

complex (tetracyanoethylene)Ir(CO)Cl(PPh₃)₂.^{22,23} All have acute C–Ir–C angles, linear Cl–Ir–CO units, and P–Ir–P angles near 115°.

The finding that the iridium ion is bound to an a–b edge of C₇₀ is not unexpected in light of the structural information on (η²-C₆₀)Pt(PPh₃)₂⁶ and (η²-C₆₀)Ir(CO)Cl(PPh₃)₂.⁷ In both of those structures it was noted that metal binding was accompanied by local distortion of the C₆₀ so that the two carbon atoms involved in coordination were pulled out from the C₆₀ surface. In the idealized C₇₀ structure, simple geometric considerations show that the a–b bond is the most accessible bond for coordination of this sort. The other C–C bonds at 6:6 ring fusions (c–c, d–e, and e–e) all have a more flattened local structure, which would require much larger distortion to accommodate metal coordination. Thus while eight isomeric forms of (η²-C₇₀) coordination by metal centers are possible, we suspect that coordination at the a–b bond will be most favored as found here. Given the success of our efforts in obtaining ordered crystals of (η²-C₆₀)Ir(CO)Cl(PPh₃)₂ and a single isomer of (η²-C₇₀)Ir(CO)Cl(PPh₃)₂, it appears that Ir(CO)Cl(PPh₃)₂ will be a useful reagent for obtaining crystalline samples of the higher fullerenes whose structures remain to be determined.²⁴

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Supplementary Material Available: Drawings of **1** showing atomic numbering, details of the data collection and refinement of the structure, and tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions of **1** (16 pages); listing of observed and calculated structure factors for (η-C₇₀)Ir(CO)Cl(PPh₃)₂ (34 pages). Ordering information is given on any current masthead page.

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Allylbarium in Organic Synthesis: Unprecedented α-Selective and Stereospecific Allylation of Carbonyl Compounds

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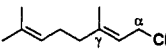
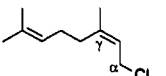
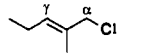
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The organometallic compounds of heavier alkaline-earth metals have found little application in organic synthesis, since they do not offer any advantages over Grignard reagents.¹ We have been interested in using barium or strontium reagents with the anticipation that such species should exhibit stereochemical stability

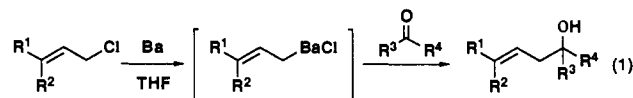
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Table I. Regio- and Stereoselective Allylation of Carbonyl Compounds with Allylic Barium Reagents Prepared from Allylic Chlorides^a

allylic chlorides ^b	carbonyls	yield, % ^c	α : γ ^d	E : Z ^d
(E)- ^γ C ₇ H ₁₅ CH=CHCH ₂ Cl	PhCHO	80	97 : 3	>99 : 1
	^γ C ₈ H ₁₁ CHO	82	98 : 2	97 : 3
	(E)-PhCH=CHCHO	73 ^e	94 : 6	98 : 2
(Z)- ^γ C ₇ H ₁₅ CH=CHCH ₂ Cl	Cyclohexanone	95	99 : 1	99 : 1
	Acetophenone	94	96 : 4	99 : 1
	^γ C ₈ H ₁₁ CHO	75	86 : 14	2 : 98
(Z)- ^γ CH ₃ CH=CHCH ₂ Cl	Cyclohexanone	89	75 : 25	2 : 98
	^γ C ₈ H ₁₁ CHO	56	77 : 23	1 : 99
		PhCHO	90	92 : 8
^γ C ₈ H ₁₁ CHO		90	94 : 6	>99 : 1
Cyclohexanone		98	89 : 11	>99 : 1
	PhCHO	89	94 : 6	2 : 98
	^γ C ₈ H ₁₁ CHO	73	96 : 4	< 1 : 99
	Cyclohexanone	98	91 : 9	< 1 : 99
	^γ C ₈ H ₁₁ CHO	64	94 : 6	>99 : 1
	Cyclohexanone	92	96 : 4	99 : 1

^a Allylation was carried out by using an allylic chloride, barium, and carbonyl compound (2, 2, and 1 equiv, respectively) at -78 °C for 30 min. ^b Stereochemically pure (>99%) allylic chlorides were used. ^c Isolated yield. ^d Determined by GC analysis. ^e 1,4-Adduct was also obtained in 14% yield.

markedly different from that of the ordinary magnesium reagent.² Herein, we disclose the first direct preparation of allylbarium by reaction of in situ generated barium metal with various allylic chlorides,³ and regio- and stereoselective allylation of carbonyl compounds using these allylmetals (eq 1).



Highly reactive barium was readily prepared by the reduction of barium iodide⁶ with 2 equiv of lithium biphenylide⁷ in dry THF at room temperature for 30 min. The dark brown suspension thus obtained was exposed to allylic chlorides at -78 °C. A slightly exothermic reaction takes place immediately to give a reddish suspension of allylic barium. The barium reagent reacts with a variety of carbonyl compounds cleanly at -78 °C in a few minutes to produce the homoallylic alcohol with remarkably high α-selectivity and retention of stereochemistry of the starting halides. It is well established that the corresponding magnesium or calcium reagent gave the γ-substituted product predominantly and the allylation with the lithium reagent was less selective.⁸ Table I summarizes the results obtained for the reaction of a variety of carbonyl compounds with barium reagents generated from E- or Z-allylic chlorides in THF at -78 °C. All reactions resulted in high yields with remarkable α-selectivities not only with aldehydes but also with ketones. In marked contrast to the allylmagnesium or allyllithium, the double-bond geometry of the allylbarium was

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(7) Highly reactive calcium has been prepared by the lithium biphenylide reduction of CaBr₂ or CaI₂; see: Wu, T.-C.; Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1990**, 55, 5045.

(8) α:γ ratios of the products obtained by the reaction of benzaldehyde with geranylmetals: M = Mg, α:γ = <1:99 (99% yield); M = Ca, α:γ = 8:92 (38% yield); M = Li, α:γ = 47:53 (36% yield); M = Ce, α:γ = 72:28 (52% yield); preliminary results by A. Yanagisawa, S. Habaue, and H. Yamamoto.

completely retained in each case.²

A representative experimental procedure is given by the reaction of benzaldehyde with geranylbarium reagent: To a suspension of anhydrous BaI₂⁶ (435 mg, 1.1 mmol) in THF (5 mL) was added at room temperature a preformed lithium biphenylide, prepared from freshly cut lithium (16 mg, 2.3 mmol) and biphenyl (360 mg, 2.3 mmol) in THF (5 mL), and the reaction mixture was stirred for 30 min at room temperature. To the resulting brown suspension of barium powder in THF was slowly added a solution of geranyl chloride (170 mg, 0.98 mmol) in THF (1.5 mL) at -78 °C. After being stirred for 30 min, the mixture was treated with a solution of benzaldehyde (40 μL, 0.39 mmol) in THF (1 mL) at -78 °C and stirred for another 30 min at this temperature. To the mixture was added 1 N HCl, and the organic material was extracted with ether. The combined organic extracts were dried (MgSO₄) and concentrated, and the crude product was purified by column chromatography on silica gel (hexane-ethyl acetate, 5:1) to afford the homoallylic alcohol (86 mg, 90% yield); the α:γ and E:Z ratios were determined to be 92:8 and 98:2, respectively, by GC analysis.

The extraordinary α-selectivity and stereospecificity of the carbonyl addition of barium reagent provide an unprecedented route to homoallylic alcohols and are broadly applicable in organic synthesis.^{9,10} Further work on the reaction with barium reagent is now being done.

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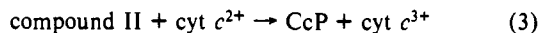
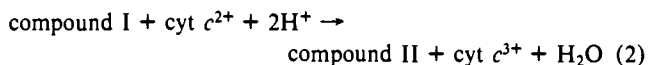
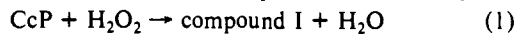
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Intramolecular Electron Transfer from the Heme to the Radical Site Does Not Occur in Compound II of Yeast Cytochrome *c* Peroxidase during Catalytic Turnover^{†,‡}

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Yeast cytochrome *c* peroxidase is a ferric heme containing enzyme which catalyzes the decomposition of H₂O₂ to H₂O, utilizing reduced cytochrome *c* (cyt *c*²⁺) as an electron source.¹ Classically, the reaction is thought to proceed in three stages:^{2,3}



[†]This work was supported by NIH Grant DK15057 (to G.T.).

[‡]The abbreviations used are as follows: CcP, yeast cytochrome *c* peroxidase; cyt *c*³⁺ and cyt *c*²⁺, the ferric and ferrous oxidation states of cytochrome *c*; et, electron transfer.

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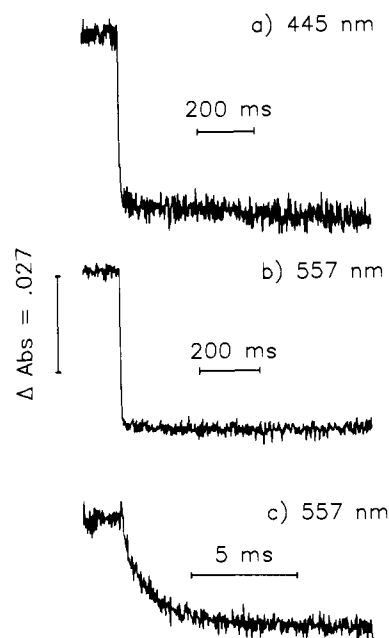


Figure 1. Laser flash generated transients for the reduction of compound I by cyt *c*²⁺. Experiments were performed in a 4.2 mM phosphate buffer (pH 7.4) containing 0.5 mM EDTA and 0.1 mM 5-deazalumiflavin *N*-3-propanesulfonate; compound I (20 μM) was generated by titration of ferric CcP immediately prior to the flash experiment. The concentration of horse cyt *c*³⁺ was 20 μM for all traces.

Compound I is relatively stable⁴ and contains two oxidizing equivalents.^{2a,5} One of these is an oxyferryl heme⁶, in which the iron atom has a formal oxidation state of 4+. The other is an organic free radical (R^{•+})^{5b,7} localized on an amino acid residue(s) of somewhat controversial identity; however, the most likely candidate is Trp-191.⁸ A transient porphyrin π-cation radical may be formed prior to transfer of the oxidizing equivalent to the amino acid side chain.⁹

The location of the oxidizing equivalent in compound II is also controversial.^{2c,3} Stopped-flow measurements of ferrocyanide reduction suggest that R^{•+} reacts approximately five times faster than the oxyferryl site.^{2c,10} When ferric CcP is reduced to the ferrous state and then oxidized with H₂O₂, a stable oxyferryl species without an oxidized amino acid side chain is produced.¹¹ Reaction of this species with F⁻ results in reduction of the heme Fe to the ferric state with a rate constant of 0.11 s⁻¹, due to intramolecular et from an unknown amino acid.^{11b} A rate constant of 20 s⁻¹ has been calculated for the oxidation of the ferric heme

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