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Metal-Mediated Decarbonylation and Dehydration of Ketose Sugars

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Ketose sugars can be decarbonylated and/or dehydrated by the action of certain metal complexes. Fructose reacts with 1 equiv of $RhCl(PPh_3)_3$ (**1**) in *N*-methyl-2-pyrrolidinone (NMP) at 130 °C to give furfuryl alcohol, $Rh(CO)Cl(PPh_3)_2$ (**2**), and a small amount of 1-deoxyerythritol. 1,3-Dihydroxyacetone consumes 2 equiv of **1**, giving methane and ca. 2 mol of **2**. With *manno*-2-heptulose the primary product is 2,7-anhydro-*manno*-2-heptulopyranose. The mechanisms of these unusual reactions have been studied by using ^{13}C-labeling experiments and model reactions employing Pd(II) and HCl. Attempts to make the reactions catalytic using $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)_2]^+[BF_4]^-$ in place of **1** were not successful. The use of NMP as a solvent offers some advantages in the acid-catalyzed synthesis of certain carbohydrate dehydration products, as exemplified by the conversion of *manno*-2-heptulose to its 2,7-anhydride and of 2-deoxyglucose to 1-(2-furanyl)-1,2-ethanediol.

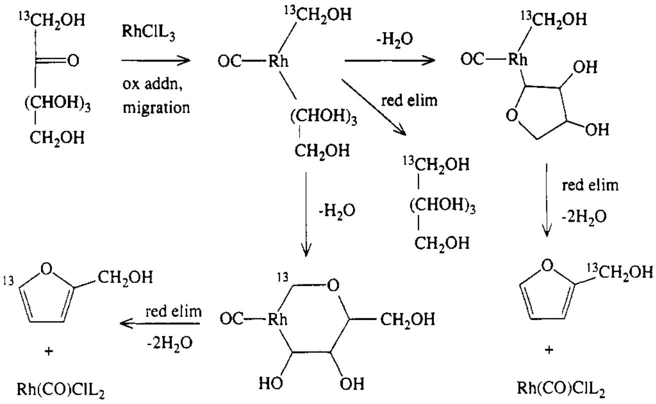
Introduction

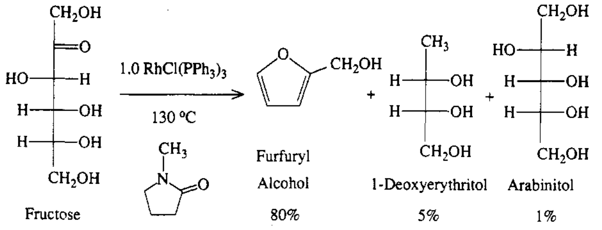
Aldehydes are readily decarbonylated by a number of metal complexes, most notably, chlorotris(triphenylphosphine)rhodium(I) (**1**).[1] We have recently shown that this reagent is even reactive enough to decarbonylate aldose sugars,[2] solutions of which contain only a few hundredths of a percent free aldehyde functionality due to intramolecular hemiacetal formation.[3] In contrast, the only unambiguous demonstrations of ketone decarbonylations employing **1** have involved activated substrates such as carboxylic acid anhydrides, α-keto aldehydes, and β-keto esters.[4,5] We thought that the α-hydroxyl substituents in ketose sugars might also provide sufficient activation to effect metal-mediated decarbonylations. In fact, reactions of **1** with ketoses proved to be more complicated than with aldoses and involve dehydrations as well as decarbonylations.[6] These findings have significant implications for future studies of metal-mediated reactions of carbohydrates directed at both fine synthesis and biomass conversion.

Results and Discussion

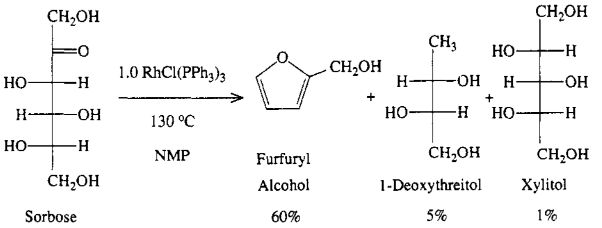
Stoichiometric Ketose Decarbonylations. Treatment of fructose[7] with 1 equiv of $RhCl(PPh_3)_3$ in *N*-methyl-2-pyrrolidinone (NMP) solution at 130 °C for 4–12 h leads to greater than 90% yields of $Rh(CO)Cl(PPh_3)_2$ (**2**) but only about 1% of the simple decarbonylation product arabinitol. Instead, the primary sugar-derived product is furfuryl alcohol (eq 1). The isomeric ketose sorbose behaves similarly (eq 2). The idealized stoichiometry for these reactions (eq 3) indicates that both decarbonylation and dehydration are occurring.

Scheme I. Mechanisms 1 and 2 for Fructose Decarbonylation–Dehydration





(1)



(2)

$$C_6H_{12}O_6 + \underset{\mathbf{1}}{RhCl(PPh_3)_3} \rightarrow C_5H_6O_2 + \underset{\mathbf{2}}{Rh(CO)Cl(PPh_3)_3} + 3H_2O + PPh_3 \quad (3)$$

The three-carbon ketose 1,3-dihydroxyacetone is also decarbonylated by **1** but again yields only a few percent

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[1] (a) Baird, M. C.; Nyman, C. J.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 348. (b) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968,** *90,* 99. (c) Tsuji, J.; Ohno, K. *Synthesis* **1969,** *1,* 157.

[2] (a) Andrews, M. A.; Klaeren, S. A. *J. Chem. Soc., Chem. Commun.* **1988,** 1266. (b) Andrews, M. A.; Gould, G. L.; Klaeren, S. A. *J. Org. Chem.* **1989,** *54,* 5257.

[3] Angyal, S. J. *Adv. Carbohydr. Chem. Biochem.* **1984,** *42,* 15.

[4] An early report on the decarbonylation of various solvents such as cyclohexanone by **1** did not identify the organic products (Rusina, A.; Vlcek, A. A. *Nature (London)* **1965,** *206,* 295). We believe that most of these results are more likely due to reactions of **1** with aldehydic oxidation impurities in the solvents.

[5] (a) Kaneda, K.; Azuma, H.; Wayaku, M.; Teranishi, S. *Chem. Lett.* **1974,** 215. (b) Akhrem, I. S.; Vartanyan, R. S.; Afanas'eva, L. V.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983,** 1346 (*Chem. Abstr.* **1983,** *99,* 121658y). (c) Akhrem, I. S.; Vartanyan, R. S.; Kotlyar, L. E.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977,** 253 (*Chem. Abstr.* **1977,** *86,* 170805j).

[6] A preliminary account of portions of this work is found in ref 2a.

[7] D and L configurational designators have been suppressed throughout the paper since they are immaterial to the chemistry reported. The actual sugars used are noted in the introduction to the Experimental Section.

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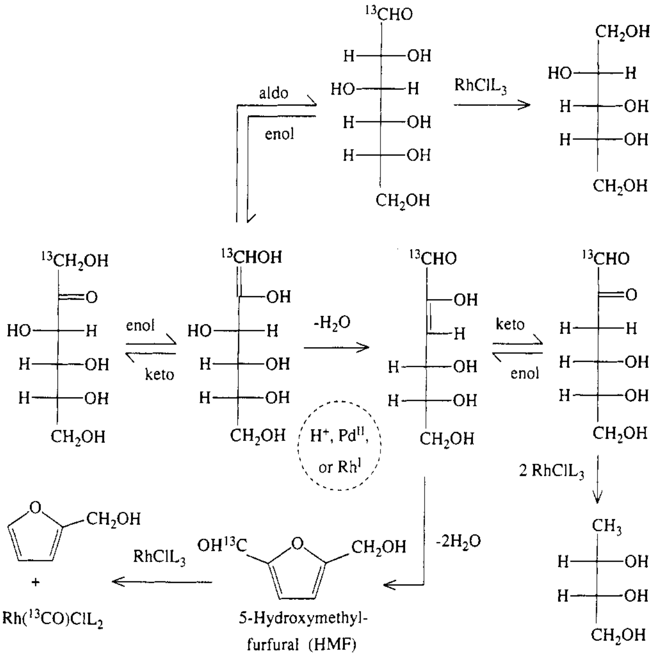
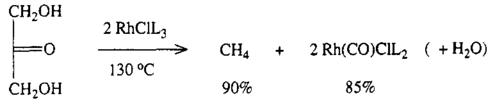
Scheme II. Mechanism 3 for Fructose Decarbonylation–Dehydration (Observed)



of the simple decarbonylation product ethylene glycol. Experiments instead reveal that the reaction proceeds according to eq 4, consuming *2 equiv* of $RhCl(PPh_3)_3$ to


(4)

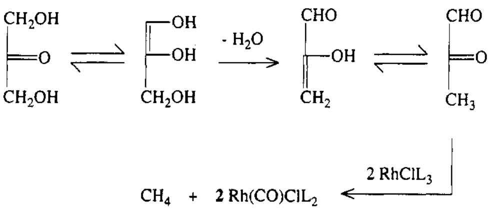
$$\mathrm{HOCH_2C(=O)CH_2OH} \xrightarrow[130\ ^\circ C]{2\,RhClL_3} \underset{90\%}{CH_4} + \underset{85\%}{2\,Rh(CO)ClL_2}\ (+H_2O) \qquad (4)$$

give carbonyl complex **2** (85%) and *methane* (ca. 90%). Decarbonylation of the C_4 ketose tetrulose by **1** is very slow, even at 130 °C, and gives a mixture of products, primarily glycerol and ethanol.

Mechanism of Decarbonylation–Dehydration Reactions. A ^{13}C isotope labeling experiment was devised that could distinguish between three plausible explanations for the unusual ketose decarbonylation products observed. Two related mechanistic scenarios (Scheme I), both based on analogies to known aldehyde decarbonylation[1,8] and hydroxyalkyl dehydration[9] chemistry, predict incorporation of a [1-^{13}C]fructose label into two different positions of the product furan. A third mechanistic scenario (Scheme II), based on ketose dehydration[10] and aldehyde decarbonylation[1,8] reactions, predicts yet another fate for the ^{13}C label, incorporation into the rhodium carbonyl ligand.

The experimental results show that the reaction of **1** with [1-^{13}C]fructose yields essentially unlabeled furfuryl alcohol (^{13}C NMR, GC–MS) and **2** containing 86% ^{13}C in the carbonyl group (IR). These findings rule out significant participation by the mechanisms given in Scheme I. Further support for the mechanism given in Scheme II comes from (a) the observation of residual amounts of the

Scheme III. Mechanism for Dihydroxyacetone Dehydration–Decarbonylation



5-(hydroxymethyl)furfural intermediate at the end of the reaction when fructose is used in excess and b) the formation of small amounts of 1-deoxyerythritol. (A corresponding product, tentatively identified as 1-deoxythreitol, is seen in the decarbonylation of sorbose.) The formation of these deoxyalditols is readily explained by partitioning of the initial enol aldehyde intermediate between cyclization to furans (which leads to the major furfuryl alcohol product) and retro-enolization to give 3-deoxy-2-hexosuloses.[10a] The latter would be readily doubly decarbonylated to give the observed 1-deoxytetritols (Scheme II, lower right).[11] Methane is presumably formed from 1,3-dihydroxyacetone via similar reactions (Scheme III), but this is harder to prove since in this case isotopic labeling studies cannot discriminate between mechanisms corresponding to those shown in Schemes I and II.

Several other observations are of interest in the context of the mechanism established for these reactions. First, the enediol derived from fructose is a known intermediate in the interconversion of fructose and glucose (Scheme II, top).[10b] Decarbonylation of the glucose so formed from the enediol would account for the ca. 1% yield of the simple decarbonylation product arabinitol.[2] Consistent with this hypothesis, the arabinitol derived from [1-^{13}C]fructose appeared to be unlabeled (GC–MS). (Arabinitol formed via the route shown in the center of Scheme I would be labeled.) It is noteworthy that no furfuryl alcohol is detected in the decarbonylation of glucose by **1**.[2]

A second observation concerns the fact that simple thermolysis of fructose in NMP at 130 °C does not lead to formation of the 5-(hydroxymethyl)furfural (HMF) intermediate of Scheme II (bottom center), implicating **1** as an agent in this transformation as well as in the subsequent decarbonylation. The potential for metal catalysis of this reaction is demonstrated by an experiment using the Pd(II) complex $Pd(CH_3CN)_2Cl_2$ (**3**) as a model for the Rh(I) complex **1**. Thus **3** was found to be an effective catalyst for the conversion of fructose into HMF at only 70 °C, the reaction stopping there since Pd(II) is not an effective decarbonylation reagent. A plausible vehicle for this would be stabilization/activation of the enol intermediates by coordination of these electron-rich alkenes to an electrophilic metal.

It would appear, however, that complexes **1** and **3** may be more accurately described as dehydration catalyst precursors. Product formation in the reaction of **1** with fructose only takes place after an induction period during which time noticeable amounts of fructose are consumed without formation of significant amounts of either HMF or furfuryl alcohol.[12] It has not been possible to unam-

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[8] Decarbonylation of aldehydes by 1 involves oxidative addition of the aldehyde C–H bond to give an acyl hydride, alkyl migration to form a carbonyl alkyl hydride, and finally reductive elimination to give 2 and the appropriate alkane. (a) Kampmeier, J. A.; Harris, S. H.; Mergelsberg, I. *J. Org. Chem.* **1984**, *49*, 621. (b) Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640. (c) Walborsky, H. M.; Allen, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 5465.

[9] Hydroxyalkyl complexes are known to undergo facile dehydration reactions with alcohols to give ethers: Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

[10] (a) Feather, M. S.; Harris, J. F. *Adv. Carbohydr. Chem. Biochem.* **1973**, *28*, 161. (b) de Bruijn, J. M.; Kieboom, A. P. G.; van Bekkum, H. *Sugar Tech. Rev.* **1986**, *13*, 21.

[11] This would also account for about half of the ^{12}CO-containing 2 formed in the reaction of 1 with [1-^{13}C]fructose. The remaining ^{12}CO material presumably comes from other small side reactions represented by the ca. 5% unidentified products observed.

[12] Some variation in reaction time with different lots of solvent and/or catalyst has been observed, with the ultimate yield of furfuryl alcohol and 2 being inversely dependent on the time required to achieve complete consumption of sugar, presumably due to parasitic sugar decomposition reactions.

biguously identify the active catalyst in this system, but several observations are relevant. Dehydration of fructose to HMF in aqueous solutions is typically an acid-catalyzed reaction,[10a] and a control experiment using HCl shows that this is also true in NMP. One possibility, therefore, is that chloride complexes **1** and **3** react with the sugar hydroxyl groups and/or solvent impurities to generate small amounts of HCl which then catalyzes the formation of HMF from fructose.[13] As expected, the intentional addition of 0.15 equiv of HCl to reactions of **1** with fructose greatly accelerates the formation of furfuryl alcohol. HMF can then be observed as an intermediate, and the reaction is complete in good yield within 15–30 minutes. Additional evidence in favor of the role of metal-generated acid as the primary catalyst is the inability of Rh(I) complexes not containing halide ligands to effect the formation of significant amounts of HMF or furfuryl alcohol from fructose, even at 130 °C (vide infra).

Attempts to confirm the role of adventitious acid by quenching these reactions with basic inhibitors proved unsuccessful for a variety of reasons. Pyridine bases are unsuitable traps since even their weak conjugate acids are efficient catalysts for the conversion of fructose to 5-(hydroxymethyl)furfural.[14] The conjugate acids of stronger noncoordinating bases such as 2,2,6,6-tetramethylpiperidine do not catalyze the dehydration of fructose, but addition of the base to the rhodium–fructose reaction opens new reaction paths leading to retro-aldol and transfer hydrogenation products. *Regardless of whether the active dehydration catalyst in this system is the metal itself or a derived acid, future studies of metal-mediated reactions of carbohydrates will need to either circumvent or exploit this rather ubiquitous metal–sugar reactivity pattern.*

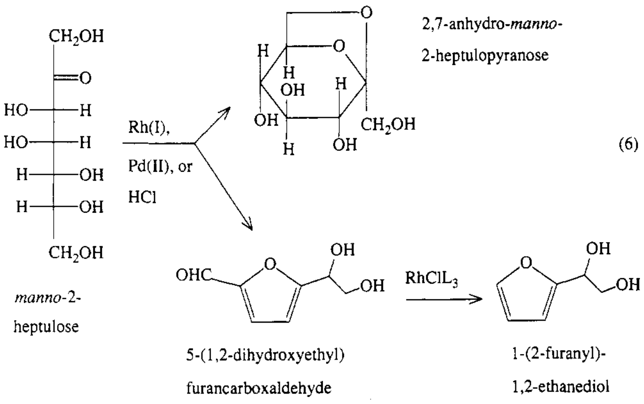
Catalytic Decarbonylations. Although the ketose decarbonylations proceed in an unusual fashion, it seemed worthwhile to attempt making the reactions catalytic. For example, catalytic conversion of fructose to furfuryl alcohol could provide an alternative to the existing preparation of this polymer precursor based on the reduction of furfural. More fascinating, but also more speculative, would be the conversion of fructose to a methane–carbon monoxide gaseous fuel via retro-aldol cleavage to dihydroxyacetone[10b] and subsequent catalytic dehydration/decarbonylation (eq 5).

$$C_6H_{12}O_6 \rightarrow 2HOCH_2COCH_2OH \rightarrow 2CH_4 + 4CO + 2H_2O \quad (5)$$

The most kinetically active aldehyde decarbonylation catalysts found in the literature are the metalloporphyrins studied by James and co-workers.[15] The free-radical characteristics of these systems, however, did not seem well-suited to the functionally rich sugars involved in the present work. We therefore chose to investigate the complexes $[Rh(Ph_2P(CH_2)_nPPh_2)_2]^+[BF_4]^-$ (**4a**, $n = 2$; **4b**, $n = 3$) because of their similarity to **1**. While these rhodium(I) cations have been reported to be long-lived and effective aldehyde decarbonylation catalysts,[16] the reaction conditions involve relatively concentrated solutions in nonpolar solvents at temperatures substantially higher than those required for stoichiometric decarbonylations with **1**.

Preliminary model studies using **4a** showed that it was a very poor catalyst for the decarbonylation of the hydroxyaldehyde HMF in NMP, giving less than one turnover to furfuryl alcohol after 22 h at 155 °C. (For comparison, **1** effected the quantitative stoichiometric decarbonylation of the same aldehyde in 24 h at only 70 °C in the same solvent.) Changing to the less coordinating solvent tetraglyme increased the reactivity of **4a** significantly, giving 7.3 turnovers in 20 h at 155 °C. A final increment in activity was obtained by switching to the more efficient catalyst **4b** (12 turnovers in 6 h at 155 °C in tetraglyme). Unfortunately, the cationic, chelated phosphine complexes proved ineffective at catalyzing the initial cyclodehydration of fructose to HMF. An attempt at bimetallic catalysis using both $Pd(CH_3CN)_2Cl_2$ and **4b** gave less than 20% conversion of fructose to HMF and almost no furfuryl alcohol. In all cases, mass balance problems and black deposits indicated that decomposition reactions were also occurring. In view of these poor results, detailed catalytic studies of the more difficult to analyze dihydroxyacetone system were not undertaken. These findings, together with those of our related studies of aldose decarbonylation,[2b] point out the need for the development of better aldehyde decarbonylation catalysts.

Dehydration of *manno*-2-Heptulose. The readily available C_7 ketose *manno*-2-heptulose was treated with **1** with the expectation, by analogy with fructose, of obtaining 1-(2-furanyl)-1,2-ethanediol.[17] While a little of this compound is formed (8% yield), the primary product (33% yield) was identified as 2,7-anhydro-*manno*-2-heptulopyranose[18] (eq 6). These results are consistent with Pd(II) and HCl model studies that show the formation of small amounts of the furan glycol precursor 5-(1,2-dihydroxyethyl)furancarboxaldehyde[19,20] and up to 65% yields of the anhydride.



(6)

Use of NMP in Sugar Dehydration Reactions. In the course of these model studies, it became apparent that a number of well-known sugar dehydration reactions might be carried out in NMP solution much more effectively than in water. While it was beyond the scope of the present work to develop this into a complete synthetic procedure, we report here our observations for future consideration

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(13) Addition of methanol, an impurity in an early lot of NMP, did not significantly affect the reaction. Water appeared to be a slight inhibitor, rather than a promoter.

(14) Fructose can be converted to 5-(hydroxymethyl)furfural by pyridinium hydrochloride in a solid-state reaction (Fayet, C.; Gelas, J. *Carbohydr. Res.* **1983**, *122*, 59). Present work confirms that this also occurs in NMP solution.

(15) Belani, R. M.; James, B. R.; Dolphin, D.; Rettig, S. J. *Can. J. Chem.* **1988**, *66*, 2072.

(16) (a) Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 7083. (b) Doughty, D. H.; Anderson, M. P.; Casalnuovo, A. L.; McGuiggan, M. F.; Tso, C. C.; Wang, H. H.; Pignolet, L. H. *Adv. Chem. Ser.* **1982**, *No. 196*, 65.

(17) (a) Albano, E.; Horton, D.; Tsuchiya, T. *Carbohydr. Res.* **1966**, *2*, 349. (b) Gonzalez, F.; Lesage, S.; Perlin, A. S. *Carbohydr. Res.* **1975**, *42*, 267. (c) Marco, J. L. *J. Chem. Res., Synop.* **1988**, 382.

(18) Zissis, E.; Stewart, L. C.; Richtmyer, N. K. *J. Am. Chem. Soc.* **1957**, *79*, 2593.

(19) Fayet, C.; Gelas, J. *Heterocycles* **1983**, *20*, 1563.

(20) Cf. acid-catalyzed reactions of *altro*-2-heptulose (sedoheptulose): (a) Richtmyer, N. K.; Pratt, J. W. *J. Am. Chem. Soc.* **1956**, *78*, 4717. (b) Zill, L. P.; Tolbert, N. E. *J. Am. Chem. Soc.* **1954**, *76*, 2929.

by others. For example, treatment of *manno*-2-heptulose with catalytic amounts of concentrated aqueous hydrochloric acid in NMP solution gives the anhydride in about 50% yield, a marked improvement in the ca. 9%, equilibrium-limited yield previously obtained by using water as the solvent.[18] Similarly, an authentic sample of 1-(2-furanyl)-1,2-ethanediol was readily obtained by the acid-catalyzed cyclodehydration of 2-deoxyglucose without formation of acetate byproducts as observed when the same reaction is conducted in acetic acid.[21] We believe that this technique could prove quite useful for the synthesis of a number of other carbohydrates and carbohydrate-derived compounds.

Experimental Section

General Data. Sugars were used as obtained (Sigma, D-fructose, L-sorbose, D-*manno*-2-heptulose; Aldrich, L-*glycero*-tetrulose (L-erythrulose), 1,3-dihydroxyacetone; Pfanstiehl, 2-deoxy-D-glucose; Cambridge Isotope: 99% enriched [1-^{13}C]-D-fructose). Commercial furans were obtained from Aldrich. $RhCl(PPh_3)_3$,[22] **4a** and **4b**,[23] and $Pd(CH_3CN)_2Cl_2$[24] were prepared as described. *N*-Methyl-2-pyrrolidinone (Aldrich HPLC grade) was dried over 4-Å molecular sieves. All experiments were assembled in an argon-filled glovebox. Most reactions were conducted in 25-mL screw-cap Erlenmeyer flasks equipped with Teflon-faced silicone rubber septa. Catalytic runs employing an argon sweep utilized 5-mL Kontes Airless-ware (TM) micro reaction flasks equipped with a septum port, magnetic stir-bar, and a water-cooled 14/20 West condenser connected via a U-shaped vacuum distillation adapter to a 25-mL round-bottom flask immersed in ice water. A steady stream of argon was bubbled through the reaction solution by inserting an 20-gauge needle through the septum port, the exit gases flowing out the vacuum distillation take-off adapter to a mercury bubbler. Capillary GC analyses were performed employing trimethylsilylation and O-methyloximation techniques as described elsewhere.[25] NMR spectra were obtained on a Bruker AM-300 using solvent peaks as internal reference ([^{1}H]DMSO at δ 2.49, [^{13}C]DMSO δ 39.5, $^{13}CH_3$ of NMP at δ 18.06). $Rh(CO)Cl(PPh_3)_2$ was identified by comparison with an authentic sample[26] and quantitated by its characteristic infrared CO stretch at 1977 cm^{-1}.

Decarbonylation of Fructose by $RhCl(PPh_3)_3$. Complex 1 (156 mg, 168 μmol), fructose (30 mg, 170 μmol), and GC internal standard(s) (tetradecane (20 μL) or durene/bibenzyl (45 mg/60 mg)) were heated in NMP or *N*,*N*-dimethylacetamide (5 mL) for 2–12 h at 130–140 °C. The deep red solution changed to orange or yellow only as the reaction neared completion. IR: **2** (90–99% yield). GC: furfuryl alcohol (40–80% yield, confirmation by ^{1}H NMR and GC–MS), 1-deoxyerythritol[27] (ca. 3–5%, confirmation by GC–MS of tris(trimethylsilyl ether) and partial ^{1}H NMR),[2b] arabinitol (1–3%, confirmation by GC–MS of pentakis(trimethylsilyl ether)), and an unknown (ca. 5%). Up to 5–10% yield of an unidentified, non-carbonyl-containing sugar species formed and then disappeared as the reaction proceeded. Best results were obtained with NMP that had been distilled from BaO; worst results were obtained with NMP containing visible molecular sieve dust.

Decarbonylation of [1-^{13}C]Fructose. Complex 1 (38.3 mg, 41.4 μmol) and [1-^{13}C]fructose (7.4 mg, 41 μmol) were heated in NMP (1 mL) at 130 °C for 2 h to give a yellow solution. IR: $Rh(^{13}CO)Cl(PPh_3)_3$ (30.9 μmol) and $Rh(^{12}CO)Cl(PPh_3)_3$ (5.1 μmol) (86:14). (A control reaction of 1 alone in NMP indicates that no more than 1 μmol of the [^{12}C]-**2** formed could be due to reaction with solvent impurities.) A ^{13}C {^{1}H} NMR spectrum (NMP/acetone-d_6) showed a large doublet due to [^{13}C]-**2** at δ 187.7 (J_{Rh-C} = 73.6 Hz) and only small peaks due to furfuryl alcohol, all at about natural abundance level. A GC–MS spectrum of a silylated aliquot of the reaction mixture also indicated negligible (< ca. 5%) incorporation of ^{13}C into the furfuryl alcohol and the arabinitol.

Decarbonylation of Sorbose. Complex 1 (153 mg, 166 μmol), sorbose (30.4 mg, 169 μmol), durene (45 mg), and bibenzyl (68 mg) were heated in NMP (5 mL) for 6 h to give a yellow-orange solution. IR: **2** (94%). GC: furfuryl alcohol (59%), 1-deoxythreitol[27] (ca. 5%, tentative identification by comparison of its tris(trimethylsilyl ether) GC–MS and GC retention time with those of 1-deoxyerythritol together with consideration of sorbose stereochemistry), xylitol (ca. 1%, confirmation by GC–MS of pentakis(trimethylsilyl ether)), and an unknown (ca. 5%).

Decarbonylation of 1,3-Dihydroxyacetone. Complex 1 (194.5 mg, 210 μmol) and 1,3-dihydroxyacetone (9.5 mg, 105 μmol) were heated in NMP (5 mL) for 7.5 h at 130 °C. The deep red solution turned orange as the reaction approached completion. The reaction mixture was cooled to room temperature and 10 μL of cyclopentane added as an internal GC standard. After the mixture was stirred for 0.5–1 h to equilibrate the cyclopentane between the gas and liquid phases, the gas phase was sampled and analyzed by GC giving an average methane yield of 95%. On the basis of calibration mixtures prepared by adding known amounts of methane and cyclopentane to NMP in an identical reaction flask, the error in this determination is estimated to be about 10–15%. Methane identification was confirmed by GC–MS (m/z = 16, 15, 14, 13, and 12). The liquid phase was analyzed by IR giving an 85% yield (179 μmol) of $Rh(CO)Cl(PPh_3)_2$. In a similar reaction, ethylene glycol (ca. 5% yield) was found in the liquid phase by GC.

Decarbonylation of Tetrulose. Complex 1 (150 mg, 163 μmol), tetrulose (25 mg syrup, ca. 157 μmol by GC analysis), durene (45 mg), and bibenzyl (62 mg) were heated in *N*,*N*-dimethylacetamide (5 mL) for 23 h to give a red solution. GC: unreacted tetrulose (60 μmol, 62%), glycerol (38 μmol, 24%), ethanol (ca. 15 μmol, 10%), and ca. 1–2% each of erythrose, erythritol, threitol, and ethylene glycol. Similar results were obtained by using NMP as solvent.

Decarbonylation of 5-(Hydroxymethyl)furfural. Complex 1 (155 mg, 168 μmol), HMF (23.4 mg, 186 μmol), durene (50 mg), and bibenzyl (64 mg) were heated in NMP (5 mL) at 70 °C. GC (reaction time, HMF, furfuryl alcohol): 2 h, 96 μmol, 89 μmol (48%); 24 h, 27 μmol, 166 μmol (99%).

Studies of Reaction Variables in Fructose Cyclodehydration and Decarbonylation. A. Fructose + 1. In a reaction of fructose (17.1 mg, 95 μmol), 1 (80.8 mg, 87 μmol), and bibenzyl (30 mg) at 130 °C in NMP (2.5 mL), GC analysis vs time gave the following (time, fructose consumed, furfuryl alcohol formed): 45 min, 13%, <1%; 2.5 h, 47%, 11%; 9 h, 91%, 52%).

B. Fructose + 1 + H_2O. In a reaction similar to A with H_2O (10 μL, 550 μmol) added, GC analysis gave the following (time, fructose consumed, furfuryl alcohol formed): 45 min, 12%, <1%; 2.5 h, 39%, 12%; 9 h, 83%, 45%.

C. Fructose + 1 + MeOH. In a reaction similar to A with MeOH added (10 μL, 250 μmol), GC analysis gave the following (time, fructose consumed, furfuryl alcohol formed): 45 min, 17%, <1%; 2.5 h, 56%, 20%; 9 h, 93%, 59%.

D. Fructose + 1 + HCl. In a reaction similar to A with concentrated aqueous HCl (1.2 μL, 14 μmol) added, GC analysis gave the following (time, fructose consumed, HMF present, furfuryl alcohol formed): 5 min, 100%, 11%, 74%; 30 min, 100%, 0%, 81%.

E. Fructose + Pyridinium Hydrochloride. In a reaction similar to A without 1 but with pyridinium hydrochloride (4.4 mg, 38 μmol) added, GC analysis gave the following (time, fructose consumed, HMF formed): 5 min, 100%, 82%.

F. Fructose + HCl. Concentrated aqueous HCl (3.5 μL, 40 μmol) was added to a solution of fructose (62.3 mg, 346 μmol) and bibenzyl (75 mg) in NMP (5.2 mL) and the mixture heated to 70 °C. GC analysis (time, fructose consumed, HMF formed): 20 min, 58%, 39%; 1 h, 86%, 67%; 3 h, 99%, 78%.

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[21] Hirsch, J.; Feather, M. S. *J. Carbohydr., Nucleosides, Nucleotides* **1979**, *5*, 573.

[22] Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

[23] (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1437. (b) James, B. R.; Mahajan, D. *Can. J. Chem.* **1979**, *57*, 180. (c) Slack, D. A.; Greveling, I.; Baird, M. C. *Inorg. Chem.* **1979**, *18*, 3125.

[24] Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 5913.

[25] (a) Biermann, C. J., McGinnis, G. D., Eds. *Analysis of Carbohydrates by GLC and MS*; CRC Press: Boca Raton, FL, 1988. (b) Andrews, M. A. *Carbohydr. Res.* **1989**, *194*, 000.

[26] Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

[27] Chaby, R.; Szabo, L. *Tetrahedron* **1971**, *27*, 3197.

G. Fructose + $Pd(CH_3CN)_2Cl_2$. In a reaction similar to F with complex **3** (11.1 mg, 42.8 μmol) used in place of HCl, GC analysis gave the following (time, fructose consumed, HMF formed): 20 min, 36%, 4%; 1 h, 62%, 31%; 3 h, 89%, 64%. Comparable results were obtained in an in situ ^{13}C NMR study.

H. Fructose + 1 + 2,2,6,6-Tetramethylpiperidine. In a reaction similar to A with 2,2,6,6-tetramethylpiperidine (15 μL, 89 μmol) added, GC analysis after 28 h gave fructose (7.5 μmol), 1,3-dihydroxyacetone (12.8 μmol), glycerol (2.8 μmol), arabinitol (3.6 μmol), mannose (1.1 μmol), 1,4-gluconolactone (12.7 μmol), glucose (1.2 μmol), mannitol (2.0 μmol), glucitol (1.0 μmol), and 1,4-mannonolactone (9.4 μmol).

Catalytic Decarbonylation of 5-(Hydroxymethyl)furfural. A. With 4a in NMP. Complex **4a** (37.9 mg, 38.4 μmol), HMF (45.8 mg, 363 μmol, **4a**:HMF = 1:9.5), and bibenzyl (75 mg) were dissolved in NMP (4.2 mL) in a micro reaction flask. The yellow solution was stirred and heated at 155 °C for 22 h under an argon purge. No products were found in the trap by GC analysis. Liquids in the condenser were washed back into the reaction vessel and the dark brown reaction solution analyzed by GC: HMF (291 μmol, 24% reaction), furfuryl alcohol (24 μmol, 7%, 0.6 turnover).

B. With 4a in Tetraglyme. Complex **4a** (21.1 mg, 21.4 μmol), HMF (55.0 mg, 436 μmol, **4a**:HMF = 1:20.4), durene (49 mg), and 1,2-diphenoxyethane (DPE, 100 mg) were dissolved in tetraethylene glycol dimethyl ether (3 mL, Aldrich Gold Label) in a micro reaction flask. The yellow solution was stirred and heated at 155 °C under an argon purge. The durene sublimed into the condenser. At 5 h, the solution was brownish yellow and GC analysis (vs DPE internal standard) showed HMF (290 μmol, 37% reaction) and furfuryl alcohol (23 μmol, 1.1 turnovers, not counting any product trapped in the condenser). After 22 h the reaction mixture was black and the argon purge needle had plugged. GC analysis of the trap showed that it contained furfuryl alcohol (34 μmol, 1.6 turnovers). Liquids in the condenser were washed back into the reaction vessel, and the black reaction solution was analyzed by GC: HMF (19 μmol, 96% reaction), furfuryl alcohol (122 μmol, 5.7 turnovers). Total furfuryl alcohol: 156 μmol, 7.3 turnovers, 36%.

C. With 4b in Tetraglyme. Complex **4b** (20.8 mg, 20.5 μmol), HMF (69.5 mg, 551 μmol, **4b**:HMF = 1:26.9), and bibenzyl (60 mg) were dissolved in tetraethylene glycol dimethyl ether (3.3 mL) in a micro reaction flask. The yellow solution was stirred and heated at 155 °C for 6 h under an argon purge. GC analysis of the trap showed that it contained furfuryl alcohol (7 μmol, 0.3 turnover). Liquids in the condenser were washed back into the reaction vessel, and the brown reaction solution was analyzed by GC: HMF (45 μmol, 92% reaction), furfuryl alcohol (237 μmol, 11.6 turnovers), and 2,5-furandimethanol (4 μmol). Total furfuryl alcohol: 244 μmol, 11.9 turnovers, 44%.

Reaction of Fructose with 4a and 4b. Complex **4a** (Cl^- salt) (15.7 mg, 16.8 μmol), fructose (30.3 mg, 168 μmol), durene (45 mg), and bibenzyl (65 mg) were heated in NMP (5.2 mL) in a screw-capped Erlenmeyer at 130 °C for 22 h. The solution remained yellow. GC: fructose (40 μmol, 76% reaction), HMF (15.6 μmol, 10%, 0.9 turnover), 1,3-dihydroxyacetone (ca. 2%), and four unknowns (ca. 3–15%). A similar reaction with **4a** (BF_4^- salt) gave a 4% yield of HMF after 4 h. A similar reaction with **4b** gave essentially no HMF after 4 h at 130 °C even though 17% of the starting fructose disappeared.

Attempted Catalytic Decarbonylation of Fructose. Complex **4b** (21.0 mg, 20.7 μmol), $Pd(CH_3CN)_2Cl_2$ (7.4 mg, 28.5 μmol), fructose (178 mg, 985 μmol), and bibenzyl (95 mg) were heated in tetraglyme (3.8 mL) at 155 °C under an argon purge. The yellow solution rapidly turned greenish yellow and then black, and liquid droplets appeared in the condenser. GC analysis after 5 min showed that only 29 μmol (3%) of the fructose remained and that only 170 μmol (17%) of HMF had formed. After 2 h, the condensate was washed back into the flask and GC analysis showed that all of the fructose had been consumed yielding only 101 μmol of HMF (10%) and a trace of furfuryl alcohol (3 μmol).

Acid-Catalyzed Dehydration of 2-Deoxyglucose. 2-Deoxyglucose (29.3 mg, 178.5 μmol) and bibenzyl (68 mg) were dissolved in NMP (5.0 mL) and heated at 130 °C for 1 h at which time GC analysis indicated that no reaction had occurred. Concentrated aqueous HCl (2 μL, 20 μmol) was added and the mixture heated for 1 h at which time GC analysis showed the complete disappearance of the starting sugar to give 1-(2-furanyl)-1,2-ethanediol (128 μmol based on a response factor equal to that of the isomeric 2,5-furandimethanol, 72%) together with two unknowns (ca. 10%). The reaction was cooled and the solvent removed by bulb-to-bulb vacuum distillation at ca. 50 °C. The last few drops of distillate were observed to be yellow and were collected separately and found by GC to contain bibenzyl and the furanyl glycol. The distillation residue was a mixture of white crystals and yellow-brown gum identified by GC and NMR as bibenzyl and the furanyl glycol.

1-(2-Furanyl)-1,2-ethanediol. ^1H NMR (DMSO-d_6): agreed with literature values.[17b] ^{13}C NMR (DMSO-d_6):[28] δ 156.2 (m, J = ca. 3.5 Hz, C-2), 141.5 (d of d of d, J = 202.7, 10.8, 7.2 Hz, C-5), 110.0 (d of d of d, J = 174.3, 13.5, 4.3 Hz, C-4), 105.9 (d of m, J = 174.8 Hz, C-3), 67.7 (d of d, J = 140, 3 Hz, CHOH), 64.4 (t of d, J = 141.0, 4.6 Hz, CH_2OH). Mass spectrum of bis(trimethylsilyl ether): m/z (relative intensity) 272 (M^+, 3.7), 257 ($[M - CH_3]^+$, 1.4), 182 ($[M - Me_3SiOH]^+$, 0.3), 169 ($[M - CH_2OSiMe_3]^+$, 100), 147 ($[Me_3SiO{=}SiMe_2]^+$, 28.8), 73 ($[Me_3Si]^+$, 65.6).

Catalytic Dehydration of *manno*-2-Heptulose. Concentrated aqueous HCl (3.8 μL, 44 μmol) was added to a solution of *manno*-2-heptulose (77.2 mg, 367 μmol) and bibenzyl (70 mg) in NMP (5.1 mL) and the mixture heated to 70 °C. The solution gradually became yellow and then orange. Heating was continued for 5 h although GC analysis later indicated that the reaction was essentially complete within 1 h. The primary product was 2,7-anhydro-*manno*-2-heptulopyranose (182 μmol based on a response factor equal to that of the isomeric 2,7-anhydro-*altro*-2-heptulopyranose, 50% (identification by comparison of ^{13}C NMR with literature data[29] and by comparison of its GC–MS with that of 2,7-anhydro-*altro*-2-heptulopyranose)). A slightly earlier eluting product (ca. 7%) appeared by GC–MS to be an isomeric anhydride, presumably the 2,7-anhydro-*manno*-2-heptulofuranose.[20] Another minor product (ca. 5%) was identified as 5-(1,2-dihydroxyethyl)-2-furancarboxaldehyde by comparison of its two isomeric *O*-methyloxime bis(trimethylsilyl ether)s' GC retention times with an authentic sample[19] and by GC–MS of the same derivatives: major (syn?) isomer, m/z (relative intensity) 329 (M^+, 1.2), 298 ($[M - OMe]^+$, 2.6), 226 ($[M - CH_2OSiMe_3]^+$, 100), 163 (5.0), 147 ($[Me_3SiO{=}SiMe_2]^+$, 14.5), 136 (13.2), 122 (20.2), 105 (6.0), 73 ($[Me_3Si]^+$, 26.1); minor (anti?) isomer very similar except m/z 136 (5.5), 122 (6.0). Several other small unidentified products were also observed.

An analogous reaction using complex **3** in place of HCl proceeded very similarly at 80 °C but was somewhat cleaner, giving a 65% yield of the main anhydride, a 15% yield of the minor anhydride, and a ca. 5% yield of the furancarboxaldehyde.

2,7-Anhydro-*manno*-2-heptulopyranose. Mass spectrum of tetrakis(trimethylsilyl ether): m/z (relative intensity) 375 ($[M - Me_3SiOH - CH_3]^+$, 0.2), 333 (5.1), 243 (4.5), 217 (13), 205 (11.2), 204 (55.8), 191 (24.6), 147 (20.2), 143 (12.1), 129 (11.5), 103 (10.7), 73 (100).

2,7-Anhydro-*altro*-2-heptulopyranose. Mass spectrum of an Aldrich sample derivatized as its tetrakis(trimethylsilyl ether): m/z (relative intensity) 375 ($[M - Me_3SiOH - CH_3]^+$, 0.5), 333 (2.5), 243 (3.6), 217 (38.1), 205 (16.5), 204 (84.2), 191 (12.2), 147 (23.1), 143 (5.4), 129 (10.7), 103 (10.7), 73 (100).

Reaction of *manno*-2-Heptulose with $RhCl(PPh_3)_3$. Complex **1** (153 mg, 165 μmol), *manno*-2-heptulose (35.1 mg, 167 μmol), durene (45 mg), and bibenzyl (60 mg) were dissolved in NMP (5.0 mL) and heated at 130 °C for 23 h. IR: complex **2** (59%). GC: *manno*-2-heptulose (<1%), 2,7-anhydro-*manno*-2-heptulopyranose (55 μmol, 33%), 1-(2-furanyl)-1,2-ethanediol (14 μmol, 8%), and a number of small unidentified products.

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(28) Assignments based on comparison with furfuryl alcohol: Hearn, M. T. W. *Aust. J. Chem.* **1976**, *29*, 107.

(29) Ritchie, R. G. S.; Cyr, N.; Perlin, A. S. *Can. J. Chem.* **1976**, *54*, 2301. Personal correspondence with Professor Perlin confirms our observations that the chemical shift of C-6 is 77.6 ppm, not 78.6 ppm, and that at higher field strengths C-3 and C-7 are partially resolved.

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Registry No. 1, 14694-95-2; 2, 13938-94-8; 4a, 53450-79-6; 4b, 70196-21-3; D-fructose, 57-48-7; furfuryl alcohol, 98-00-0; 1-deoxyerythritol, 4144-94-9; D-arabinitol, 488-82-4; D-sorbose, 87-79-6; 1-deoxythreitol, 122920-28-9; xylitol, 87-99-0; 1,3-dihydroxyacetone, 96-26-4; methane, 74-82-8; L-*glycero*-tetrulose, 533-50-6; glycerol, 56-81-5; ethanol, 64-17-5; 5-(hydroxymethyl)furfural, 67-47-0; 2-deoxy-D-glucose, 154-17-6; 1-(2-furanyl)-1,2-ethanediol, 19377-75-4; D-*manno*-2-heptulose, 3615-44-9; 2,7-anhydro-*manno*-2-heptulopyranose, 7739-21-1; 2,7-anhydro-*manno*-2-heptulofuranose, 122844-56-8; 5-(1,2-dihydroxyethyl)-2-furancarboxaldehyde, 98546-42-0; 2,7-anhydro-*altro*-2-heptulopyranose tetrakis(trimethylsilyl ether), 122844-57-9.

Synthesis and Electrophilic Properties of Neutral Molybdenum Formyl Complexes $Mo(C_5Me_5)(CO)_2(PR_3)CHO$: Access to Secondary Heterocarbene Compounds

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The neutral formyl complexes $MoCp^*(CO)_2(L)CHO$ (**3a**, L = CO; **3b**, L = $P(OPh)_3$; **3c**, L = PPh_3; **3d**, L = PPh_2Me; **3e**, L = PMe_3) are conveniently synthesized by sodium borohydride reduction of the corresponding metal carbonyl $[MoCp^*(CO)_3(L)^+PF_6^-$ (**2a–e**) in cold methanol. These thermally unstable species are isolated in 90% yield as a mixture of microcrystals of both cis and trans isomers, the selectivity (cis/trans) ranging from 10/90 (PPh_3) to 95/5 (PMe_3). The X-ray crystal structure of **3e** recorded at 128 K shows that it crystallizes in the monoclinic space $P2_1/c$ with unit cell parameters $a = 14.580$ (8) Å, $b = 8.244$ (12) Å, $c = 15.991$ (8) Å, $\beta = 94.28$ (5)°, and $Z = 4$. The structure was solved and refined (3402 reflections) to the final values for residual $R = 0.051$ and $R_w = 0.044$. The perpendicular orientation of the Cp* and CHO ligands evidenced from the crystal data is also assumed to be the favored conformation in solution, from the temperature dependence of the $^3J_{PH}$ coupling constants for the formyl proton resonance. Monitoring the thermal decomposition of the cis/trans mixture of the compounds **3b–e** by variable-temperature ^1H NMR experiments shows a greater stability for the cis isomers and an evolution to the related metal hydride complexes by specific loss of the ligand located trans with respect to the formyl group. Mechanistic implications of these features are discussed. The formyl complexes **3c** and **3d** undergo an electrophilic O-addition with CH_3SO_3F, CF_3CO_2H, and $Me_3SiOSO_3CF_3$ affording specifically the corresponding secondary oxycarbene complexes $[MoCp^*(CO)_2(L)(CHOR)]^+X^-$ (**4**, L = PPh_3, R = Me; **6**, L = PPh_3, R = H; **7**, L = PPh_2Me, R = $Si(CH_3)_3$) which are isolated for the more thermally stable compounds **4** and **7** and all fully characterized.

Introduction

Since the first synthesis, by an indirect route, of a formyl complex as reported by Collman and Winter,[1] many formyl transition-metal complexes have been obtained. These have attracted intense interest, especially in connection with synthesis gas chemistry.[2] The less stable neutral transition-metal formyl complexes have been prepared by hydride reduction of coordinated CO. The most detailed studies were performed by Graham,[4] Gladysz,[5] and Casey[6] on piano-stool CpRe carbonyl complexes. The key role of the solvent and of the Lewis acid associated with the hydridic reagent were emphasized in the preparation and

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(1) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089. (c) Casey, C. P.; Neuman, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5375. Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (d) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545. Tam, W.; Wong, W, K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

(2) (a) Henrici-Olive, G.; Olive, S. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 3, pp 391–434. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (d) Muetterties, E. L.; Stein, J. J. *Chem. Rev.* **1979**, *79*, 479. (e) Ponec, V. *Catal. Rev.—Sci. Eng.* **1978**, *18*, 151. (f) Kung, H. *Catal. Rev.—Sci. Eng.* **1980**, *22*, 235. (g) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic: New York, 1984. (h) Rofer-De Poorter, C, K. *Chem. Rev.* **1981**, *81*, 447. (i) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(3) When we were submitting the manuscript, a related paper by Gibson and co-workers appeared. Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.

(4) (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (b) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9. (c) May, C. J.; Graham, . A. G. *J. Organomet. Chem.* **1982**, *234*, C49.

(5) (a) Tam, W.; Lin, G. Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525. (b) Tam, W.; Lin, G. Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (c) Gladysz, J. A.; William, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1. (d) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5608. (e) Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596.

(6) (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395. (b) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (d) Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3371.

0276-7333/89/2308-2708$01.50/0