stable zerovalent complexes $M(CNAr)_6$, while the alkyl isocyanides favor retention of these metals in the divalent state, either as $M(CNR)_6^{2+}$ or $M(CNR)_7^{2+}$.

Dichloromethane solutions of $[Cr(CNR)_7](PF_6)_2$ show an irreversible oxidation close to +1.15 V ($E_{p,a}$ = +1.12 V for R = $C_6H_{11}$ and +1.16 V for R = $CMe_3$).[20] This oxidation to $Cr(CNR)_7^{3+}$ is followed by the loss of an isocyanide ligand and the formation of $Cr(CNR)_6^{3+}$, as identified through the appearance of the three couples (Figure 1b) which characterize these six-coordinate cations. Note that the rate of ligand loss is quite slow (as measured by peak currents), since considerable amounts of the seven-coordinate cation remain following completion of the single CV scan.[21] The decomposition of the $Cr(CNR)_7^{3+}$ ions following their electrochemical generation (possibly by a simple EC mechanism)[22] contrasts with the much greater stability of the analogous molybdenum and tungsten species. Solutions containing the $Mo(CNR)_7^{3+}$ and $W(CNR)_7^{3+}$ cations may be generated electrolytically[7] and decompose at much slower rates.

An alternative ligand loss mechanism is the spontaneous conversion of solutions of the unoxidized $Cr(CNR)_7^{2+}$ cations to $Cr(CNR)_6^{2+}$. This change can be monitored by cyclic voltammetry (on dichloromethane solutions of the complexes using switching potentials of +0.90 and −1.6 V) and, in the case of the formation of $[Cr(CNC_6H_{11})_6](PF_6)_2$ from $[Cr(CNC_6H_{11})_7](PF_6)_2$, was also followed by $^1H$ NMR spectroscopy. The cyclohexyl resonances at $\delta \sim 1.50$ and $\sim 4.35$ in the the diamagnetic seven-coordinate complex (data recorded in acetone-$d_6$ at room temperature relative to $Me_4Si$) collapse and new, broad resonances centered at $\delta$ 1.4, 3.25, and 5.4 emerge as the paramagnetic complex $[Cr(CNC_6H_{11})_6](PF_6)_2$ is formed.[23]

The XPS Cr $2p_{3/2}$ binding energies of the six- and seven-coordinate complexes are very similar (576.6 ± 0.2 eV),[24] being significantly higher than those we have measured for the phenyl isocyanide species $Cr(CNPh)_6^+$ and $Cr(CNPh)_6$ (575.3 and 574.5 eV, respectively). Accordingly, this smooth increase of $E$(Cr 2p) with increase in oxidation state implies that neither Cr to $\pi^*$-(CNR) nor Cr to $\pi^*$(CNAr) back-bonding is particularly dominant in influencing the charge at the metal center. If it were then with PhNC a significantly better $\pi$-acceptor ligand than RNC, Cr to $\pi^*$(CNPh) back-bonding in $Cr(CNPh)_6$ and $Cr(CNPh)_6^+$ might well be expected to increase the Cr 2p binding energies to a point where they approach those of $Cr(CNR)_6^{2+}$. This we do not observe.

Preliminary studies point to a rich substitution chemistry for these new alkyl isocyanide complexes of Cr(II). Among the complexes already isolated are $[Cr(CNCMe_3)_5P(OMe)_3](PF_6)_2$ and $[Cr(CNR)_{5+x}(dppe)](PF_6)_2$, where $x$ = 1 or 2, R = $CMe_3$ or $C_6H_{11}$, and dppe = 1,2-bis(diphenylphosphino)ethane. Further work is in progress and will be reported in detail at a later date.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE79-09233) for research support and Professor S. J. Lippard for providing us with the information presented in ref 18.

(20) A reduction wave at $E_{p,c}$ = +0.65 V which is associated with the seven-coordinate cation overlaps that arising from the reduction $Cr(CNR)_6^{3+} + e \rightarrow Cr(CNR)_6^{2+}$ (see Figure 1b).

(21) From the CV shown in Figure 1b, it is apparent that while $Cr(CNC_6H_{11})_6^{3+}$ is formed by ligand loss following the oxidation of $Cr(CNC_6H_{11})_7^{2+}$, the peak curents associated with the cathodic sweep are less than that which characterizes the oxidation $Cr(CNC_6H_{11})_7^{2+} \rightarrow Cr(CNC_6H_{11})_7^{3+} + e$. Accordingly, there must be partial decomposition of $Cr(CNC_6H_{11})_7^{3+}$ and/or $Cr(CNC_6H_{11})_6^{3+}$ to some electrochemically inactive species by a second unidentified mechanism.

(22) E means an electrochemical reaction, either an oxidation or a reduction, while C means a chemical reaction. Thus an EC reaction is an electrode process followed by a chemical reaction.

(23) Detailed temperature-range $^1H$ NMR spectroscopic measurements of the $[Cr(CNR)_7](PF_6)_2 \rightleftarrows [Cr(CNR)_6](PF_6)_2 + CNR$ equilibria are currently under way.

(24) X-ray photoelectron spectra (XPS) were measured on a Hewlett-Packard 5950A instrument as described in detail elsewhere.[25] Spectra were recorded at 250 K with the use of a cold probe and the Cr 2p binding energies are internally referenced to an aliphatic C 1s binding energy of 285.0 eV for the isocyanide ligands.

(25) Hamer, A. D.; Walton, R. A. *Inorg. Chem.* **1974**, *13*, 1446.

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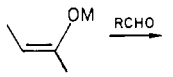
*Received July 21, 1980*

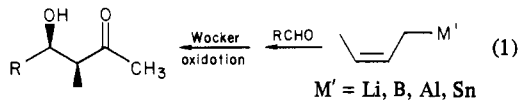
## Erythro-Selective Addition of Crotyltrialkyltins to Aldehydes Regardless of the Geometry of the Crotyl Unit. Stereoselection Independent of the Stereochemistry of Precursors

*Sir:*

One of the most challenging problems for the synthetic organic chemist today is control of stereochemistry in conformationally nonrigid open-chain compounds. Especially, attention is focused on erythro-selective synthesis of $\beta$-hydroxycarbonyl compounds which may be applicable to the synthesis of macrolide antibiotics.[1] The hitherto known solution to this problem is to use the addition reaction of (i) (*Z*)-metal enolates[2] or (ii) (*Z*)-2-alkenylmetal derivatives[3] to aldehydes (eq 1). However, an important problem



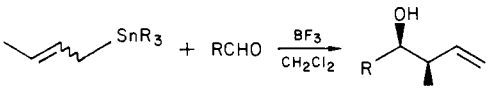

M = Li, Mg, Zn, B, Al, Si




(1)

M′ = Li, B, Al, Sn

that arises from these approaches is the stereochemical control (*Z* configuration) of the starting materials, which still remains difficult despite numerous efforts in this kind of chemistry.[2,3] We report an entirely new approach to the stereoselection via the Lewis acid mediated addition[4] of crotyltrialkyltins to aldehydes, where it does not matter if the stereochemistry of the crotyl unit is either cis or trans (eq 2).




(2)

1 erythro selectivity >90%

(1) For review articles, see: (a) Bartlett, P. A. *Tetrahedron*, **1980**, *36*, 3. (b) Masamune, S. *Aldrichimica Acta* **1978**, *11*, 23.

(2) Li: (a) Kleschick, W. A.; Buse, C. T.; Heathcock, C. H. *J. Am. Chem. Soc.* **1977**, *99*, 247. (b) Buse, C. T.; Heathcock, C. H. *Ibid.* **1977**, *99*, 8109. (c) Meyers, A. I.; Reider, P. J. *Ibid.* **1979**, *101*, 2501. (d) Dubois, J. E.; Fellmann, P. *Tetrahedron Lett.* **1975**, 1225. (e) Mulzer, J.; Segner, J.; Bruntrup, G. *Ibid.* **1977**, 4651. (f) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066. Li, Mg, and Zn: (g) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. B: (h) Fenzl, W.; Köster, R.; Zimmermann, H. J. *Justus Liebigs Ann. Chem.* **1975**, 2201. (i) Masamune, S.; Mori, D.; Horn, D. V.; Brooks, D. W. *Tetrahedron Lett.* **1979**, 1665. (j) Hirama, M.; Masamune, S. *Ibid.* **1979**, 2225. (k) Horn, D. V.; Masamune, S. *Ibid.* **1979**, 2229. (l) Hirama, M.; Garvey, D. S.; Lu, L. D.; Masamune, S. *Ibid.* **1979**, 3937. (m) Evans, D. A.; Vogel, E.; Nelson, J. V. *J. Am. Chem. Soc.* **1979**, *101*, 6120. Al: (n) Jeffrey, E. A.; Meisters, A.; Mole, T. J. *J. Organomet. Chem.* **1974**, *74*, 373. Aluminum (*Z*)-enolates give threo derivatives in contrast with other enolates. (o) Maruoka, K.; Hashimoto, S.; Kitagawa, Y.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 7705. Si and Ti: (p) Mukaiyama, T.; Banno, K.; Narasaka, K. *Ibid.* **1974**, *96*, 7505. (q) Chan, T. H.; Aida, T.; Lau, P. W. K.; Gorys, V.; Harpp, D. N. *Tetrahedron Lett.* **1979**, 4029.

(3) Li: (a) Hayashi, T.; Fujitaka, N.; Oishi, T.; Takeshima, T. *Tetrahedron Lett.* **1980**, 303. B: (b) Hoffmann, R. W.; Ladner, W. *Ibid.* **1979**, 4653. (c) Hoffmann, R. W.; Zeiss, H. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 306. Al: (d) Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2118. Sn: (e) Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1972**, *35*, c20. (f) Yatagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548.

(4) Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919.

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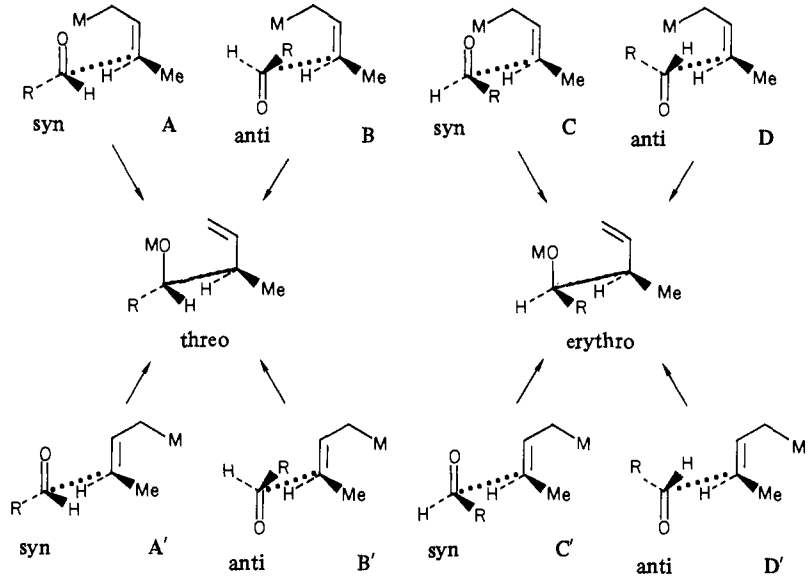
Scheme I




It is well-recognized that crotyl organometallic compounds (M = Li,[5] Mg,[6] Zn,[6a,b] Cd,[6a,b] and B[7]) react with aldehydes (RCHO) to give a mixture of *erythro*- and *threo*-β-methylhomoallyl alcohols though the stereoselectivity slightly increases as the steric hindrance of R increases. It is generally believed that the reaction proceeds through a cyclic transition state in which the metal cation can interact with the partially negative oxygen[8] and hence that the stereodefined (*Z*)-crotyl organometallic compounds selectively produce erythro derivatives. Actually, this proves to be practical with lithium,[3a] boron,[3b,c] aluminum,[3d] and tin.[3e,f] During these investigations,[3f] we discovered that the reaction of crotyltrialkyltins with aldehydes gives selectively erythro derivatives irrespective of the geometry of crotyltins (eq 2). The results are summarized in Table I.

As is apparent from Table I, the erythro-selective (>90%) condensation is realized regardless of the steric effect of the substituent R of aldehydes and of the geometry of the crotyl unit. Such an independence from the stereochemistry of the starting materials is particularly useful for synthetic application and, more importantly, highly interesting for the mechanistic consideration. Scheme I shows the transition states leading to erythro and threo derivatives,[9] in which the chelate formation between Sn and oxygen (or $-OBF_3$ group) is not important.[10] It is easily decided that, among eight possible geometries, two configurations (**D** and **D'**) leading to the erythro isomer must be favored for steric reasons. Consequently, the present reaction system presumably does not involve a conventional cyclic mechanism;[11] the previous reaction via Li,[3a,5] Mg,[6] Zn,[6a,b] Cd,[6a,b] B,[3b,c,7] Al,[3d] Si,[12] and Sn[3e] must proceed more or less through such a mechanism.

Table I. Erythro-Selective Synthesis of β-Methylhomoallyl Alcohols[a]

| crotyltin[b] (trans and/or cis) | aldehyde | yield of 1,[c] % | erythro/threo ratio |
|---|---|---|---|
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t*) | $C_6H_5CHO$ | 90 | 98:2[d] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t* 90%, *c* 10%) | $C_6H_5CHO$ | 90 | 98:2[d] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t* 60%, *c* 40%) | $C_6H_5CHO$ | 90 | 96:4[d] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*c*) | $C_6H_5CHO$ | 90 | 99:1[d] |
| $CH_3CH=CHCH_2SnMe_3$ (*t*) | $C_6H_5CHO$ | 90 | 95:5[d] |
| $CH_3CH=CHCH_2SnMe_3$ (*t*) | $(CH_3)_2CHCHO$ | 89 | 95:5[e] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t*) | $(CH_3)_2CHCHO$ | 90 | 91:9[e] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t*) | $(C_2H_5)_2CHCHO$ | 92 | 98:2[e] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t*) | $(CH_3)_2CHCH_2CHO$ | 90 | 90:10[e] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t*) | $CH_3CH_2CHO$ | (87) | 91:9[e] |
| $CH_3CH=CHCH_2Sn(n\text{-}Bu)_3$ (*t*) | $CH_3CHO$ | (82) | 91:9[e] |

[a] All reactions were performed as described in the text. All products were fully identified by spectroscopic methods and by comparison with the authentic materials. [b] Prepared according to ref 13 and 3f. [c] Isolated yield (GLPC yield). [d] Determined by $^1H$ NMR spectra. [e] Determined by GLPC (CW 6000, 2 m).

(5) Rautenstrauch, V. *Helv. Chim. Acta* **1974**, *57*, 496.

(6) (a) Abenhaim, D.; Basch, E. H.; Freon, P. *Bull. Soc. Chim. Fr.* **1969**, 4038, 4042. (b) Abenhaim, D.; Basch, E. H. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *267*, 87. (c) Felkin, H.; Gault, Y.; Roussi, G. *Tetrahedron* **1970**, 3761.

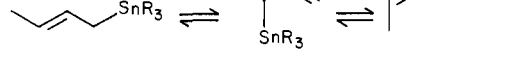
(7) Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2292.

(8) On the contrary, Felkin has reported that allylic organomagnesium compounds react with carbonyl derivatives according to the mechanism of noncyclic bimolecular electrophilic substitution ($S_E2'$). See ref 6c and Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. Felkin, H.; Frajerman, C. *Tetrahedron Lett.* **1970**, 1045. Cherest, M.; Felkin, H.; Frajerman, C. *Ibid.* **1971**, 379.

(9) Similar consideration is made on aldol addition: Mulzer, J.; Bruntrup, G.; Finke, J.; Zippel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7723.

(10) In the absence of a coordinating cation, threo products are obtained from (*Z*)-enolates: ref 2a and Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265. Very low stereoselection is observed in protic media: Fellmann, P.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 1349. Dubois, J. E.; Fort, J. F. *Ibid.* **1972**, *28*, 1653. See also Naruta, Y. *J. Am. Chem. Soc.* **1980**, *102*, 3774.

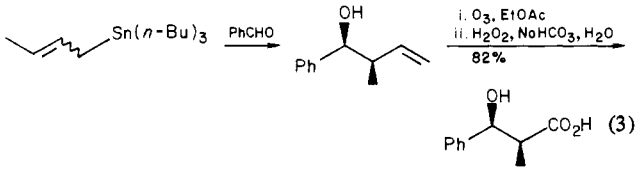
(11) If the *trans*-crotyltin undergoes a facile isomerization to the cis isomer via 1,3-tin migration, the erythro selectivity can be understood through the cyclic transition state.[3f] Such a possibility is eliminated by the following experiments. (i) The reaction of *trans*-crotyltributyltin (trans 90, cis 10) (1.2 mmol) with benzaldehyde (1 mmol) in the presence of $BF_3{\cdot}OEt_2$ (1 mmol) was quenched immediately at −78 °C with MeOH–$H_2O$. The isomerization of the recovered crotyltin was not detected. (ii) The reaction of the isomeric 1-methylallyltin, independently prepared by the method of ref 13, with benzaldehyde under the same condition produced 1-phenylpent-3-en-1-ol in high yield.




(12) Titanium tetrachloride mediated reaction of crotyltrimethylsilane with propanal produced a mixture of erythro (60%) and threo (40%) isomers. This may be due to the fact that the affinity of Si toward oxygen atoms is higher than that of Sn, and hence that the reaction via Si involves more or less the cyclic transition state. For the affinity of Si and Sn, see: Itoh, K.; Matsuzaki, K.; Ishii, Y. *J. Chem. Soc. C* **1968**, 2709. Itoh, K.; Fukumoto, Y.; Ishii, Y. *Tetrahedron Lett.* **1968**, 3199. The addition of crotyl bromide to aldehydes with chromous ion provides the threo products regardless of the geometry of the starting material: Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3179. Buse, C. T.; Heathcock, C. H. *Tetrahedron Lett.* **1978**, 1685.

The preparation of *erythro*-2-methyl-1-phenylbut-3-en-1-ol is representative. To a solution of benzaldehyde (2 mmol, 0.22 mL) in dry $CH_2Cl_2$ (4 mL) was added $BF_3{\cdot}OEt_2$ (4 mmol, 0.52 mL) at -78 °C under $N_2$. Subsequently, crotyltributyltin[13] (2 mmol, 0.8 mL) was added, and the reaction mixture was allowed to warm to 0 °C. The reaction was quenched with $H_2O$, and the organic phase was separated, dried, and condensed. Filtration through a column of silica gel with petroleum ether–ether (10:1) as an eluant gave the desired product in an essentially pure form: 0.29 g, 90%, bp 80–85 °C (0.5 mmHg) (Kugelrohr).

An important application of the present procedure is to use the allylic tin route as a synthetic equivalent of the (*Z*)-enolate route. For example, to obtain the erythro product, the enolate route inherently requires the presence of a bulky substituent at the $\alpha$ position as well as the stereochemically pure *Z* geometry. Further, the stereoselectivity of ester enolate condensation is generally low.[2b] These difficulties are overcome by using the allylic tin route (eq 3). We are currently studying the related reaction of tin enolates with carbonyl derivatives and will report this work shortly.[14]



(3)

(13) Crotyltins were prepared according to M-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976**, *121*, 155; Ibid. **1976**, *121*, 169.

(14) Note **Added in Proof**: In a communication that appeared subsequent to submission of this manuscript, Professor Noyori and co-workers report that an acylic transition state may be involved in the reaction of enol silyl ethers with acetals in the presence of catalytic amounts of $Me_3SiOTf$; Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248. We also learned that the similar stereoselection of allylic tin derivatives was observed by Professor Koreeda, University of Michigan, private communication.

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*Received May 19, 1980*

## Hydrido–Formyl Complexes of Iridium. The First Cationic Formyl Complex and Its Reduction to a Stable Cis-Hydrido–Methyl Compound

*Sir:*

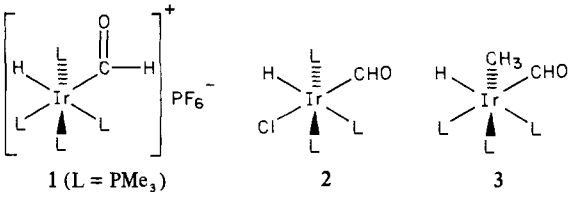
We have recently found that a series of remarkably stable Ir(III) hydrido–formyl complexes can be easily synthesized from the reactions of formaldehyde[1] with several Ir(I) compounds. These hydrido–formyl complexes[2] and the products derived from their subsequent reactions have ligands in the metal coordination sphere which are possible intermediate species in CO–$H_2$ reduction chemistry (e.g., the Fischer–Tropsch reaction).[3] The compounds to be described are, therefore, of great interest both in their own right and also as model systems for certain CO reduction reactions which occur in compounds of the later transition metals.[3]

(1) A hydrido–formyl complex of osmium has been prepared from a formaldehyde complex and reported by: Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505.

(2) Hydrido–benzoyl complexes of Ir(III) have been reported by: Rauchfuss, T. B. *J. Am. Chem. Soc.* **101**, *1979*, 1045–1047. Hydrido–acyl and benzoyl complexes of Fe(II) were reported by: Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *Ibid.* **101**, 1979, 1742–1751.

(3) For recent reviews see: Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. Henrici-Olive, G.; Olive, S. *Angew. Chem.* **1976**, *88*, 144–150; *Angew. Chem., Int. Ed. Engl.* **1973**, *15*, 136–141.

Stirring a red tetrahydrofuran (THF) solution[4] of $[Ir(P(CH_3)_3)_4]PF_6$[5,6] with an equimolar amount or slight excess of solid paraformaldehyde[7] at room temperature results in slow decolorization over about 4 h. The final product, $[Ir(H)(HCO)(P(CH_3)_3)_4]PF_6$ (**1**), is very sparingly soluble in THF and is obtained in 60–80% yield as a white or pale yellow precipitate. Compound **1** was recrystallized from acetone solution by the vapor diffusion of hexane and decomposed when heated to 146 °C (vide infra). The IR spectrum of **1** (Nujol) has sharp, characteristic absorption peaks at 2622 (m, $\nu_{C-H}$), 2072 (s, $\nu_{Ir-H}$), and 1600 $cm^{-1}$ (s, $\nu_{C=O}$). The $^1H$ NMR spectrum[8] of **1** (pyridine-$d_5$ or $CD_2Cl_2$) consists of a complex pattern at $\delta$ 14.0 (doublet, $J$ = 50 Hz, of multiplets, pseudoquintets, $J$ = 5 Hz), a doublet of quartets centered at $\delta$ -12.0 ($J_{H-P,trans}$ = 123, $J_{H-P,cis}$ = 18 Hz), and a multiplet at $\delta$ 1.35. The hydrido and formyl ligands are therefore cis, since the hydrido $^1H$ NMR signal is only consistent with a structure containing a trimethylphosphine ligand trans to the hydride. This assignment of the structure of **1** has been confirmed by a single-crystal X-ray structure determination, details of which will be published elsewhere.[9] The $^{13}C$ NMR spectrum (acetone-$d_6$) of the $^{13}C$-labeled complex (prepared by using $^{13}C$ paraformaldehyde, Merck Isotopes) consists of a doublet of triplets of doublets, $J_{C-P,trans}$ = 83 Hz, $J_{C-P,cis(cis\ to\ H)}$ = 5.4 Hz, $J_{C-P,cis(trans\ to\ H)}$ = 10 Hz, centered at 225.40 ppm. From the $^1H$ NMR spectrum of the $^{13}C$-labeled complex, $J_{C-H}$ = 150 Hz. The $^{31}P\{^1H\}$ NMR spectrum of **1** is an $A_2MX$ pattern.[10]




A closely related hydrido–formyl complex, $IrCl(H)(HCO)(P(CH_3)_3)_3$ (**2**), is obtained from the reaction of $IrCl(C_8H_{14})(P(CH_3)_3)_3$[6] with an equimolar amount of paraformaldehyde in THF. The product was precipitated in 54% yield from THF by the addition of pentane to give a pale yellow solid. From the IR and $^1H$ NMR spectra of **2**,[11] the structure is readily deduced and is illustrated as shown. Compound **2** melts with decomposition at 130 °C.

A third hydrido–formyl complex, $Ir(CH_3)(H)(HCO)(P(CH_3)_3)_3$ (**3**), was prepared by the analogous reaction of $Ir(CH_3)(P(CH_3)_3)_4$[12] with paraformaldehyde, followed by recrystal-

(4) The Ir(I) complexes used as starting materials are sensitive to oxygen. Solvents were dried and degassed prior to use, and reactions were performed using standard inert atmosphere techniques.

(5) Analytically pure material was prepared by adding 1 equiv of $P(CH_3)_3$ to a THF solution of $IrCl(C_8H_{14})(P(CH_3)_3)_3$[6] in the presence of excess $NaPF_6$, filtering after several hours, and crystallizing (slow vapor diffusion of hexane). Further characterization of this compound will be presented in future publications: Herskovitz, T.; Ittel, S. D.; Tulip, T. H.; Thorn, D. L., to be published.

(6) Herskovitz, T; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615–1616. Herskovitz, T. *Ibid.* **1977**, *99*, 2391–2392. English, A. D.; Herskovitz, T. Ibid. **1977**, *99*, 1648–1649.

(7) Paraformaldehyde was obtained from Aldrich and was used without further purification after degassing in vacuum. The inevitable presence of traces of moisture is not detrimental; small amounts of added water appear to accelerate the reaction.

(8) All chemical shifts are relative to external $Me_4Si$. $^1H$ NMR spectra were measured at ambient temperature (~34 °C) with Varian EM390 and Varian HR220 spectrometers. Satisfactory C, H analyses have been obtained for compounds **1**, **2**, and **3**.

(9) Thorn, D. L.; Harlow, R. L., to be published.

(10) $^{31}P\{^1H\}$ NMR spectrum of **1** (pyridine-*d*, ambient temperature): triplet ($J$ = 21 Hz) at $\delta$ -52.0, distorted quartet ($J$ ~21 Hz) at $\delta$ -55.8, quartet ($J$ ~19 Hz) at $\delta$ -69.0. Chemical shifts are in ppm relative to external $H_3PO_4$ with a positive shift signifying a larger resonance frequency. The $PF_6^-$ resonance is centered at $\delta$ -143.2 ($J_{P-F}$ = 710 Hz).

(11) IR of **2** (Nujol) 2585 (m), 1990 (s), and 1600 (s) $cm^{-1}$. $^1H$ NMR of **2** ($C_6D_6$): formyl H, triplet ($J$ = 7 Hz) of doublets ($J$ = 3 Hz) at $\delta$ 15.0; hydrido H, doublet ($J$ = 140 Hz) of triplets ($J$ = 20 Hz) at $\delta$ -9.2; $P(CH_3)_3$, triplet ($J$ = 4 Hz) at $\delta$ 1.46, 18 H; doublet ($J$ = 8 Hz) at $\delta$ 1.30, 9 H.

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