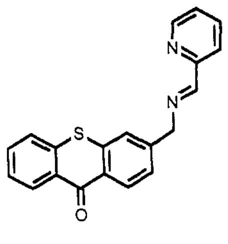
Not all catalytic reactions with **2** show such high turnovers. Chlorination of **3** at C-9, or of **4** at C-9, were successful with Ni^{2+} and **2** because of metal coordination to the OH but required stoichiometric amounts.[1] We have now devised a new template catalyst that indeed performs the important C-9 chlorination of **3** with reasonable turnovers. At the same time, we have developed evidence, described in the accompanying paper, that the remarkably high turnovers sometimes observed with **2** and with the new template result from a special new bifunctional chlorination mechanism.

Since the eventual decomposition of **2** involves replacement of iodine by chlorine,[1] we examined the use of sulfur atom templates that might be more stable. The diphenyl sulfide[3] analogue **5** was too easily oxidized, and even a related thiophene[4] system **6** showed only 10^4 turnovers with **1**. However, the thioxanthone template **7** was an excellent catalyst. Substrate **1** was 80% converted to C-9 chlorosteroid, with 20% recovered **1**, when 15 mM **1** was irradiated with 3 equiv. of $PhICl_2$ and 5 equiv. of undissolved KOAc in CH_2Cl_2 with 15×10^{-9} mM Ni^{2+} and 15×10^{-12} mM **7** for 10 min (275-W sunlamp) at 0 °C (or at 20 °C) and then allowed to react further[5] without irradiation for 1.5 h. Thus 10^{11} to 10^{12} turnovers of **7** are occurring. Template **7** also catalyzed the C-9 chlorination of **3** and **4**, with ca. 10^2 turnovers.



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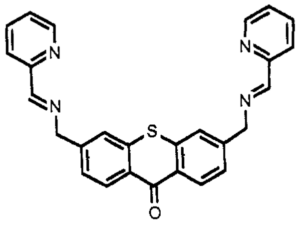

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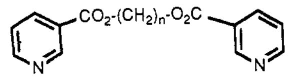
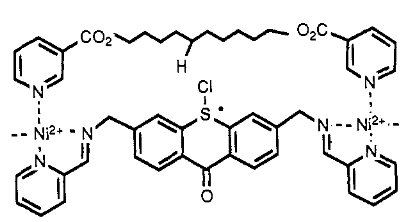


9a: n = 10

9b: n = 6

9c: n = 4



Thioxanthone **7** was easily prepared by reaction of thiosalicylic acid with *N*-(*m*-iodobenzyl)acetamide (irradiation)[6] followed by intramolecular acylation and further obvious steps. In a similar way, using *N*-(*m*-iodobenzyl)acetamide and Na_2S and then $COCl_2$, we were able to prepare **8**. This species carries two M^{2+} binding groups, so its double Ni^{2+} or Cu^{2+} complex can coordinate both ends of a flexible substrate and chlorinate the middle.[7]

Indeed, reaction of the decane-1,10-diol derivative **9a** at 15 mM with 3 equiv of $PhICl_2$ and 5 equiv of KOAc along with 15×10^{-4} mM **8** and 30×10^{-3} mM Ni^{2+} $(ClO_4^-)_2$ under irradiation for 1 h at 0 °C afforded the monochlorinated **9a** with 32% recovered **9a** (at 15×10^{-3} mM **8**, no **9a** is detected). By methods we have described earlier[8] we were able to establish that the chlorination occurs essentially exclusively at the middle carbon C-5, as expected if **9a** coordinates to a fully extended conformation of the **8**-[Ni^{2+}]$_2$ complex. This conformation is apparently the preferred one, because of electrostatic repulsion[9] by the Ni^{2+} ions, since the shorter hexanediol and butanediol derivatives **9b** and **9c** are not chlorinated by the **8**-[Ni^{2+}]$_2$ complex. Models show that they should also be able to bind at both ends and be chlorinated, if the template does not have the fully extended conformation.

This work shows that catalytic templates based on the thioxanthone system can have even better turnover numbers with steroids, compared with aryl iodide templates. Even a simple underivatized steroid such as **3** can be catalytically functionalized. The thioxanthone system also easily carries more than one binding group, as in **8**, to permit selective catalytic reactions on flexible substrates. In the accompanying paper[10] we will describe the evidence that some thioxanthone or aryl iodide catalyses involve a novel bifunctional mechanism.

Acknowledgment. This work has been supported by the NSF.

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[3] Breslow et al. (Breslow, R.; Wife, R. L.; Prezant, D. *Tetrahedron Lett.* **1976**, 925) report use of an attached diphenyl sulfide group in the radical relay reaction.

[4] Cf., for use of a thiophene template: Breslow, R.; Heyer, D. *J. Am. Chem. Soc.* **1982**, *104*, 2045.

[5] The reaction requires this additional time to go to completion. Such a dark reaction, initiated by irradiation, is not sensible for a normal free radical chain process but is expected for the mechanism proposed in the following paper.

[6] Cf.: Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173-3174.

[7] For selective benzophenone attack on a flexible chain oriented by double coordination, see: Breslow, R.; Rajagopalan, R.; Schwarz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2905.

[8] Breslow, R.; Rothbard, J.; Herman, F.; Rodriguez, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 1213.

[9] By standard calculations (Cf.: Tanford, C. *J. Am. Chem. Soc.* **1957**, *79*, 5348; a modification of, Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506, 513) we find the interaction energy is large enough (ca. 2.7 kcal/mol) to account for this conformational preference.

[10] Breslow, R.; Mehta, M. P. *J. Am. Chem. Soc.*, following paper in this issue.

A Novel Bifunctional Chlorination Mechanism in Template Catalyzed Directed Functionalization with High Effective Molarities and Rates Approaching Diffusion Control

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Received June 13, 1986

We have described the catalytic chlorination of 3-α-cholestanyl nicotinate (**1**) by mixed-metal complexes with an aryl iodide[1] template (**2**) and a thioxanthone[2] template (**3**). These reactions showed very high catalytic turnovers, ca. 10^9 and 10^{11}–10^{12} respectively, but this might simply mean that loss of catalyst through side reactions occurs only very slowly. However, the reactions also involve astonishing apparent effective molarities (EM's) of the catalysts.

At a concentration of 15×10^{-9} mM the catalyst **2**, in a mixed complex, performs an essentially complete (>99%) selective chlorination on 15 mM **1** with 3 equiv. of $PhICl_2$. However, in control reactions under the same conditions uncomplexed aryl iodides such as **2** in the absence of M^{2+}, or PhI itself in the presence of Ni^{2+}, do not perform *any* intermolecular reaction (<4%) even at 15 mM aryl iodide. In such controls we begin to see random intermolecular attack only with 50 equiv of $PhICl_2$ chlorinating

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[1] Breslow, R.; Mehta, M. P. *J. Am. Chem. Soc.* **1986**, *108*, 2485-2486.

[2] Breslow, R.; Mehta, M. P. *J. Am. Chem. Soc.*, preceding paper in this issue.

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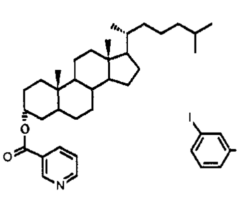

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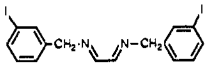

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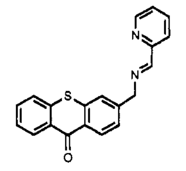

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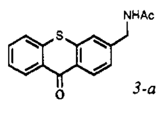

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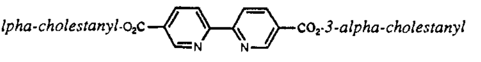

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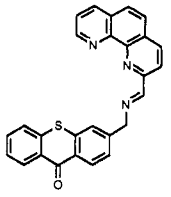

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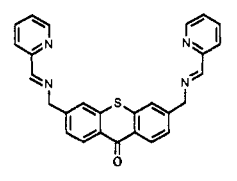

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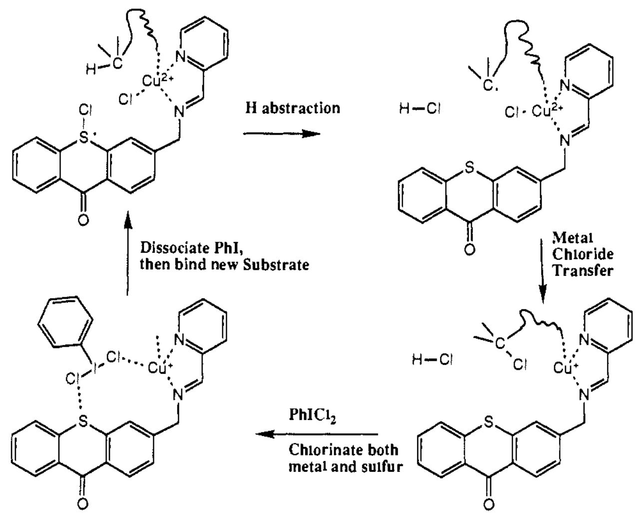
agent. Similarly, the complexed thioxanthone **3** performs a directed chlorination at 15 × 10^{-12} mM, but uncomplexed thioxanthone derivative **4**, or **3** without M^{2+}, can be added at 15 mM to control reactions without effect: the steroid **1**, or the corresponding benzoate, are not attacked by 3 equiv. of $PhICl_2$ under any conditions examined.

The ratio of a first-order rate constant (for intramolecular or intracomplex reaction) to a second-order rate constant (for the corresponding bimolecular reaction) is normally expressed as the effective molarity for the first-order case.[3] Since the catalyzed reaction occurs with very low concentrations of complexing catalyst while no reaction occurs with high concentrations of noncomplexing analogues, our reactions have apparent EM's of at least 10^{10} M (**2**) or 10^{13} M (**3**): Such enormous EM's are precedented for a very few intramolecular reactions with rigid proximity, but out of the question for flexible systems such as the metal complexes of **2** or **3** with **1**.[3] Thus, something special must be going on.[4]

We see two classes of reactions. In those with such abnormally high apparent EM's only three sites on the metal are occupied by catalyst and substrate, and a fourth metal site is within reach of the substrate position being attacked. This is true for the Ni^{2+} or Cu^{2+} mixed complexes of **2** or **3** with **1**. By contrast, we see normal EM's in all cases that do not meet these criteria. For example, with substrate **5** the catalyst **2** has an EM of only 10^3, and all M^{2+} sites are occupied. Similarly, with substrate **1** the catalyst **6** has an EM of only 10^4, and again there is no free fourth M^{2+} site. In the accompanying paper[2] we describe chlorination of two hydroxy steroids by catalyst **3** with EM's of 10^3 M; here there is a free fourth M^{2+} position in the mixed complex, but it is not within reach of C-9 where chlorination occurs. For these normal cases the radical relay mechanism within a mixed complex is probably occurring. In the abnormal cases a new mechanism must be involved.

It is likely that the free M^{2+} site carries a chloride ion in our system. It is well-known[5] that Cu^{2+} chlorides can chlorinate carbon radicals, and this is probably also true for Ni^{2+} chloride.[6]

Scheme I. Metal and Sulfur Template Atoms Cooperate Both in a Sequential Reaction with the Substrate and in a Simultaneous Reaction with $PhICl_2$



However, in its simplest form invoking only this radical trapping cannot explain our results. In control reactions with Ni^{2+} complexed to **1** but without template there is no intermolecular attack under our normal reaction conditions. Furthermore, a catalyst performing 10^{11} turnovers in 6000 s, even at a diffusion-controlled rate, must be reacting only with species whose concentration exceeds 1.5 mM. Thus there is enough time for reaction with substrate, but no possibility of reaction with a free radical of low concentration.

The most attractive explanation entails cooperative reaction by template $ArICl^\bullet$ or $Ar_2SCl^\bullet$ and metal in attack on the C–H bond and also in subsequent reaction with $PhICl_2$. Some evidence for this is seen in the studies with **7**, which can bind two M^{2+} ions. In the accompanying paper[2] we have reported evidence that with two bound Ni^{2+} ions **7** has an extended conformation, with the Ni^{2+} not near sulfur. We find that **7**, with two bound Ni^{2+}, chlorinates **1** with only 10^4 turnovers. By contrast, with *one* Ni^{2+} it need not have the extended conformation and it gives ca. 10^{10} turnovers, similar to the results with **3**. Thus for very high turnovers, and EM's, the Ni^{2+} and sulfur must be close.

It is geometrically impossible for the complexed metal to bind to the sulfur atom of **3** and essentially impossible for them to share a single chlorine atom. Thus we propose that both the sulfur and the metal carry their own chlorines and that these cooperate in a bifunctional sequential substitution reaction, as Scheme I shows. Then in the critical step the resulting M(I) species reacts with $PhICl_2$ in a concerted reaction forming M(II) chloride, iodobenzene, and the template chlorine radical.[7] This bifunctional double chlorination avoids the formation of free $PhICl\cdot$ and its subsequent bimolecular reaction with a free template, as occurs in reactions without the bifunctional metal/template complex. Thus bifunctional complexed reactions occur at *two stages* of the process, leading to the remarkably high overall preference for the intracomplex reaction.

As expected from this, the Cu(I) complex of template **3** reacts directly (degassed) with $PhICl_2$ to chlorinate **1** (10^6 turnovers within 10 min), without need for the irradation that is needed to start the Cu(II) or Ni(II) reactions. There are a number of other predictions based on this bifunctional mechanism that can help establish it in detail. However, the general conclusion that the high EM's and rates of some of our reactions require a bifunctional

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(3) Cf.: Kirby, A. J. *Adv. Phys. Org. Chem.* **1981**, *17*, 183–276. Page, M. I. *Chem. Soc. Rev.* **1973**, *2*, 295.

(4) We first realized the need for some special explanation while attempting to answer a particularly penetrating question posed by Prof. Michael McBride, Yale University.

(5) Kochi, J. In Free Radicals; Kochi, J., Ed.; Wiley-Interscience:New York, 1973, Vol. I, chapter 11.

(6) Some radical chemistry that interconnects Ni(II) and Ni(I) is known (Tsou, T. T.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 1930–1937). Alternatively, the steroid radical might add to Ni(II); bifunctional reaction of this organometal intermediate with $PhICl_2$ would lead to R–Cl and the recharged catalyst.

(7) When the template is an aryl iodide, there would be an equilibrium between template chlororadical and $PhICl^\bullet$ in the encounter complex; the equilibrium is displaced by template-directed attack on substrate.

mechanism, with good proximity of the organic and inorganic catalytic centers, seems clear. It is a process with considerable synthetic potential beyond the examples reported here.

Acknowledgment. Support of this work by the NSF is gratefully acknowledged.

Preparation, Characterization, and Structure of $Fe_4(CO)_{12}[Au(PPh_3)]_2BH$: An Iron-Gold Borido Cluster Violating the H/AuPR$_3$ Structural Analogy

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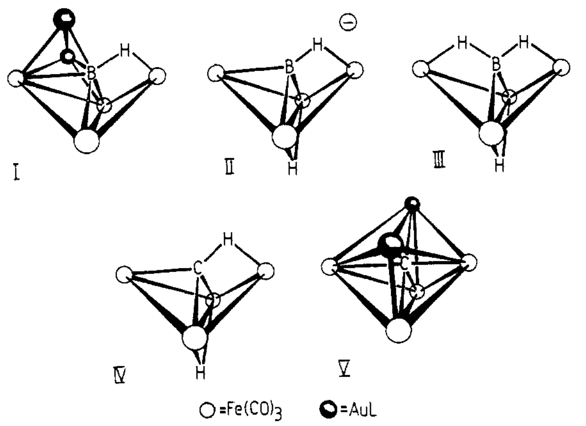
Metallaboranes are predominantly exemplified by boron-rich rather than metal-rich clusters, and in a variety of cases, replacement of BH_2 for isoelectronic CH units in a metallaborane leads to a known organometallic cluster.[1] However, in contrast to metallaboranes, metal–carbon clusters also include a category of compound in which a carbon atom is fully or partially encapsulated by metal atoms: the so-called metal carbide clusters.[2,3] The replacement of metal cluster[4-7] and, to a far lesser extent, borane cluster[8] hydrogen atoms by gold(I) phosphine[4,5,9] has been exploited to synthesize some novel compounds with structures often related to the parent hydrogen-containing species via direct H/AuL (L = PR_3) substitution. Indeed, it has been noted that the structures of transition-metal–gold clusters can be used directly to model the analogous transition-metal hydrides[4,10] and to "isolate" isomers which are unstable as the hydride cluster but stable after H/AuL replacement.[4] To our knowledge, no H/AuL replacement has been reported for a metallaborane. Here we report the synthesis of $Fe_4(CO)_{12}[Au(PPh_3)]_2BH$ (I).

I was prepared by the addition of $[HFe_4(CO)_{12}BH]PPN$[11] (II) (PPN = bis(triphenylphosphine)iminium) (0.04 mmol) in 4 mL of CH_2Cl_2 to an excess of $Au(PPh_3)Cl$. After 30 min of stirring at room temperature, solvent was removed and the product extracted from PPNCl and unreacted $Au(PPh_3)Cl$ with diethyl ether. The major product[12] was a green-brown, moderately air sensitive, neutral material collected as the first band after elution with hexanes/CH_2Cl_2 (1:2) on a silica gel column. A single crystal suitable for X-ray diffraction was grown from CH_2Cl_2 layered with hexane.[13]

Table I. Selected Distances (Å) and Angles (deg) from I

Distances			
Au(1)–Au(2)	2.943 (1)	Fe(4)–C(12)	2.42 (1)
Au(1)–Fe(1)	2.630 (1)	Au(1)–B	2.36 (1)
Au(1)–Fe(2)	2.852 (2)	Au(2)–B	2.35 (1)
Au(2)–Fe(2)	2.606 (1)	Fe(1)–B	2.07 (1)
Fe(1)–Fe(2)	2.720 (2)	Fe(2)–B	2.00 (1)
Fe(1)–Fe(3)	2.671 (2)	Fe(3)–B	2.01 (1)
Fe(1)–Fe(4)	2.578 (2)	Fe(4)–B	2.13 (1)
Fe(2)–Fe(4)	2.708 (2)	Au(1)–P(1)	2.299 (3)
Fe(3)–Fe(4)	2.655 (3)	Au(2)–P(2)	2.302 (2)
Fe(1)–C(12)	1.75 (1)		
Angles			
Au(1)–Au(2)–B	51.4 (3)	Au(2)–B–Fe(4)	125.5 (6)
Au(1)–Au(2)–Fe(2)	61.5 (0)	Fe(1)–Fe(2)–Fe(4)	56.7 (1)
Au(2)–Au(1)–B	51.2 (3)	Fe(1)–Fe(2)–B	49.1 (3)
Au(2)–Au(1)–Fe(1)	98.0 (0)	Fe(1)–Fe(3)–Fe(4)	57.9 (1)
Au(2)–Au(1)–Fe(2)	53.4 (0)	Fe(1)–Fe(3)–B	50.1 (3)
Au(1)–Fe(1)–B	58.8 (3)	Fe(1)–Fe(4)–Fe(2)	61.9 (1)
Au(2)–Fe(2)–B	59.7 (3)	Fe(1)–Fe(4)–Fe(3)	61.3 (1)
Au(2)–B–Fe(1)	144.4 (5)	Fe(1)–Fe(4)–B	51.1 (3)
Au(2)–B–Fe(2)	73.0 (4)	Fe(1)–B–Fe(2)	83.8 (4)
Au(2)–B–Fe(3)	126.6 (5)		
Au(1)–Fe(1)–Fe(2)	64.4 (0)	Fe(1)–B–Fe(3)	81.8 (5)
Au(1)–Fe(1)–Fe(3)	84.4 (1)	Fe(1)–B–Fe(4)	75.7 (4)
Au(1)–Fe(1)–Fe(4)	110.8 (1)	Fe(2)–Fe(1)–Fe(3)	94.0 (1)
Au(1)–Fe(2)–B	54.8 (3)	Fe(2)–Fe(1)–Fe(4)	61.4 (1)
Au(1)–Fe(2)–Fe(1)	56.3 (0)	Fe(2)–Fe(1)–B	47.0 (4)
Au(1)–Fe(2)–Fe(4)	100.8 (1)	Fe(2)–Fe(4)–Fe(1)	61.9 (1)
Au(1)–B–Au(2)	77.3 (3)	Fe(2)–Fe(4)–Fe(3)	97.7 (1)
Au(1)–B–Fe(1)	72.5 (4)	Fe(2)–B–Fe(3)	158.9 (6)
Au(1)–B–Fe(2)	81.3 (4)	Fe(2)–B–Fe(4)	81.8 (5)
Au(1)–B–Fe(3)	108.8 (6)	Fe(3)–Fe(1)–Fe(4)	60.7 (1)
Au(1)–B–Fe(4)	145.3 (5)	Fe(3)–Fe(1)–B	48.2 (3)
Au(2)–Fe(2)–Au(1)	65.1 (0)	Fe(3)–Fe(4)–B	48.2 (4)
Au(2)–Fe(2)–Fe(1)	104.4 (1)	Fe(4)–Fe(3)–B	52.1 (3)
Au(2)–Fe(2)–Fe(4)	97.2 (1)		

The X-ray crystal structure of I (Figure 1) shows the near encapsulation of the boron by six metal atoms. Selected bond parameters are given in Table I. The "butterfly" of iron atoms present in II[11] and in its conjugate acid, III,[14] is retained in I. The boron resides 0.37 (1) Å above the Fe(2)- - -Fe(3) wingtip axis.[15]



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(1) Housecroft, C. E.; Fehlner, T. P. *Adv. Organomet. Chem.* **1982**, *21*, 57.

(2) Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.

(3) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1.

(4) Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* **1981**, *103*, 7648.

(5) Bateman, L. W.; Green, M.; Mead, K. A.; Mills, R. M.; Slater, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2599.

(6) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237 and references therein.

(7) Horwitz, C. P.; Holt, E. M.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8136 and references therein.

(8) Wynd, A. J.; Robins, S. E.; Welch, D. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 819. Beckett, M. A.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1984**, 1427.

(9) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171.

(10) Hall, M. B.; Halpin, C. F. *J. Am. Chem. Soc.* **1986**, *108*, 1695.

(11) Housecroft, C. E.; Fehlner, T. P. *Organometallics* **1986**, *5*, 379.

(12) $Fe_4(CO)_{12}[Au(PPh_3)]_2BH$: 28.7-MHz ^{11}B NMR ($(CD_3)_2CO$, 20 °C) δ +141.3 (br s, fwhm = 185 Hz, $\{^1H\}$ fwhm = 110 Hz, $J_{BH} \simeq 90$ Hz); 36.2-MHz ^{31}P NMR ($(CD_3)_2CO$, –70 °C) δ +53.0; 89.56-MHz ^1H NMR ($(CD_3)_2CO$, 20 °C) δ +7.57–7.25 (m, 30 H, Ph), –9.1 (br, 1 H, FeHB); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2056 m, 2009 vs, 1996 vs, 1967 m, 1925 sh.

(13) Crystal data for I: $C_{48}H_{31}Au_2BFe_4P_2O_{12}$, $M_r = 1489.8$, triclinic, $P\bar{1}$, $a = 10.870$ (3) Å, $b = 12.114$ (3) Å, $c = 20.466$ (6) Å, $\alpha = 80.23$ (2)°, $\beta = 83.17$ (2)°, $\gamma = 73.40$ (2)°, $V = 2537.9$ Å^3, $Z = 2$, $D_c = 1.949$ g cm^{-3}, λ(Mo Kα) = 0.710 73 Å, $\mu = 70.2$ cm^{-1}, green-black, 0.24 × 0.30 × 0.37 mm, 293 K. Nicolet R3m/μ diffractometer with graphite monochromator. Corrections for decay (linear, 4%) and absorption (empirical, $T_{max}/T_{min} = 2.23$). Of 8320 reflections collected (max $2\theta = 48°$), 7942 were unique $R_{int} = 1.2\%$), and 5474 were considered observed with $F_o \geq 3\sigma(F_o)$. Phenyl rings; rigid, planar constraint. All non-hydrogen atoms anisotropic; hydrogen atoms idealized; isotropic contributions (H atom on boron ignored). Refinement of 550 parameters: $R_F = 4.49\%$, $R_{wF} = 5.20\%$, GOF = 1.102, $\Delta/\sigma = 0.08$, $\Delta\rho = 1.13$ e Å^{-3} (1.28 Å from Au(2)). All programs in SHELXTL and P3 program libraries (Nicolet Corp., Madison, WI).

(14) Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825.

(15) In III, the boron lies 0.31 Å above the wingtip Fe–Fe axis.

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