of carbon monoxide in the reaction mixture does not modify the stereochemistry of this complex, since both directly cross-coupled products **2** and ketone **3** are produced at intermediate carbon monoxide pressures. Carbon monoxide diverts the allylpalladium(II) complex to ketone **3**.

Since CO insertion into a palladium-carbon bond is known to proceed with retention of configuration at carbon,[16] the overall inversion of stereochemistry observed in the formation of ketone **3** requires that oxidative addition to palladium(0) proceeds with inversion at carbon. Thus, in the formation of the cross-coupled product **2** the subsequent steps of transmetalation and reductive elimination must proceed with net retention. Since reductive elimination from palladium has been shown[14,17] to proceed with retention, the stereochemistry is most likely fixed (retention) in the transmetalation step. This stereochemistry is consistent with that observed in the palladium-catalyzed coupling of the cis allyl ester with phenyl and hexenyl allanes.[18]

Acknowledgment. This research was supported by Grants CHE-8003336 and CHE-8305468 from the National Science Foundation. The 360-MHz NMR spectra were obtained at the Colorado State University Regional NMR Center, funded by the National Science Foundation Grant CHE-78-18581.

Supplementary Material Available: Listing of spectral data and elemental analyses (1 page). Ordering information is given on any current masthead page.

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(15) Oxidative additions to Pd(0) take place with inversion in the case of allylic esters (Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611) and benzyl chloride (Wong, P. K.; Lau, K. S. Y.; Stille, J. K. *Ibid.* **1974**, *96*, 5956).

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Direct Conversion of Organic Halides to Aldehydes with Carbon Monoxide and Tin Hydride Catalyzed by Palladium

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Received August 19, 1983
Revised Manuscript Received October 14, 1983

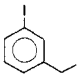
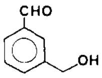
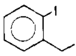
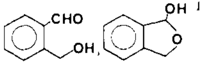
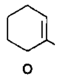
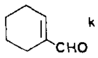
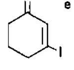
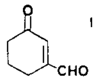
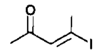
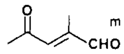
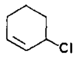
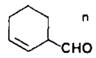
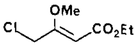
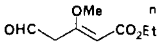
Although the uncatalyzed reduction of acid chlorides to aldehydes by tributytin hydride yields a mixture of aldehydes and esters,[1] the introduction of a palladium catalyst directs the reduction under mild conditions nearly exclusively to the aldehyde in high yield, even in the presence of other reducible groups.[2] The suggested mechanism[2] for the catalytic reaction involved sequential rapid oxidative addition of the acid chloride to the palladium(0) catalyst followed by transmetalation with tin hydride, to yield an acylpalladium hydride, and reductive elimination.

These results suggested that an organic halide could be catalytically converted directly to an aldehyde in the presence of carbon monoxide and tributyltin hydride. The transformation of a variety of organic halides to aldehydes does in fact take place with these reagents under mild reaction conditions (1-3 atm of CO, 50 °C) to give good yields of aldehydes (Table I).

$$\mathrm{RX} + \mathrm{CO} + n\text{-}\mathrm{Bu_3SnH} \xrightarrow[50\,^\circ\mathrm{C}]{\mathrm{Pd(0)}} \mathrm{RCHO} + n\text{-}\mathrm{BuSnX}$$

Aryl, benzyl, vinyl, and allyl halides can be converted to aldehydes, and other functional groups in the molecule (nitro, ketone, ester, and alcohol) remain unaffected under these reaction conditions. Closely related to this reaction is the palladium-catalyzed conversion of vinyl or aryl halides to aldehydes by carbon monoxide and hydrogen (1:1); this reaction, however, requires higher temperatures (~100 °C) and pressures (1200-1500 psi).[3]

Table I. Formylation of Organic Halides[a]

halide	solvent	*P* CO, atm	product(s)	% yield[b]
C_6H_5I	toluene	1	C_6H_5CHO	95[c]
p-MeC_6H_4I	"	1	p-MeC_6H_4CHO	100
o-MeC_6H_4I	"	1	o-MeC_6H_4CHO	70
p-BrC_6H_4I	THF	3	p-BrC_6H_4CHO C_6H_5Br C_6H_6	88 (70) 9 4
p-$MeOC_6H_4I$	toluene	1	p-$MeOC_6H_4CHO$	100 (77)
p-$NO_2C_6H_4I$	"	3	p-$NO_2C_6H_4CHO$ $C_6H_5NO_2$	38 62
	"	1	 [i] $C_6H_5CH_2OH$	(76) 12
	"	1	 [j] $C_6H_5CH_2OH$	(55) 20
$C_6H_5CH_2Br$	THF	1	$C_6H_5CH_2CHO$ $C_6H_5CH_3$	75 12
 [d]	toluene	1	 [k]	89 (53)
 [e]	"	3	 [l]	83
 [f]	"	3	 [m]	95
 [g]	"	3	 [n]	65
 [h]	THF	3	 [n]	86

[a] Reactions were run at 50 °C with tetrakis(triphenylphosphine)-palladium(0), 3.5-4 mol %. All compounds gave satisfactory spectra (IR, ^{1}H NMR, ^{13}C NMR) and GC retention times by comparison to authentic samples or known compounds. [b] Yields determined by GC; isolated yields in parentheses. [c] The same yield was obtained with either tetrakis(triphenylphosphine)-palladium(0) or bis(dibenzylidene acetone)palladium (3.7 mol %) plus 8.7 mol % triphenylphosphine. [d] Pross, A.; Sternhall, S. *Aust. J. Chem.* 1970, *23*, 989. [e] Piers, E.; Grierson, J. R.; Lau, C. K.; Nagakura, I. *Can. J. Chem.* 1982, *60*, 210. [f] Piers, E.; Nagakura, I. *Synth. Commun.* 1975, 193. [g] Grob, C. A.; Knu, H.; Gagneux, A. *Helv. Chim. Acta* 1957, *40*, 130. [h] DuBois, G. E.; Crosby, G. A.; Stephenson, R. A. *J. Med. Chem.* 1981, *24*, 408. [i] Leznoff, C. C.; Wong, J. Y. *Can. J. Chem.* 1973, *51*, 3756. [j] Rieche, A.; Schultz, M. *Justus Liebigs Ann. Chem.* 1962, *653*, 32. [k] Kraus, J. L.; Sturtz, G. *Bull. Soc. Chim. Fr.* 1971, *11*, 4012. [l] Quesada, M. L.; Schlessing, R. H. *Synth. Commun.* 1976, *6*, 555. [m] This compound has the correct spectra (NMR, IR) and analysis. [n] The product of reaction by NMR. However, the double bond isomerizes in conjugation with aldehyde function on workup.

The reaction with tin hydride and carbon monoxide has the advantage over a sequence in which a main group organometallic such as an organolithium or Grignard reagent is used to convert organic halides to aldehydes in that other reactive functionality may be present. The use of disodium tetracarbonylferrate to convert aliphatic halides and sulfonates to aldehydes is limited to substrates that do not contain other groups susceptible to reaction with the strong ferrate nucleophile.[4] The tin hydride reaction has the advantage that an acid chloride is not the sub-

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strate, and therefore the organic halide and/or aldehyde can carry functional groups, such as alcohol, that would have to be protected in the presence of the acid chloride. Allyl chlorides are converted to aldehydes without double-bond migration to the α,β-position.

In the conversion of 2-iodobenzyl alcohol to the corresponding aldehyde, the acylpalladium complex (**1**), under the reaction conditions, apparently undergoes a transmetalation reaction and reductive elimination of the acylpalladium hydride much faster than direct reductive elimination to the lactone.[5] A limiting side reaction in the conversion of halides to aldehydes appears to be the direct reduction of the halide without carbon monoxide insertion. This reduction proceeds only very slowly under the standard reaction conditions in the absence of a palladium catalyst. The slow addition of tributyltin hydride to the reaction mixture under carbon monoxide is necessary in order to optimize the ratio of aldehyde to reduced product, and the reduction also can be suppressed somewhat by increasing the carbon monoxide pressure. For example, the conversion of 4-bromoiodobenzene to 4-bromobenzaldehyde by the slow addition of 1 equiv of tributyltin hydride gives a 73% yield under 1 atm CO and an 88% yield under 3 atm. The reduction pathway becomes more serious with an aryl halide that is a good electron acceptor (one-electron transfer) and/or carries $+\sigma$ substituents. The yields of 4-nitrobenzaldehyde and nitrobenzene from 4-nitroiodobenzene are 9% and 84%, respectively, under 1 atm of carbon monoxide but 38% and 62% under 3 atm.

1

Typically, reactions were run under a balloon of carbon monoxide or in a pressure bottle (3 atm) with 1–5 mmol of the organic halide in 2–5 mL of THF or toluene per mmol of halide and 3.5–4 mol % of tetrakis(triphenylphosphine)palladium(0). A 10-mL solution of an equimolar amount of tributyltin hydride (plus a 10% excess) in the appropriate solvent was added via syringe pump over a 2.5–4-h period while maintaining the reaction mixture at 50 °C. After the addition was completed, the tributyltin halide was removed by conversion to the insoluble tributyltin fluoride.[6] The aldehydes were purified by radial or flash column chromatography.

Acknowledgment. This research was supported by a Grant CHE-8305468 from the National Science Foundation.

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Aqueous Tungsten(VI) Alkyl Chemistry

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We have recently reported reactions between neopentylidyne complexes and water to give oxo neopentylidene complexes of the type $W(O)(CHCMe_3)(PR_3)_2Cl_2$.[1] We became interested in the possibility of analogous reactions in the absence of potentially problematical phosphine ligands and therefore began exploring the hydrolysis of simple tungsten(VI) neopentylidyne complexes. We report here two examples of hydrolysis to give oxo neo*pentyl* complexes that are stable to ~180 °C in air and to further hydrolysis.

When a large excess of water is added to a concentrated solution of $W(CCMe_3)(CH_2CMe_3)_3$[2] in tetrahydrofuran white crystals form in ~30 min and can be isolated in ~90% yield. Analytical, NMR, and mass spectral data[3] suggest that this hydrocarbon-soluble product has the empirical formula $W_2O_3(CH_2CMe_3)_6$ (**1**). Since its IR spectrum shows no peaks characteristic of terminal oxo ligands in the region 1000–850 cm^{-1} we thought that the three oxo ligands were bridging, an unprecedented situation. However, preliminary X-ray studies[4] show that **1** contains the more logical linear O=W—O—W=O unit with a trigonal arrangement of neopentyl ligands about each metal. The absence of a peak ascribable to a W=O stretching mode in the 1000–850-cm^{-1} region has precedent[5] and will be discussed elsewhere.[4] If less than 2.5 equiv of H_2O are added to $W(CCMe_3)(CH_2CMe_3)_3$ the yield of **1** is reduced and $W(CCMe_3)(CH_2CMe_3)_3$ remains; we have not yet observed any intermediates.

$W_2O_3(CH_2CMe_3)_6$ is remarkably stable in air and to aqueous hydrolysis. After several weeks in air it becomes pale yellow, but the IR and NMR spectra of the pale yellow material are identical with those of the initial sample of white **1**. Recrystallization of the yellow material from pentane yields white crystals. $W_2O_3(CH_2CMe_3)_6$ can be recovered in high yield from THF after treatment with excess aqueous HCl (pH ~4) or NaOH (pH ~10) for 48 h, but it does not survive 1 N HCl or NaOH under the same conditions. In the air it begins to decompose on a melting point stage at ~180 °C.

Treatment of $W(CCMe_3)(CH_2CMe_3)_3$ with excess D_2O yields $W_2O_3(CH_2CMe_3)_4(CD_2CMe_3)_2$, as shown by ^{13}C NMR. At 67.89 MHz the signal for $CD_2\mathit{C}Me_3$ is found ca. 0.20 ppm upfield from that for $CH_2\mathit{C}Me_3$ in the proton-decoupled spectrum and their ratio is 1:2, respectively. No quaternary carbon signal for $CHD\mathit{C}Me_3$ could be found. The weak quintet signal (J_{CD} = 18 Hz) for $\mathit{C}D_2CMe_3$ is observed 1.36 ppm upfield of the large singlet for $\mathit{C}H_2CMe_3$, and again no signal ascribable to $\mathit{C}HDCMe_3$ could be observed. Although we cannot be certain that one CD_2CMe_3 ligand is on each metal, that certainly seems most plausible. We propose a mechanism for hydrolysis of $W(CCMe_3)(CH_2CMe_3)_3$ in which the neopentylidyne ligand is doubly protonated and there is no interconversion of neopentyl and neopentylidene ligands in reaction intermediates. The simplest version is shown in Scheme I.

$W_2O_3(CH_2CMe_3)_6$ is not stable to HCl in dichloromethane. Typically a mixture of **1** and the product, $W(O)(CH_2CMe_3)_3Cl$,[6] is obtained, since $W(O)(CH_2CMe_3)_3Cl$ readily and quantitatively reacts with water to reform **1**. Pure $W(O)(CH_2CMe_3)_3Cl$ can be isolated if Me_3SiCl is present to remove the water (eq 1); it

$$0.5W_2O_3(CH_2CMe_3)_3 \xrightarrow[Me_3SiCl]{HCl} W(O)(CH_2CMe_3)_3Cl \xrightarrow[\text{or LiOH}]{H_2O} \mathbf{1} \qquad (1)$$

is stable to HCl in dichloromethane. It is also possible to convert $W(O)(CH_2CMe_3)_3Cl$ into **1** by reacting it with 1 equiv of LiOH in THF. This provides some evidence that two molecules of $W(O)(OH)(CH_2CMe_3)_3$ condense to give **1** and 1 equiv of water.

Hydrolysis of $W(CCMe_3)(OCMe_3)_3$[2] in THF produces an

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(3) Anal. Calcd for $W_2C_{30}H_{66}O_3$: C, 42.77; H, 7.89. Found: C, 42.76; H, 7.73. ^1H NMR (C_6D_6) δ 1.98 (s, 2, $C\mathit{H}_2CMe_3$), 1.31 (s, 9, CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 91.89 (t, J_{CW} = 93 Hz, $\mathit{C}H_2CMe_3$), 35.42 (s, J_{CW} = 48 Hz, $\mathit{C}Me_3$), 32.90 (q, $C\mathit{Me}_3$); IR (Nujol) 760 (w), 680 cm^{-1} (vs); FD Mass Spectrum M + 1 ion at *m/e* 843. (M + 1 ions are not uncommon in FD mass spectrometry; see: Beckey, H. D. "Principles of Field Ionization and Field Desorption Mass Spectroscopy"; Pergamon Press: New York, 1977.)

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