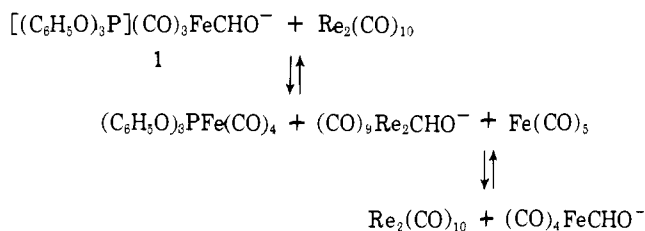


(m-s) cm^{-1} . The observation of four different MCO resonances in the low temperature ^{13}C NMR¹⁵ of **4** establishes the cis geometry of the compound: ^{13}C NMR (THF- d_8 , -53°C , 0.07 M, $\text{Cr}(\text{acac})_3$), δ 7.6 (NCH_2CH_3), 52.1 (NCH_2CH_3), 188.8, 194.4, 199.0, 203.2 (relative intensity: 0.9, 0.8, 4.7, 2.5 ReCO), 264.2 (ReCHO).¹⁹

Solutions of **4** as well as the solid were found to be sensitive to fluorescent laboratory lights. Photolysis of a THF solution of **4** in an NMR tube produces a metal hydride ($\delta -7.1$) in 81% yield as determined by NMR. Preparative photolysis of **4** gave **5** in 38% yield after recrystallization. The dinuclear rhenium hydride,¹⁶ $\text{Et}_4\text{N}^+ \text{cis}-(\text{CO})_9\text{Re}_2\text{H}^-$ (**5**) was more conveniently prepared by reaction of $\text{K}^+\text{HB}(\text{O}-i\text{-Pr})_3^-$ with $\text{Re}_2(\text{CO})_{10}$ at $45\text{--}50^\circ\text{C}$ for 3 h under fluorescent laboratory lighting. Aqueous basic workup, cation exchange with $\text{Et}_4\text{N}^+\text{Br}^-$ and recrystallization from THF-hexane gave **5** in 33% yield.¹³ Elemental analysis,¹⁷ IR, and ^1H NMR established the gross structure of **5**: ^1H NMR (acetone- d_6) δ 1.40 (tt, $J = 7.2$, $J_{\text{NH}} = 1.5$ Hz, 12 H, NCH_2CH_3), 3.50 (q, $J = 7.2$ Hz, 8 H, NCH_2CH_3), -7.10 (s, 1 H, ReH); IR (THF) 2078 (vw), 2028 (m), 1972 (s), 1924 (w-m), 1888 (m) cm^{-1} ; IR (KBr) 2082 (vw), 2028 (m), 2004 (m), 1968 (s), 1931 (m), 1912 (m), 1865 (ms), 1733 (w) cm^{-1} . The observation of five different MCO resonances in the low temperature ^{13}C NMR¹⁸ of **5** establishes the cis geometry of the compound: ^{13}C NMR (THF- d_8 , -70.6°C , 0.07 M, $\text{Cr}(\text{acac})_3$), δ 7.7 (NCH_2CH_3), 52.1 (NCH_2CH_3), 189.9, 195.4, 199.0, 201.1, 202.0 (relative intensity: 1.1, 0.9, 0.9, 3.8, 2.3 ReCO).

Transformylation reactions between various metal formyl and metal carbonyl compounds indicate the following order of stability of formyl complexes relative to their metal carbonyl precursors: $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}^+(\text{CO})_4\text{FeCHO}^- > \text{Et}_4\text{N}^+ \text{cis}-(\text{CO})_9\text{Re}_2\text{CHO}^- > \text{Et}_4\text{N}^+ \text{trans}-[\text{C}_6\text{H}_5\text{O}_3\text{P}](\text{CO})_3\text{-FeCHO}^-$. The possibility that these transformylations proceed via decarbonylation to give a metal hydride which then transfers hydride to a metal carbonyl is excluded since the reaction of **1** with $\text{Re}_2(\text{CO})_{10}$ or $\text{Fe}(\text{CO})_5$ is faster than decomposition of **1** to $(\text{CO})_4\text{FeH}^-$ and since $\text{Et}_4\text{N}^+(\text{CO})_4\text{FeH}^-$ does not react with $\text{Re}_2(\text{CO})_{10}$, $\text{Fe}(\text{CO})_5$, or $(\text{CO})_4\text{FeP}(\text{OC}_6\text{H}_5)_3$ under the reaction conditions.



Acknowledgment. Support from the Division of Basic Energy Sciences of the Department of Energy is gratefully acknowledged. We thank Professor John Gladysz (UCLA) for informing us of his similar results prior to publication.

Supplementary Material Available: Preparation of **4** and **5** (2 pages). Ordering information is given on any current masthead page.

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- (3) C. P. Casey and S. M. Neumann, unpublished results.
- (4) $\frac{1}{8}$ in. \times 20 ft 20% UCON 50 HB 280X on 60/80 Chrom P column at 85°C .
- (5) The formation of formaldehyde on acidification of $(\text{CO})_4\text{FeCHO}^-$ solutions has been previously reported by Collman⁹ and confirmed by us.¹
- (6) $\frac{1}{4}$ in. \times 15 ft 10% Ethofat 60/25 on 40/60 Fluoropak 80 column at 110

- $^\circ\text{C}$. H_2 (6-10%) was also observed and attributed to the presence of a similar amount of $\text{Et}_4\text{N}^+(\text{CO})_4\text{FeH}^-$ in the starting material.
- (7) K. Bombauch and W. Bull, *Anal. Chem.*, **34**, 1237 (1962).
- (8) **1** reacts with excess formaldehyde in THF to give a 73% yield of methanol.
- (9) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973).
- (10) Yields by gas chromatography on $\frac{1}{8}$ in. \times 30 ft 20% UCON 50 HB 280X on 60/80 Chrom P column at 70°C (heptane) and 155°C (octanal).
- (11) Gladysz has observed that $(\text{CO})_9\text{Mn}_2\text{CHO}^-$ (formed in situ from $\text{Mn}_2(\text{CO})_{10}$ and $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$) reacts with $\text{Fe}(\text{CO})_5$ to give $(\text{CO})_4\text{FeCHO}^-$: J. A. Gladysz, G. M. Williams, W. Tam, and D. L. Johnson, *J. Organomet. Chem.*, **140**, c1 (1977).
- (12) Yield was determined by using the signal for the $\text{P}(\text{OC}_6\text{H}_5)_3$ group as an internal standard.
- (13) Detailed procedures for these preparations are included as supplementary material. See paragraph at end of paper regarding supplementary material.
- (14) Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_{10}\text{Re}_2$: C, 27.58; H, 2.70; N, 1.79; Re, 47.51. Found: C, 26.34; H, 2.49; N, 1.40; Re, 48.66.
- (15) The thermal decoupling of nuclear quadrupole moments has been previously reported for metal carbonyl compounds: (a) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **80**, C31 (1974); (b) M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. LiShingMan, and J. Takats, *J. Am. Chem. Soc.*, **98**, 4810 (1976).
- (16) For a survey of known hydridocarbonyl complexes of rhenium, see (a) D. Gulsto, *Inorg. Chim. Acta Rev.*, **6**, 91 (1972); (b) M. Bennett, A. Graham, J. Hoyano, and W. Hutcheon, *J. Am. Chem. Soc.*, **94**, 6232 (1972).
- (17) Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_9\text{Re}_2$: C, 27.02; H, 2.80; N, 1.85; Re, 49.28. Found: C, 27.11; H, 3.01; N, 1.73; Re, 48.98.
- (18) At ambient probe temperatures, broadening by the Re quadrupole causes the three upfield carbonyl resonances to disappear and the two downfield resonances to broaden and merge to a broad singlet at δ 201.1.
- (19) NOTE ADDED IN PROOF. In higher resolution ^{13}C NMR of **4**, the peak at 199.0 was resolved into two resonances separated by 3.6 Hz. Five MCO resonances were also observed in the ^{13}C NMR $\text{Li}^+ \text{cis}-(\text{CO})_9\text{Re}_2\text{CHO}^-$ (THF- d_6 , -57°C , 0.07 M, $\text{Cr}(\text{acac})_3$): δ 189.1, 194.5, 199.4, 200.1, 203.6 (relative intensity: 0.9, 1.4, 3.5, 1.2, 1.9 ReCO), 284.3 (ReCHO).

Charles P. Casey,* Stephen M. Neumann

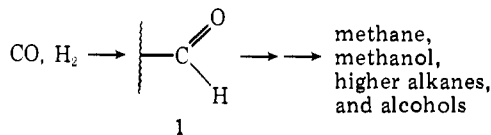
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Received December 16, 1977

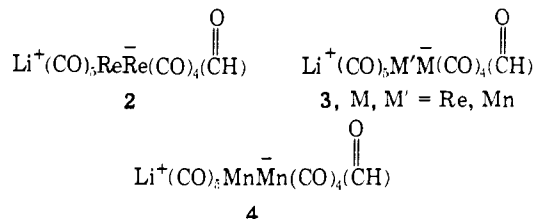
Binuclear and Mixed Metal Formyl Complexes: Isolation, Characterization, and Chemistry

Sir:

Carbon monoxide-hydrogen gas mixtures can be transformed by heterogeneous catalysts at high temperatures and pressures to methane, alcohols, and gasoline (Fischer-Tropsch process).¹⁻³ The initially formed intermediate in these reactions is believed to be the surface-bound formyl **1**.^{3,4}

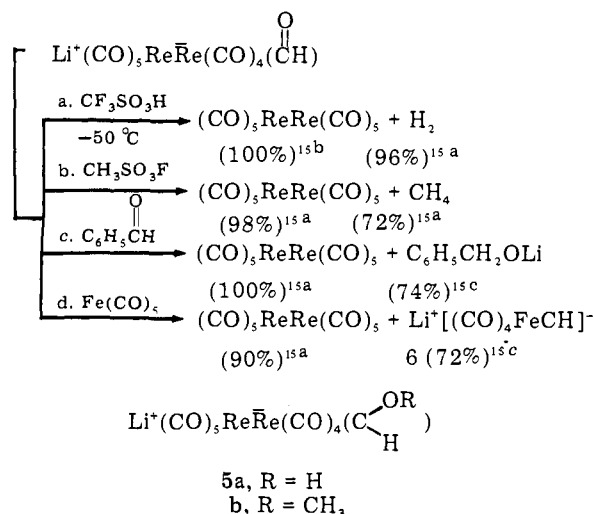


The rational development of milder, homogeneous, and more selective Fischer-Tropsch-type processes⁵ requires the study of homogeneous homologues of **1** and other surface-bound intermediates on the reaction coordinate between CO and alkanes and alcohols. In this communication, we report (a) the synthesis of the first isolable binuclear formyl complex (**2**) by reaction of $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$ with $\text{Re}_2(\text{CO})_{10}$, (b) the availability of the kinetically less stable mixed metal formyl complex **3** by reaction of $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$ with $\text{ReMn}(\text{CO})_{10}$, (c) reactions which establish **2** and **3** as potent hydride donors, and (d) the formation of formaldehyde and methanol from $\text{K}^+\text{-2}$.



The addition of 1.0 equiv of $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}^{\text{6a}}$ to $\text{Re}_2(\text{CO})_{10}$ in THF in a ^1H NMR tube at room temperature resulted in a new resonance at δ 15.78 (80–98% yield; *p*-di-*tert*-butylbenzene reference and internal standard). This type of chemical shift has been previously established as characteristic of anionic formyl complexes.^{7–11} The product was isolated by vacuum removal of the THF until apparent dryness, taking the residue up in a minimum of ether, and adding pentane. A light yellow powder formed, which after vacuum drying analyzed correctly for a THF solvate of **2**¹² (60–75% isolated yield; dec pt 80–90 °C; sealed tube). The formyl ^1H NMR resonance was shifted to δ 15.97 in the spectrum of *isolated 2*. Further evidence for the formyl ligand was provided by characteristic ^{13}C NMR^{7,10,11} (286.5 ppm, 1:5 THF: C_6D_6 ; $J_{^{13}\text{C}-\text{H}} = 123 \pm 1$ Hz) and IR^{7–11} ($\nu_{\text{C}=\text{O}}$ 1529 (m) cm^{-1} , THF) absorbances. Carbonyl ^{13}C NMR resonances (202.5, 198.4, 193.5 ppm; relative height 1.5:1.5:1) and IR absorbances ($\nu_{\text{C}=\text{O}}$ 2090 (w), 2030 (m), 1973 (s), 1940 (m), 1905 (m) cm^{-1}) suggest that the di-substituted rhenium in **2** is *trans*.^{13,14,23}

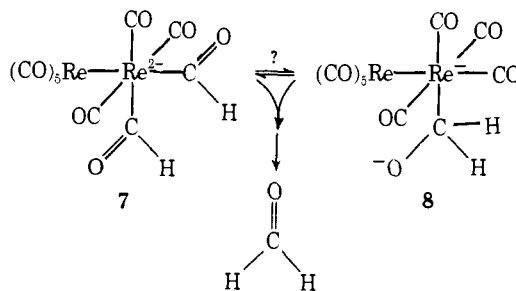
Scheme I. Hydride Transfer Reactions of the Rhenium Formyl **2**



Reactions of **2** with organic and inorganic substrates were investigated (Scheme I). Protonation of **2** at -50°C with $\text{CF}_3\text{SO}_3\text{H}$ (reaction a) gave immediate evolution of H_2 and formation of $\text{Re}_2(\text{CO})_{10}$. No formaldehyde could be detected, nor was ^1H NMR evidence for hydroxycarbene **5a** observed. Reaction of **2** with $\text{CH}_3\text{SO}_3\text{F}$ (reaction b) yielded methane and not **5b**. Reduction of benzaldehyde to benzyl alcohol was also observed (reaction c). Treatment of **2** with $\text{Fe}(\text{CO})_5$ (reaction d) afforded the known formyl complex $[(\text{CO})_4\text{Fe}(\text{COH})]^-$ (**6**). Although **6** was originally prepared by formylation of $[\text{Fe}(\text{CO})_4]^{2-}$, more recently we⁸ and others^{10,11} have shown that salts of **6** may be synthesized by attack of various hydride donors upon $\text{Fe}(\text{CO})_5$. Thus it is unlikely that actual migration of a formyl ligand from rhenium to iron occurs. Together, the reactions in Scheme I indicate that **2** is a strong, broad-spectrum hydride donor.

The addition of 1.0 equiv of $\text{K}(\text{sec-C}_4\text{H}_9)_3\text{BH}^{\text{6b}}$ to $\text{Re}_2(\text{CO})_{10}$ afforded the potassium salt of **2** in situ (^1H NMR δ 16.03; IR 2092 (w), 2023 (m), 1972 (s), 1933 (m), 1897 (m), 1547 (m) cm^{-1}). The addition of a second equivalent resulted in the formation of a new rhenium complex over the course of 10 min, which was isolated as an orange powder by solvent removal and precipitation from THF/hexane. No protons were present by ^1H NMR, and microanalysis indicated the empirical formula $\text{K}_2\text{Re}_2(\text{CO})_9$ ¹⁶ (92% yield; dec pt 120–140 °C), a previously reported dianion.¹⁷ Also formed in this reaction was formaldehyde, isolated in 21% yield as its dimedone de-

rivative. When $\text{Re}_2(\text{CO})_{10}$ was reacted with 3.0 equiv of $\text{K}(\text{sec-C}_4\text{H}_9)_3\text{BH}$ (which does not react with $\text{K}_2\text{Re}_2(\text{CO})_9$), methanol was isolated in 38% yield as its 3,5-dinitrobenzoate. Possible precursors to formaldehyde include **7** and **8**. This reaction is not restricted to binuclear formyls, as methanol is produced under similar conditions from $\text{K}^+ \cdot \text{6}$.¹⁸ These reactions^{16b} indicate that, although **2** is a hydride donor, it is still subject to further hydride attack.



Formyl **2** exhibits surprising thermal stability relative to previously prepared anionic formyl complexes.^{8,9} After 55 h at 55°C in THF in a sealed ^1H NMR tube, it was only 50% decomposed. When the decomposition of **2** was carried out at 90°C without solvent, $\text{Re}_2(\text{CO})_{10}$ (47–52%)^{15a} was formed. No gases, formaldehyde, methanol, or butanol could be detected.

The addition of 1.0 equiv of $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$ to $\text{ReMn}(\text{CO})_{10}$ at -20°C in THF in a ^1H NMR tube resulted in a new resonance at δ 14.30 (98%;^{15b} one sharp peak to -60°C) to which we assign the overall structure **3**. Since **3** decomposes quite rapidly at room temperature by an apparent first-order mechanism ($k_{\text{obsd}} = 9.73 \times 10^{-4} \text{ s}^{-1}$ at 32°C), its isolation has been impeded. While the IR is suggestive of a single structure (THF, 2072 (w), 2011 (m), 1970 (s), 1906 (m), 1872 (m), 1579 cm^{-1} (m)), the ^{13}C NMR indicates that two formyl complexes are present (-30°C , 5:1 THF: C_6D_6 (relative area), 285.1 (14), 284.1 (13), 199.0 (8), 197.4 (4), 192.4 (6), 191.3 (4), 189.2 (17), 187.2 ppm (7)). These may be *cis-trans* isomers or a mixture of manganese and rhenium formyls.¹⁹ Regardless of the precise composition, formyl **3** duplicates exactly the chemistry of **2** depicted in Scheme I. The predominant decomposition product of **3** is $\text{ReMn}(\text{CO})_{10}$ (42%).^{15a} No $\text{LiMn}(\text{CO})_5$, $\text{LiRe}(\text{CO})_5$, $\text{HMn}(\text{CO})_5$, or $\text{HRe}(\text{CO})_5$ are formed.

Observations which complement the foregoing results have been described by Casey.²⁰ The principal conclusions from our study are as follows: (a) With the synthesis of **4** previously reported by us,⁸ a series of three homologous binuclear formyl complexes (**2–4**) are now readily available. Their kinetic stability increases with rhenium content; in general, rhenium forms stronger bonds than manganese.²¹ (b) Reactions a–d (Scheme I) with *isolated 2* firmly establish that anionic formyl complexes can act as *direct* hydride donors. Although similar reactions were observed with a variety of thermally unstable formyl complexes generated with $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$,^{8,9} by-product $(\text{C}_2\text{H}_5)_3\text{B}$ represents a possible mediator of the hydride transfer process.²² Also, the previous observation of Collman and Winter that $\text{PPN}^+ \cdot \text{6}$ reduces 1-iodooctane to octane⁷ should be reinterpreted as a hydride displacement. (c) Formyl **2** is subject to further reduction by hydride donors, as evidenced by the formation of formaldehyde and methanol. (d) The availability of **2–4** should facilitate syntheses of models for other surface-bound intermediates on the reaction coordinate between CO and alkanes and alcohols. This line of investigation is under active pursuit in this laboratory.

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dation instrumentation support (CHE 76-05926; Bruker 200 MHz NMR) is also gratefully acknowledged. We thank Professor C. P. Casey (University of Wisconsin) for details of related studies in his laboratory.

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- (12) Anal. Calcd for $C_{14}H_{19}LiO_{11}Re_2$: C, 22.95; H, 1.24; Li, 0.95; Re, 50.84. Found: C, 22.76; H, 1.30; Li, 1.07; Re, 50.61. When dissolved in $CDCl_3$ (in which **2** decomposes), the 1H NMR spectrum indicated the presence of 0.93 ± 0.06 equiv of THF relative to *p*-di-*tert*-butylbenzene standard.
- (13) See E. O. Fischer, E. Offhaus, J. Müller, and D. Nöthe, *Chem. Ber.*, **105**, 3027 (1972); E. O. Fischer and E. Offhaus, *ibid.*, **102**, 2449 (1969).
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- (16) (a) Anal. Calcd for $C_9K_2O_9Re_2$: C, 15.38; K, 11.13; Re, 53.00. Found: C, 15.42; K, 11.42; Re, 53.12. IR (cm^{-1} , THF): 2033 (w), 2010 (m), 1966 (s), 1924 (s), 1880 (m), 1860 (m). (b) The reaction of $Re_2(CO)_{10}$ with 2 equiv of $Li(C_2H_5)_3BH$ yields a spectroscopically equivalent material believed to be $Li_2Re_2(CO)_8$.
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- (19) Utilization of $ReMn(CO)_{10}$ specifically ^{13}C labeled on Re or Mn does not lead to an unambiguous structure for **3**; See ref 14 for an acyl transfer reaction from manganese to rhenium.
- (20) C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, preceding paper in this issue.
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- (22) Experiments have been addressed to this point: J. A. Gladysz and J. H. Merrifield, unpublished work.
- (23) NOTE ADDED IN PROOF. The 50.32-MHz ^{13}C NMR spectrum of **2** at $-60^\circ C$ in $THF-d_6$ which is 0.06 M in $Cr(acac)_3$ (conditions for low temperature quadrupole decoupling) shows 5 carbonyl resonances (202.1, 198.6, 197.9, 193.0, 187.7 ppm; relative areas 1.6:1.2:8.2:6:0.7) indicating that **2** is likely the *cis* isomer.

J. A. Gladysz,* Wilson Tam

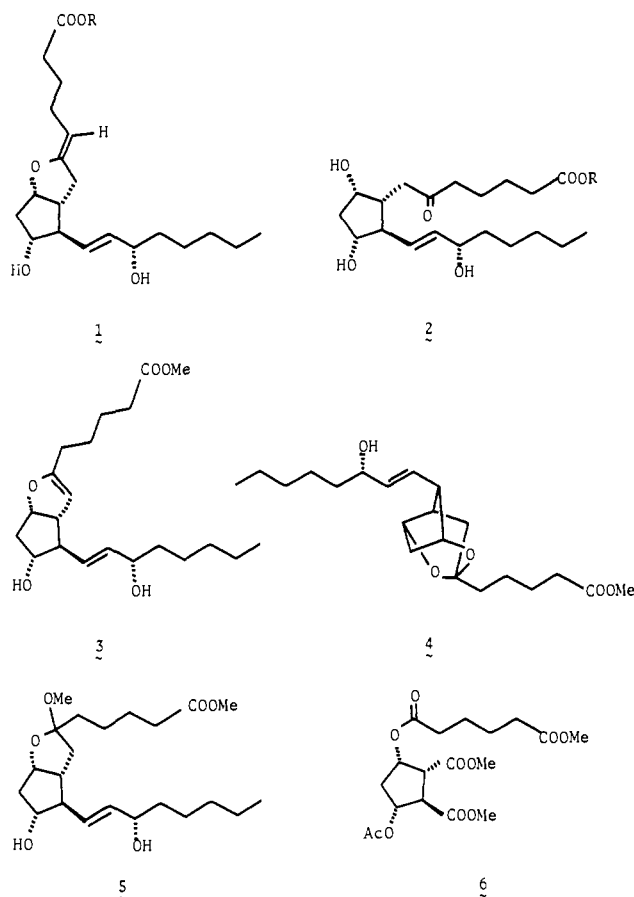
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6,9 α -Oxido-11 α ,15 α -dihydroxyprosta-6,(*E*)-13-dienoic Acid Methyl Ester and 6,9 α :6,11 α -Dioxido-15 α -hydroxyprost-(*E*)-13-enoic Acid Methyl Ester. Two Isomeric Forms of Prostacyclin (PGI₂)

Sir:

The isolation¹ and structural characterization² of prostacyclin (PGI₂, **1**, R = H) and structural characterization² of prostacyclin (PGI₂, **1**, R = H) with the discovery of its potential value in acute myocardial ischemia³ has opened a new chapter of prostaglandin research.⁴ Prostacyclin is a rather unstable molecule in aqueous, acidic or neutral media, breaking down to 6-keto-PGF_{1 α} (**2**, R = H), in equilibrium with its lactol form.^{2a} The isolation of 6-keto-PGF_{1 α} itself from various biological tissues has also been reported recently.⁵ Although **2** does not appear to be as important biologically as



is the enol form **1**, the possible regeneration of **1** from **2** would be nonetheless deserving of careful chemical and biological study. Herein we report two isomeric forms (**3** and **4**) of prostacyclin both of which were derived chemically from 6-keto-PGF_{1 α} and one of which showed a significant biological activity.

Treatment of prostacyclin methyl ester (**1**, R = Me)^{2a,6} in methanol with a small amount of acetic acid at 25 °C for 2 h, addition of excess triethylamine, extraction with ether, and concentration afforded the crude methoxy lactol **5**. The 1H NMR and IR spectra of **5** indicated the absence of 5,6-olefinic unit.⁷ The crude product was dissolved in hexamethylphosphoric triamide, and the mixture was heated at 180 °C for 14 min to effect elimination of methanol. The product was isolated from this reaction simply by extraction with ether, drying, and removing the solvent.⁸ Purification of the acid-sensitive enol ether **3** was effected by column chromatography on silica gel (EtOAc-hexane-Et₃N, 50:50:0.1), and the product **3** so obtained as a colorless oil was >98% pure by GC analysis and exhibited fully consistent 1H NMR (double-resonance technique) and IR spectra.⁹ The same enol ether was prepared from 6-keto-PGF_{1 α} methyl ester (**2**, R = Me) by an alternate sequence consisting of (1) trimethylsilylation by excess trimethylsilyldiethylamine (TMSDEA) at 25 °C for 12 h, (2) GC separation of the major component,¹⁰ and (3) removal of the remaining trimethylsilyl groups (K₂CO₃-methanol, 0 °C for 1 h) to produce after column chromatography the pure enol ether **3** (44% yield from **2**).

Independent evidence for structure **3** was obtained by the clean hydrolysis of **3** to 6-keto-PGF_{1 α} methyl ester,¹¹ a property paralleling that of PGI₂ methyl ester.^{2a} Furthermore, oxidative cleavage of the C₆-C₇ olefinic unit of **3** was effected by (1) acetylation of **3** using acetic anhydride-pyridine at 25 °C for 18 h, (2) treatment with excess ozone in chloroform at $-25^\circ C$ for 15 min followed by exposure to hydrogen peroxide-acetic acid at 50 °C for 12 h, and (3) esterification with