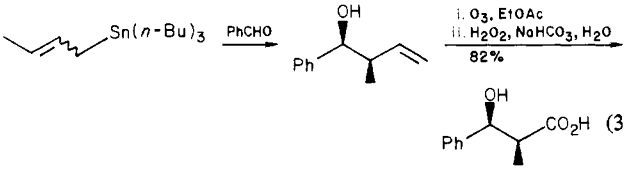
The preparation of *erythro*-2-methyl-1-phenylbut-3-en-1-ol is representative. To a solution of benzaldehyde (2 mmol, 0.22 mL) in dry CH_2Cl_2 (4 mL) was added $BF_3 \cdot OEt_2$ (4 mmol, 0.52 mL) at −78 °C under N_2. Subsequently, crotyltributyltin[13] (2 mmol, 0.8 mL) was added, and the reaction mixture 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 α 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)

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(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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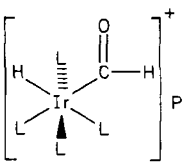
Received May 19, 1980

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

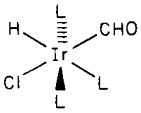
Sir:

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]

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, ν_{C-H}), 2072 (s, ν_{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 δ 14.0 (doublet, J = 50 Hz, of multiplets, pseudoquintets, J = 5 Hz), a doublet of quartets centered at δ −12.0 ($J_{H-P,trans}$ = 123, $J_{H-P,cis}$ = 18 Hz), and a multiplet at δ 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]



1 (L = PMe$_3$)



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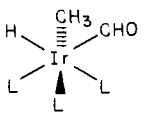

3

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-

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(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.

(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 δ −52.0, distorted quartet ($J \sim 21$ Hz) at δ −55.8, quartet ($J \sim 19$ Hz) at δ −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 δ −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 δ 15.0; hydrido H, doublet (J = 140 Hz) of triplets (J = 20 Hz) at δ −9.2; $P(CH_3)_3$, triplet (J = 4 Hz) at δ 1.46, 18 H; doublet (J = 8 Hz) at δ 1.30, 9 H.

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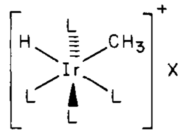
lization from toluene/hexane. Again the structure can be readily deduced from the spectral data of **3**[13] and is illustrated. The compound melts with decomposition at 135 °C.

Compounds **1**, **2**, and **3** are surprisingly robust, both in the solid state and in solution. Refluxing a THF suspension of compound **1** for several hours resulted in no significant decomposition, although the IR spectrum of the recovered solid material had a new peak at 1890 $\mathrm{cm^{-1}}$, indicating the presence of $[\mathrm{Ir(CO)(PMe_3)_4}]\mathrm{PF_6}$[14] and suggesting decomposition by loss of $\mathrm{H_2}$.[1] Decomposition was more rapid in refluxing pyridine. The differential thermal analysis[15] of a solid sample of **1** revealed slightly exothermic reactions (~0.6 kcal/mol)[15] at 146 °C followed by an endothermic reaction (~14 kcal/mol)[15] centered at about 165 °C. The reaction at 146 °C probably corresponds to the loss of $\mathrm{H_2}$, and the endothermic reaction at 165 °C involves loss of $\mathrm{PMe_3}$ and/or CO. In an attempt to reverse the $\mathrm{H_2}$ elimination from **1**, $[\mathrm{Ir(CO)(PMe_3)_4}]\mathrm{PF_6}$ was reacted with $\mathrm{H_2}$ at elevated pressures to form $[\mathrm{IrH_2(PMe_3)_4}]\mathrm{PF_6}$ with no detectable amount of **1**. Complexes **2** and **3**, similarly, are largely unchanged after warming to 60 °C for 1 h.[16]

Transition-metal formyl complexes recently have been the subject of elegant studies by several research groups.[1,17-37] Until now, all the known formyl complexes have been either anionic or neutral. Compound **1** is the first cationic formyl complex to be reported. As might be expected from its positive charge and presumed electrophilic nature, compound **1** can be readily reduced with either hydride-transfer reagents or with sodium naphthalenide to form a variety of compounds.[16] For instance, when a suspension of compound **1** in THF was reacted with an excess of borane[24,32,38-40] for 15 h at room temperature the cis hydrido–methyl Ir(III) complex, $[\mathrm{Ir(CH_3)H(P(CH_3)_3)_4}]\mathrm{PF_6}$ (**4a**), was detected in ~23% yield (NMR). It has not yet been possible to isolate



$\mathrm{L = P(CH_3)_3}$

4a, $\mathrm{X = PF_6}$

b, $\mathrm{X = BF_4}$

4a from other products[16] of the reduction, but its presence was unambiguously established by its very characteristic ^{1}H NMR spectrum, identical with that of $[\mathrm{Ir(CH_3)H(P(CH_3)_3)_4}]\mathrm{BF_4}$ (**4b**).[41] Compound **4b** was independently synthesized from the reaction of $\mathrm{Ir(CH_3)(P(CH_3)_3)_4}$[12] with $\mathrm{HBF_4}$ in diethyl ether.[41,42] The further reactions of these remarkably stable[41] cis hydrido–methyl[43-47] complexes, **3** and **4**, are under active investigation.

Acknowledgment. Discussions with Professors W. R. Roper and E. L. Muetterties, with R. A. Schunn, T. H. Tulip, W. A. Nugent, G. W. Parshall, and S. D. Ittel (of this department), and with Dr. W. Tam have been extremely beneficial to the progress of this work. I wish to especially thank T. Herskovitz for providing samples of some of the starting materials and for his continued interest and helpful comments.

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(12) Obtained analytically pure in 23% isolated yield (recrystallized from hexane) from the reaction of $\mathrm{Ir(P(CH_3)_3)_4Cl}$[6] with methyllithium; ^{1}H NMR ($\mathrm{C_6D_6}$): $\mathrm{CH_3}$, δ 0.30, quintet ($J_{\mathrm{H-P}} = 8$ Hz), 3 H; $\mathrm{P(CH_3)_3}$, δ 1.35, broad singlet, 36 H.

(13) IR of **3** (Nujol) 2490 (m), 1985 (s), 1589 (s) $\mathrm{cm^{-1}}$. ^{1}H NMR of **3** ($\mathrm{C_6D_6}$): formyl H, doublet ($J = 48$ Hz) of doublets ($J = 3$ Hz) at δ 15.2; hydrido H, doublet of triplets ($J_{\mathrm{H-P}}$ trans = 137 Hz, $J_{\mathrm{H-P}}$ cis = 21 Hz) at δ −11.1; $\mathrm{P(CH_3)_3}$, doublet ($J_{\mathrm{H-P}} = 8$ Hz), δ 1.31; doublet ($J_{\mathrm{HP}} = 7$ Hz), δ 0.99; doublet of doublets ($J_{\mathrm{H-P}} = 8$ Hz, $J_{\mathrm{H-H\ hydride}} = 1$ Hz), δ 0.95; methyl H, multiplet, δ 0.71. The methyl resonance of the complex $\mathrm{Ir(D)(DCO)(CH_3)(PMe_3)_3}$ is a well-resolved eight-line pattern.

(14) Prepared separately by the reaction of $\mathrm{Ir(P(CH_3)_3)_4PF_6}$[5] with CO at subatmospheric pressure, ν_{CO} 1890 $\mathrm{cm^{-1}}$. Anal. C, H.

(15) Experimental conditions: compound **1** (9.4 mg) was heated under $\mathrm{N_2}$ at 2 °C/min. The amounts of heat evolved or absorbed in the decomposition processes roughly correspond to ΔH for the reaction and are obtained from integration of the differential scanning calorimetric curve. However, the exothermic and endothermic regions of the curve are not cleanly separated, and probable overlap reduces the chemical significance of the integrated areas.

(16) The natures of the eventual decomposition products of **2**, **3**, and **4** and several of the reduction products of **1** are still under investigation.

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(41) Compounds **4a,b** have not yet been isolated in analytically pure form, but the ^{1}H NMR spectrum (pyridine-d_5) of **4b** provides unambiguous characterization and structural assignment. Hydrido H, δ −13.2, doublet of quartets ($J_{\mathrm{H-Ptrans}} = 138$ Hz, $J_{\mathrm{H-P,cis}}$ 20 Hz); $\mathrm{CH_3}$, δ −0.05, quartet of doublets of doublets ($J_{\mathrm{H-P,trans}} = 4$ Hz, $J_{\mathrm{H-P,cis}} = 8$ Hz, $J_{\mathrm{H-H(hydride)}} = 1$ Hz); $\mathrm{P(CH_3)_3}$, δ 1.52 (doublet, $J_{\mathrm{H-P}}$ 8.4 Hz), 1.47 [triplet (virtual coupling), $J = 3.3$ Hz], 1.31 (doublet of doublets, $J_{\mathrm{H-P}}$ 8.0 Hz, $J_{\mathrm{HH(Hydride)}} = 1$ Hz). The ^{1}H NMR spectrum of **4a** is identical. Pyridine solutions of **4a,b** are stable for days at room temperature in the absence of air. Impure solid **4b** decomposes at 190–200 °C.

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Received June 23, 1980