\mathrm{Fe}^{3+}(\mathrm{L})\mathrm{P}]} \tag{2}$$

between the α_1 and β_2 subunits within these hybrids. Our kinetic results show that anionic ligands remain bound throughout the ET cycle, and electrochemical measurements indicate that anion binding modulates the rate constants k_t and k_b through major changes in energetics. The data are consistent with a reorganization energy of λ ~ 1 eV for *both* reactions and suggest that the preexponential of k_b is enhanced over that of k_t.[7,8]

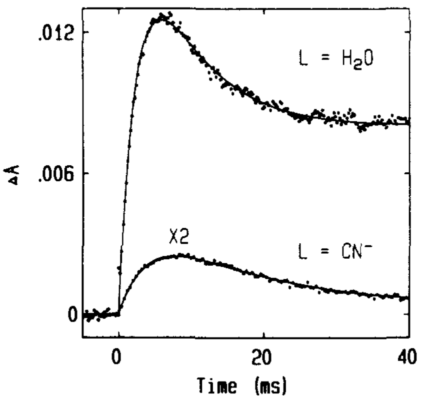

Figure 1. Kinetic progress curves monitored (λ = 435 nm, T = 278 K) for the electron-transfer intermediate (B) formed upon flash photolysis of [β(ZnP),α(Fe^{3+}(L)P)]. Experimental points (•) and nonlinear least-squares fits (solid lines) for L = H_2O and L = CN^- are presented, with absorbance changes normalized to a zero-time triplet concentration (A_0*) = 10^{-6} M. For [β(ZnP),α(Fe^{3+}(H_2O)P)], k_b = 345 (30) s^{-1}, k_p = 134 (15) s^{-1}; for [β(ZnP),α(Fe^{3+}(CN^-)P)], k_b = 243 (25) s^{-1}, k_p = 65 (8) s^{-1}.

Table I. Ligand Dependence of k_b^M and k_t^M within [MP,Fe^{3+}(L)P][a]

	k_t, s^{-1}		k_b, s^{-1}	
L	M = Zn	M = Mg	M = Zn	M = Mg
H_2O	80 (20)	30 (6)	325 (30)	155 (20)
Im[b]	75 (25)	35 (10)	300 (35)	150 (25)
CN^-	6 (3)	5 (2)	243 (25)	135 (10)
F^-	6 (4)	3 (2)	200 (35)	105 (10)
N_3^-	6 (4)	5 (3)	230 (40)	115 (15)

[a] Rate constants are the average of 5–10 measurements at 278 K. Rate constants for exogenous ligands were invariant over the concentration ranges: Im,[b] 200–500 mM; CN^- and N_3^-, 0.5–5 mM; F^-, 0.8–1.2 M. [b] For M = Mg, Im = ImH; for M = Zn, Im = 1-methylimidazole.

The rate constant for both the A* → I and the I → A processes can be determined after photoexcitation of A by analyzing the time course of the ET intermediate, I. This can only be done by monitoring the absorbance changes at an A*/A isosbestic point (λ = 435 nm for M = Zn; λ = 432 nm for M = Mg).[2a] At all other wavelengths, the transient absorbance changes are dominated by A*. In the kinetic traces of Figure 1,[9] the long-time exponential decays correspond to the net disappearance (rate constant k_p) of A*, which also can be measured by following A* directly. Deactivation of A* can occur by intrinsic triplet decay (rate constant k_D), by electron transfer (rate constant k_t), and possibly through other processes such as Forster energy transfer (rate constant k_o): $k_p = k_D + k_t + k_o$.[2b] Measurements of triplet quenching give the quenching rate constant, $k_q \equiv k_p - k_D = k_t + k_o$ which is therefore an upper bound to k_t. Recently, we noted that k_t can be determined directly by quantitation of the kinetic transient for B, whose magnitude is directly proportional to k_t.[2a] Analysis of the relatively large absorbance changes for [$(ZnP)^+$,Fe^{2+}P] (Figure 1) gives $k_t^{Zn}(H_2O)$ = 90 (30) s^{-1}, confirming, within error, the assignment[2b] of $k_t \approx k_p - k_D$ for L = H_2O. For [ZnP,Fe^{3+}(CN^-)P], both the long-time exponential fall of I and the triplet decay of A* give $k_t \leq k_q$ = 14 (4) s^{-1}; analysis of the smaller absorbance change associated with I (Figure 1) gives an even lower ET rate constant, $k_t^{Zn}(CN^-)$ = 6 (3) s^{-1}. Thus,

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[‡] Virginia Commonwealth University.

(1) (a) The symbol in brackets for the hybrid represents an [α_2,β_2] T-state tetramer of hemoglobin (Hb), in which the irons in either the α or the β chains have been replaced with M = Mg or Zn. For L = H_2O, the data refer to [β(MP),α(Fe^{3+}(L)P)]. For the remaining ligands, data were obtained for both [β(MP),α(Fe(L)P)] and [α(MP),β(Fe(L)P)] and were similar. (b) Other abbreviations: P = protoporphyrin IX; ImH = imidazole; Mb = myoglobin; k_t^M(L) and k_b^M(L) refer to the photoinitiated and thermal ET rate constants in [MP,Fe^{3+}(L)P].

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