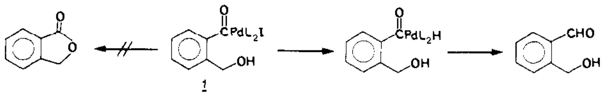
strate, and therefore the organic halide and/or aldehyde can carry functional groups, such as alcohol, that would have to be protected in the presence of the acid chloride. Allyl chlorides are converted to aldehydes without double-bond migration to the α,β-position.

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.



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.

---

[5] Cowell, A., Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4193.

[6] (a) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449. (b) Milstein, D.; Stille, J. K. *Ibid.* **1975**, *10*, 342.

Aqueous Tungsten(VI) Alkyl Chemistry

Irene Feinstein-Jaffe, Steven F. Pedersen, and
Richard R. Schrock*

Department of Chemistry, 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received July 19, 1983

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

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

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

---

[1] Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

[2] Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645.

[3] Anal. Calcd for $W_2C_{30}H_{66}O_3$: C, 42.77; H, 7.89. Found: C, 42.76; H, 7.73. ^{1}H 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.)

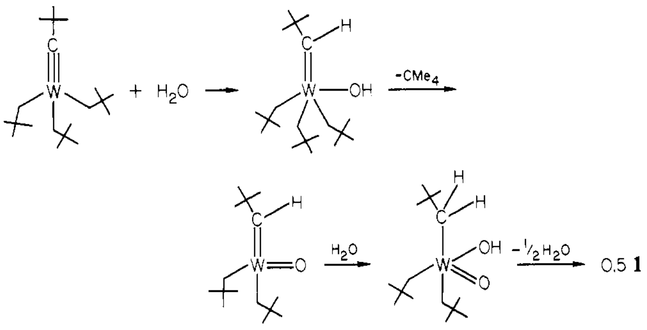
[4] Gibson, D.; Lippard, S. J.; Feinstein-Jaffe, I.; Schrock, R. R., unpublished results.

[5] Buchler, J. W.; Rohbock, K. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 1073.

[6] Kress, J. R. M.; Russell, J. M.; Wesolek, M. G.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 431.

0002-7863/83/1505-7176$01.50/0

Scheme I. Proposed Mechanism of Hydrolysis of $W(CCMe_3)(CH_2CMe_3)_3$



insoluble and as yet uncharacterized white powder. However, if the water contains 1 equiv of NaOH, a colorless solution is obtained. If tetraethylammonium hydroxide is used instead of NaOH a granular white tetraethylammonium salt is formed, which is soluble in both water and dichloromethane. IR, NMR, and FD mass spectral data all suggest that this species is $[NEt_4][WO_3(CH_2CMe_3)]$ (**2**; eq 2).[7] This complex does not darken at increased temperatures and has a melting point of 164 °C in air. It is stable in water at pH 7, but appears to be more readily hydrolyzed by aqueous acid or base than **1**. The organic product of hydrolysis of **2** by 1 N NaOH at 25 °C overnight was shown to be neopentane (1.0 (±0.1) equiv in ether layer by GLC).

$$W(CCMe_3)(OCMe_3)_3 + NEt_4OH \rightarrow \underset{\mathbf{2}}{[NEt_4][WO_3(CH_2CMe_3)]} \quad (2)$$

$W_2O_3(CH_2CMe_3)_6$ and $[WO_3(CH_2CMe_3)]^-$ can be added to the short list of d^0 complexes containing only oxo and alkyl ligands, i.e., $V(O)(CH_2SiMe_3)_3$,[8] ReO_2Me_3,[9] ReO_3Me,[10] and alkyl molybdates such as $[MoO_3Me]^-$ (observed in solution[11]). Preliminary results suggest that other tungsten(VI) alkylidyne complexes do not hydrolyze in as controlled a fashion as neopentylidyne complexes. For example, neither $W(CEt)(CH_2CMe_3)_3$[12] nor $W(CEt)(OCMe_3)_3$[13] hydrolyzes smoothly to give compounds analogous to **1** and **2**, respectively. However, $W(CPh)(OCMe_3)_3$[14] does appear to yield $[Et_4N][WO_3(CH_2Ph)]$.

The most surprising result is that **1** and **2** are so stable thermally, as well as to hydrolysis. This is likely to be a general property of such compounds since the V[8] and Re[9,10] complexes above are also reportedly stable to air and water, and $[MoO_3R]^-$ reportedly[11] hydrolyzes relatively slowly at pH 7.

We are attempting to prepare **1** and **2** by more direct routes that do not involve neopentylidyne precursors. Preparation of analogous compounds containing other hydrocarbon ligands and analogous compounds containing molybdenum has also been undertaken. We are especially interested in reactions of the alkyl ligand that are relevant to catalysis by molybdenum or tungsten oxides.

Acknowledgment. R.R.S. thanks the National Science Foundation for supporting this research (Grant CHE 81-21282), I.J. thanks the Bantrell Foundation for a postdoctoral fellowship, and S.F.P. thanks the Dow Central Research Department for a predoctoral fellowship. We also thank Dr. Catherine Costello and Dr. Henrianna Pang for obtaining FD mass spectra (NIH Grant RR317 to K. Biemann).

Registry No. 1, 87615-70-1; **2**, 87615-69-8; $W(CCMe_3)(CH_2CMe_3)_3$, 68490-69-7; $W_2O_3(CH_2CMe_3)_4(CD_2CMe_3)_2$, 87615-71-2; $W(O)(CH_2CMe_3)_3Cl$, 75846-05-8; $W(CCMe_3)(OCMe_3)_3$, 78234-36-3; NEt_4OH, 77-98-5.

---

[7] ^1H NMR (CD_2Cl_2) δ 3.35 (q, 8, NCH_2CH_3), 1.68 (s, 2, J_{HW} = 15 Hz, CH_2CMe_3), 1.34 (t, 12, NCH_2CH_3), 1.02 (s, 9, CH_2CMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 54.67 (CH_2CMe_3), 52.84 (NCH_2CH_3), 33.60 (CMe_3), 31.68 (CMe_3), 7.82 (NCH_2CH_3); IR (Nujol) 980 (vs), 925 (vs), 800 (s), 690 (vs), 655 cm^{-1} (vs). The $\{[NEt_4]_2[WO_3(CH_2CMe_3)]\}^+$ ion was observed in the FD mass spectrum.

[8] Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N. J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 532.

[9] Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488.

[10] Beattie, I. R.; Jones, P. L. *Inorg. Chem.* **1979**, *18*, 2318.

[11] Schrauzer, G. N.; Hughes, L.; Strumpach, N. *Z. Naturforsch., B* **1982**, *37b*, 380.

[12] This complex is a yellow oil prepared by reacting $W(CEt)(OCMe_3)_3$[13] with 3 equiv of $ClMgCH_2CMe_3$ followed by a 40 °C sublimation at <0.1 μm to separate it from $ClMg(OCMe_3)$: Murray, R., unpublished results.

[13] Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

[14] Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932.

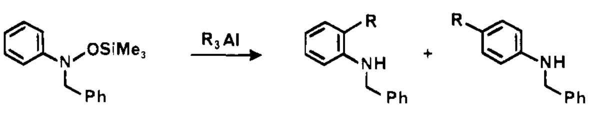
Nucleophilic Aromatic Substitution by Organoaluminum Reagents. Application to the Synthesis of Indoles

Junya Fujiwara, Yoshimi Fukutani, Hiromi Sano,
Keiji Maruoka, and Hisashi Yamamoto*

Department of Applied Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

Received August 30, 1983

Although the electrophilic aromatic substitution represented by Friedel–Crafts reaction is undoubtedly one of the most versatile synthetic procedures for construction of C–C bonds to aromatic rings,[1] the nucleophilic counterpart has been developed only to a lesser extent due to the lack of a suitable substrate for generating electron-deficient arenes.[2-5] However, by choosing the appropriate metal reagent and substrate, it could become possible to restructure the reactivity profile of the arene from nucleophile to electrophile.[4] Disclosed herein is a new and efficient method for the nucleophilic introduction of an alkyl group such as methyl or alkynyl on the aromatic nuclei of arylhydroxylamine derivatives by organoaluminum reagents (eq 1). The produced aromatic amines bearing the alkynyl moiety should serve as a promising building block for the elaboration of polyaromatics and fused heterocycles.[6]



(1)

1 2 3

The typical experimental procedure is exemplified by the alk-

---

[1] Friedel, C.; Crafts, J. M. *C. R. Hebd. Seances Acad. Sci.* **1877**, *84*, 1392, 1450. For reviews, see: Olah, G. A. "Friedel-Crafts and Related Reactions"; Interscience: New York, 1963–1965. Glatz, A. M. *Rev. Roum. Chim.* **1974**, *19*, 455.

[2] For reviews of classical nucleophilic aromatic substitution, see: Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. Hughes, E. D.; Ingold, C. K. *Quart. Rev.* (*London*) **1952**, *6*, 34. Bunnett, J. F. *Ibid.* **1958**, *12*, 1. Sauer, R.; Huisgen, R. *Angew. Chem.* **1960**, *72*, 294. Ross, S. D. *Progr. Phys. Org. Chem.* **1963**, *1*, 31.

[3] Nucleophilic aromatic alkylation of anilines and its applications to natural product synthesis: Gassman, P. G.; Gruetzmacher, G.; Smith, R. H. *Tetrahedron Lett.* **1972**, 497. Johnson, C. R.; Bacon, C. C.; Kingsbury, W. D. *Ibid.* **1972**, 501. Gassman, P. G.; Gruetzmacher, G. *J. Am. Chem. Soc.* **1973**, *95*, 588. Gassman, P. G.; Drewes, H. R. *Ibid.* **1974**, *96*, 3003. Gassman, P. G.; Gruetzmacher, G. *Ibid.* **1974**, *96*, 5487. Gassman, P. G.; van Bergen, T. J.; Gilbert, D. P.; Cue, B. W. *Ibid.* **1974**, *96*, 5495. Gassman, P. G.; van Bergen, T. J.; Gruetzmacher, G. *Ibid.* **1974**, *96*, 5512.

[4] For reviews of nucleophilic alkylation of arene–metal complexes, see: Semmelhack, M. F. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 36. Jaouen, G. In "Transition Metals Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; p 65. Semmelhack, M. F. In "Organic Synthesis. Today and Tomorrow"; Trost, B. M., Hutchinson, C. R., Eds.; Pergamon Press: New York, 1981; p 63. See also: Semmelhack, M. F.; Zask, A. *J. Am. Chem. Soc.* **1983**, *105*, 2034.

[5] Julia, M.; Le Goffic, F.; Igolen, J.; Braillage, M. *Tetrahedron Lett.* **1969**, 1569. Ohta, T.; Machida, R.; Takeda, K.; Endo, Y.; Shudo, K.; Okamoto, T. *J. Am. Chem. Soc.* **1980**, *102*, 6385. Endo, Y.; Shudo, K.; Okamoto, T. *Ibid.* **1982**, *104*, 6393.

[6] Since the amino group can be readily replaced with other functions via diazotization, the present method offers access to a variety of disubstituted aromatics.

0002-7863/83/1505-7177$01.50/0