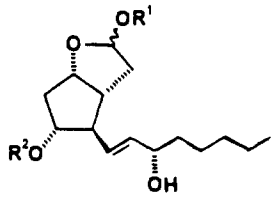
of tributyltin chloride, 2 equiv of sodium cyanoborohydride, 20 equiv of *tert*-butyl isocyanide, 0.1 equiv of AIBN, *tert*-butyl alcohol, reflux, 5 h).[9] Having the acid chain precursor masked as a cyclic acetal made the conversion of **7** to **9** an uneventful exercise via reduction to the aldehyde **8** (DIBAl-H, toluene, −20 °C; 84%), followed by keto phosphonate condensation (lithium chloride, $(i\text{-Pr})_2$NEt, diethyl 2-oxoheptylphosphonate, acetonitrile, room temperature;[10] 93%).

In the second route, radical cyclization–trapping (0.1 equiv of tributyltin chloride, 2 equiv of sodium cyanoborohydride, 7 equiv of 2-(trimethylsilyl)-1-octen-3-one, *hν* (254 nm), THF, room temperature, 10 h[11]) gave the crude trimethylsilyl ketone **10**. Volatile impurities were removed under high vacuum at 80 °C, and thermal rearrangement (140 °C, neat[12]) produced the trimethylsilyl enol ether **11**, which was oxidized (palladium acetate, acetonitrile, room temperature[13]) directly to **9**. The overall yield for these three steps was 58%.

To complete the synthesis, **9** was reduced diastereoselectively [(*S*)-BINAl-H, THF, −100 °C;[14] 89%) to the allylic alcohol **12**.



$R^1 = Et$, $R^2 = SiMe_2t\text{-Bu}$ **12**

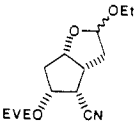
$R^1 = R^2 = H$ **13**

Hydrolysis (1.5% aqueous hydrochloric acid/THF (3:2), room temperature; 98%) gave the known dihydroxy lactol **13**.[15] Wittig reaction (potassium *tert*-butoxide, (4-carboxybutyl)triphenylphosphonium bromide, THF, room temperature;[15] 62%) produced $PGF_{2\alpha}$ (**1**) which was identical by TLC, ^{1}H NMR, ^{13}C NMR, and IR with an authentic sample.[16] The synthetic material had an optical rotation ($[\alpha]_{365}$ +78°; *c* 1.24 in 95% ethanol) essentially the same as that of the authentic $PGF_{2\alpha}$ ($[\alpha]_{365}$ +81°; *c* 1.55).

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their financial support.

Supplementary Material Available: IR and NMR spectra of compounds in this paper (29 pages). Ordering information is given on any current masthead page.

(8) We have shown that without the α-silyloxy group the trapping ratio is 34:1 (ref 2, footnote 12). In the case of **7** we were unable to detect any of the undesired α-cyano isomer. Presumably, the steric bulk of the silyloxy group leads to production of even less of the unwanted epimer. Notably, the stereochemistry of the cyano group is not crucial to the success of the prostaglandin synthesis since the required β-isomer is the more stable of the two. This assumption was key to a number of routes which were followed before the cyclization–trapping process had been developed. In one such route, explored in the (±) series, radical cyclization (Bu_3SnH, AIBN, benzene, 80 °C) was performed with a cyano group already present on the cyclopentene system. Delivery of a hydrogen atom to the convex face of the bicyclic radical intermediate set the cyano stereochemistry of the product i as α. Epimeri-



i

zation of i to the β-cyano compound was then accomplished under base catalysis (K_2CO_3, methanol, room temperature, 2 days; 73%).

(9) Much of the excess of *tert*-butyl isocyanide can be recovered by codistillation with *tert*-butyl alcohol at the end of the reaction. The distillate contains *tert*-butyl cyanide (approximately one-third as much as isocyanide) which is formed by *tert*-butyl radical-mediated isomerization of the isocyanide. Nevertheless, it can be reused after adjusting the quantity of isocyanide to compensate for the isomerization. See: Meier, M.; Rüchardt, C. *Tetrahedron Lett.* **1983**, *24*, 4671.

(10) Blanchette, M. A.; Choy, W.; Davis, J. T.; Essenfeld, A. P.; Masamune, S.; Roush, W. R.; Sakai, T. *Tetrahedron Lett.* **1984**, *25*, 2183.

(11) An additional 0.1 equiv of Bu_3SnCl was added after 4 h.

(12) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. Matsuda, T.; Sato, S.; Hattori, M.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 3215.

(13) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

(14) Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709. Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717. About 5% of the 15*R* epimer of **12** was also formed by using (*S*)-binaphthol of 91% ee. Independent reduction of the anomers of **9** allowed easy chromatographic separation of **12** from its undesired epimer.

(15) Howard, C. C.; Newton, R. F.; Reynolds, D. P.; Wadsworth, A. H.; Kelly, D. R.; Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **1980**, 852.

(16) We thank the Upjohn Co. for a sample of pure $PGF_{2\alpha}$, as its 2-amino-2-(hydroxymethyl)-1,3-propanediol salt.

Reactivity of Group 4 Acyl Complexes with Alkylaluminum Reagents: Synthesis of Zirconium Ketone Complexes

Robert M. Waymouth, Karl R. Clauser, and Robert H. Grubbs*

Contribution No. 7382, Arnold and Mabel Beckman Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

Received March 27, 1986

Transition-metal ketone complexes[1] and the closely related aldehyde[5,6] and ketene[7-9] complexes are of considerable interest because of their proposed role in CO reduction processes.[10] In this paper, we report a general and efficient synthesis of group 4 ketone complexes via the reductive alkylation of acyl complexes by alkylaluminum reagents. Mechanistic studies of this reaction reveal that aluminum reagents promote the intramolecular 1,2-migration of an alkyl group to a *cis*-acyl ligand to give ketone

(1) Transition-metal ketone complexes are generally prepared by the addition of an organic ketone to an unsaturated metal of the nickel group[2] or migration of a metal alkyl to a cis-acyl ligand.[3,4]

(2) (a) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311. (b) Hunt, M. H.; Kemmitt, R. D.; Russel, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 287. (c) Ittel, S. D. *J. Organomet. Chem.* **1977**, *137*, 223. (d) Countryman, F. R.; Penfold, B. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1598.

(3) (a) Erker, G.; Dorf, U.; Czisch, P.; Peterson, J. L. *Organometallics* **1986**, *5*, 668. (b) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29.

(4) (a) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421. (b) Evitt, E. R.; Bergman, R. G. *Ibid.* **1980**, *102*, 7003. (c) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *Ibid.* **1978**, *100*, 2716. (d) Demerseman, B.; Bouquet, B.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *93*, 199. (e) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972**, 654. (f) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101.

(5) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (b) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 278. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (d) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. (e) Roddick, D. M. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1984. (f) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846. (g) See also: Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.

(6) V: (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019. Mo: (b) *Ibid.* **1984**, *107*, 2985. (c) Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1360. (d) Brunner, H.; Wachter, J.; Bernal, I.; Creswick, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 861. Re: (e) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 1056. Fe: (f) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1984**, *B39*, 1380. Ru: (g) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. Os: (h) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53. Ni: (i) Walther, D. *Ibid.* **1980**, *190*, 393. Pt: (j) Green, M.; Howard, J. A. K.; Laguna, A.; Smart, L. E.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 278.

(7) (a) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Brownikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427. (b) Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *Ibid.* **1984**, *106*, 4050. (c) Ho, S. C. H.; Straus, D. A.; Armentrout, J.; Schaefer, W. P.; Grubbs, R. H. *Ibid.* **1983**, *105*, 2068. (e) Straus, D. A.; Grubbs, R. H. *Ibid.* **1982**, *104*, 5499. (f) Moore, E. J.; Straus, D. A.; Armentrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

(8) (a) Barger, P. T.; Santarsiero, B. D.; Armentrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *Ibid.* **1984**, *106*, 4783.

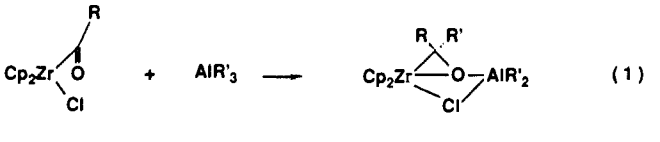
(9) (a) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 3172. (b) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173.

(10) Mazanec, T. J. *J. Catal.* **1986**, *98*, 115.

0002-7863/86/1508-6385$01.50/0

complexes. The function of the Lewis acid in these migration reactions is discussed in terms of the role of Lewis acids[22] in Fischer–Tropsch CO reduction processes. In addition, the reactivities of these complexes show them to be of considerable promise for the construction of carbon–carbon bonds.

Treatment of the acyl complexes **1** with trialkylaluminum reagents (R = Me, Et) at 0 °C in aromatic solvents affords the ketone complexes **2** in isolated yields of 60–90% (eq 1).[11,12] These



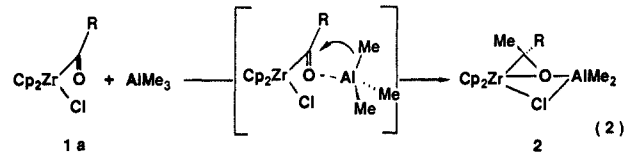
(1)

1 a R = Me
b R = Et

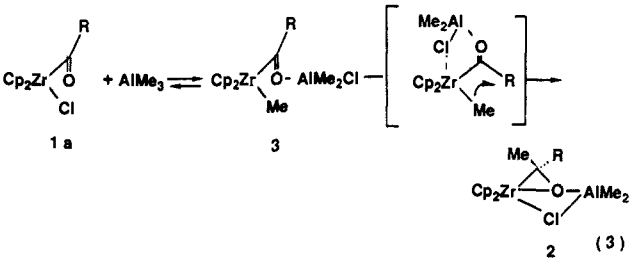
2	R	R'
a	Me	Me
b	Et	Me
c	$(CH_2)_2CMe_3$	Me
d	$(CH_2)_2CMe_3$	Et
e	c-C_6H_{11}	Me

complexes were characterized by spectral and analytical techniques, as well as by hydrolysis to the corresponding secondary alcohols.[13] The ketone complexes are thermally sensitive[14] but can be isolated at 25 °C as pale yellow or white solids that are stable under an inert atmosphere below 20 °C.

Two mechanisms for the reaction in eq 1 are presented below. The first (eq 2) involves the direct reductive alkylation of the acyl ligand by $AlMe_3$. Similar mechanisms have been proposed for reductions of acyl ligands by boranes,[15] metal hydrides,[5] and zirconium alkyls.[16] A second mechanism involves a rapid transmetalation to give the alkyl acyl complex **3**, followed by a Lewis acid promoted 1,2-migration of the alkyl group to the acyl ligand (eq 3).

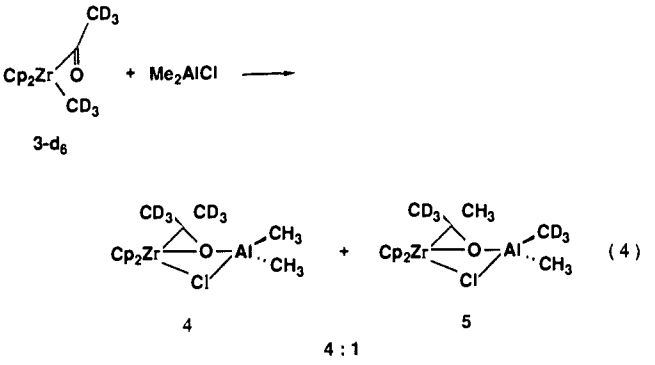


(2)



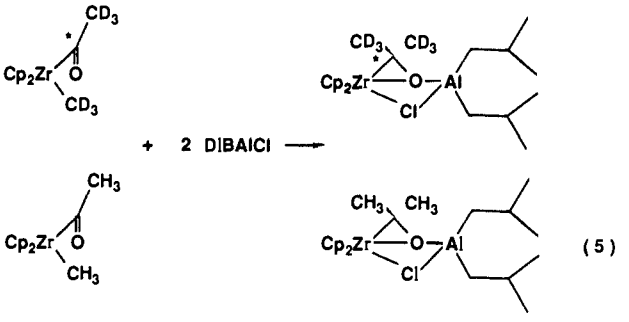
(3)

Prior to this work, there was little precedent for the second step of this latter mechanism.[17] In an effort to establish the feasibility of this step, the acyl complex **3**-d_6 was treated with Me_2AlCl at 0 °C in toluene to give the ketone complexes **4** and **5** in a ratio of 4:1 in 60% yield (eq 4). The observed product distribution



(4)

clearly shows that this reaction proceeds by a migration of the methyl group to the acyl ligand and not by transmetalation to **1** followed by direct alkylation by $Al(CH_3)_2CD_3$ (for which a ratio of 1:2 would be expected[18] for **4**:**5**). The observation of a small amount of **5** indicates that transmetalation is competitive with the reductive coupling of the alkyl and the acyl ligands. Crossover experiments (eq 5) using **3**, doubly labeled **3**-d_6-^{13}C, and diiso-



(5)

butylaluminum chloride establish that this Lewis acid induced reductive coupling of the alkyl and the acyl ligands occurs exclusively at one zirconium center.[19]

The labeling studies do not allow us, at this time, to rule out direct alkylation (eq 2) as a mechanism for formation of the ketone complexes from the chloro acyl complexes **1** (eq 1).[20] However, we have convincingly demonstrated that a novel, low-energy pathway[21] exists for formation of ketone complexes from alkyl acyl complexes **3** in the presence of a Lewis acid. A remarkable feature of the latter reactions (eq 4 and 5) is the rate enhancement observed for the migration of the alkyl group to the acyl ligand in the presence of the aluminum reagent.[17] The rate enhancements observed for CO migratory insertions in the presence of Lewis acids[22] have been rationalized[23] in terms of electronic effects in the transition state for the reaction. An equally important function

(11) Treatment of the acyl complexes **1** with $AlCl_3$ results in transmetalation of the acyl ligand from zirconium to aluminum. Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

(12) In a typical procedure, 0.563 g of **1a** (1.88 mmol) was suspended in 10 mL of 1/1 benzene/hexane and cooled to 0 °C in an ice bath. This suspension was treated with 1 mL of a 2 M toluene solution of $AlMe_3$ to give a yellow solution. Solvent was removed in vacuo at 0 °C and the pale yellow residue was washed with two 5-mL portions of pentane to give **2a** as a pale yellow powder (0.465 g, 1.31 mmol, 70%). **2a**: ^1H NMR (C_6D_6) δ 5.57 (s, 10 H), 1.49 (s, 6 H), −0.28 (s, 6 H); ^{13}C NMR (C_6D_6) δ 109.9, 80.9, 33.5, −6.32. Anal. Calcd for $C_{15}H_{22}OClZrAl$: C, 48.4; H, 6.0; Cl, 9.5. Found: C, 48.47, H, 5.96, Cl, 9.61. **2c**: ^1H NMR (C_6D_6) δ 5.68 (s, 5 H), 5.61 (s, 5 H), 1.97 (m, 2 H), 1.47 (s, 3 H), 1.35 (m, 2 H), 0.94 (s, 9 H), −0.22 (s, 3 H), −0.29 (s, 3 H); ^{13}C NMR (C_6D_6) δ 110, 109.8, 85.5, 41.4, 40.8, 30.9, 30.5, 29.7, 6.13. Anal. Calcd for $C_{20}H_{32}OClZrAl$: C, 54.31; H, 7.30. Found: C, 54.25; H, 7.26. Yield: 68%.

(13) Hydrolysis of **2e** with H_2O yields 1-cyclohexylethanol (30%, capillary GC, 50 ft SE-30 column 130 °C).

(14) The ketone complexes **2** begin to decompose in solution or in the solid state at temperatures higher than 30 °C.

(15) Van Doorn, J. A.; Masters, C.; Vogler, H. C. *J. Organomet. Chem.* **1976**, *105*, 245.

(16) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952.

(17) Erker has shown that, in the absence of Me_2AlCl, the acyl $Cp_2Zr(Ph)COPh$ isomerizes to the benzophenone complex $[Cp_2ZrOCPh_2]_2$ upon thermolysis at 70 °C for 1 h (ref 3).

(18) This ratio assumes a negligible kinetic isotope effect.

(19) The absence of crossover was confirmed by $(^1H)^{13}C$ NMR of the ketone complexes and GC–mass spectroscopy of the isopropyl alcohols obtained on hydrolysis.

(20) It is worth noting that reductions of organic carbonyls with alkylaluminum reagents, which proceed by a mechanism similar to that proposed in eq 2, require forcing conditions. Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 645.

(21) This mechanism might also be applicable to reductions observed when acyl complexes are treated with hydrido[5a,d,g] and alkyl[16] zirconium reagents.

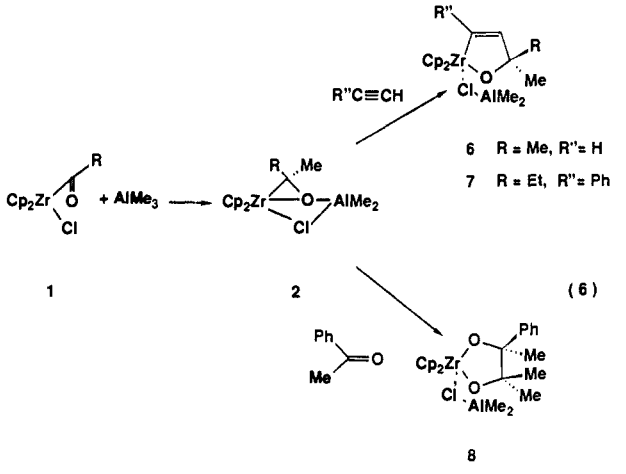
(22) (a) Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272. (b) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. (c) Correa, F.; Nakamura, R.; Stimson, R. E.; Burwell, R. L., Jr.; Shriver, D. F. *Ibid.* **1980**, *102*, 5112. (d) Shriver, D. F. In *Catalytic Activation of Carbon Monoxides*; Ford, P. C., Ed.; ACS Symposium Series 152; American Chemical Society: Washington, DC, 1981; pp 1–19. (e) Labinger, J. A.; Miller, J. S. *J. Am. Chem. Soc.*, **1982**, *104*, 6856.

(23) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

of the aluminum reagent in this case is to lower the barrier for rotation of the acyl ligand to a geometry most favorable for migration of the alkyl group (eq 3).

The role of the aluminum reagent in the isomerization of the alkyl acyl **3** to the ketone complex **2** models the behavior of Lewis-acidic metal oxides which serve as supports for heterogeneous Fischer-Tropsch catalysts. Shriver's results[22] demonstrate that molecular Lewis acids and aluminum oxides promote CO migratory insertion reactions. Our results imply that Lewis-acidic centers also promote further reduction of an acyl ligand.

The ketone complexes **2** react cleanly with acetylenes, ethylene, and ketones in reactions that promise to be of considerable synthetic utility. Treatment of the ketone complexes with acetylene or phenylacetylene generates the oxymetallacyclopentenes **6** and **7**, respectively (eq 6).[24,25] These reactions can be conveniently run in one pot starting from acyl complexes **1**. The oxymetallacycle **7** is produced regioselectively in 71% yield from the acyl **1b**. Treatment of the ketone complexes with ethylene yields saturated analogues of **6**. Hydrolysis of **6** or **7** yields the tertiary unsaturated alcohols.[26] Acetophenone reacts rapidly with the ketone complex **2a** to give **8**. The diolate **8** decomposes in solution above 10 °C but could be characterized spectroscopically[27] and by hydrolysis to the 1,2-diol $Me(Ph)C(OH)C(OH)Me_2$ (**9**) (eq 6).[28]



We have demonstrated that aluminum reagents promote the intramolecular reductive coupling of an alkyl and an acyl ligand to give ketone complexes. The aluminum reagent performs a dual role in these reactions: it acts as a reagent in the formation of the ketone complexes and it stabilizes and prevents dimerization of the ketone complexes by coordinating to the ketone ligand.[29] In the absence of coordinated Me_2AlCl, group 4 ketone complexes dimerize readily[3] and are much less reactive than the monomeric ketone complexes **2**. Further studies will investigate the role of these complexes as models for intermediates in catalytic processes and as reagents in organic synthesis.

Acknowledgment. We gratefully acknowledge the financial support of the Department of Energy and the National Institute of Health. R.M.W. was supported in part by a W.R. Grace Fellowship and a SOHIO fellowship in catalysis. K.R.C. was supported by a Summer Undergraduate Research Fellowship (SURF). We thank Dr. D. A. Straus for many helpful discussions.

Formation, Structures, and Reactivity of *cis*-Hydroxy-, *cis*-Methoxy-, and *cis*-Mercaptoiridium Hydrides. Oxidative Addition of Water to Ir(I)

David Milstein,* Joseph C. Calabrese, and Ian D. Williams

Contribution No. 4053, Central Research & Development Department, E. I. du Pont de Nemours & Company Experimental Station, Wilmington, Delaware 19898

Received May 16, 1986

Although mononuclear hydrido hydroxy complexes may play an important role in "water activation", including the water gas shift reaction,[1a,e] olefin and nitrile hydration,[1b] exchange reactions,[1b,d] and photodissociation of water,[1c] only few of them are known. The early-transition-metal complexes of this type[2] tend to dimerize, whereas the late-transition-metal complexes[1,3] tend to be unstable[1,3b,d] in the absence of excess water, probably because of an unfavorable formation constant. None of these complexes has been crystallographically characterized. We report here the isolation, properties, and crystallographic characterization, revealing some unusual features, of a stable, mononuclear hydrido hydroxy complex formed by facile water oxidative addition to Ir(I). A rare example of a mononuclear hydrido methoxy complex derived from it is also described. For comparison a hydrido mercapto complex is also presented.

Addition of excess purified water to a red suspension of $Ir(PMe_3)_4^+PF_6^-$ (**1**)[4] (Scheme I) in THF results in bleaching. Evaporation of the solvent under vacuum yields almost pure *cis*-$IrH(OH)(PMe_3)_4^+PF_6^-$ (**2**) as a white solid. Crystallization from THF by vapor diffusion of benzene leads to colorless crystals of pure **2** in 85% yield. The structure of **2** is unambiguously assigned based on IR, ^1H NMR, ^{31}P NMR, and elemental analysis.[5]

The *cis*-hydrido hydroxy **2** is air and thermally stable and does not undergo reductive elimination of water even at 100 °C. In contrast, the strongly basic *trans*-hydridohydroxyplatinum complexes[1a,b,3b] and hydridorhodium complexes containing outer-sphere hydroxide[1c,d,e] eliminate water readily, probably by deprotonation, and are stable only in the presence of a large excess of water. The cis configuration of **2** results in a relatively low tendency of the hydroxide ligand to dissociate (lack of hydride trans effect) and thus a diminished tendency to form water by deprotonation. Indeed, **2** is a relatively weak base. However, **2** undergoes ex-

(24) **6** (R = Me, R" = H): ^1H NMR (C_6D_6) δ 6.35 (d, J = 10.9 Hz, 1 H), 5.71 (d, J = 10.9 Hz, 1 H), 5.68 (s, 10 H), 1.24 (s, 6 H), -0.24 (s, 6 H); ^{13}C NMR (C_6D_6) δ 175.5 (CH), 140.4 (CH), 112.1 (Cp), 90.8 (CO), 29.3 (CH_3), -4.13 (CH_3). Anal. Calcd for $C_{17}H_{24}OClAlZr$: C, 51.30; H, 6.08; Cl, 8.91. Found: C, 51.26, H, 6.10; Cl 8.98. Yield: 55% from **1a**.

(25) **7** (R = Et, R" = Ph): ^1H NMR (C_6D_6) δ 7.24 (m, 2 H), 7.12 (m, 3 H), 5.85 (s, 5 H), 5.75 (s, 5 H), 5.43 (s, 1 H), 1.68 (m, J = 7.08 Hz, 3 H), 1.49 (m, J = 7.08 Hz, 2 H), -0.21 (s, 3 H); ^{13}C NMR (C_6D_6) δ 186.0 (C), 154.0 (Ph), 139.0 (CH), 126.2 (Ph), 113.2 (Cp), 112.6 (Cp), 92.1 (CO), 36.8 (CH_3), 28.9 (CH_2), 10.56 (CH_3). Anal. Calcd for $C_{24}H_{30}OClZrAl$: C, 59.05; H, 6.19. Found: C, 59.14; H, 6.30. Yield: 71% from **1b**.

(26) Hydrolysis of 6 with H_2O affords 2-methyl-3-buten-2-ol in 70% yield (GC).

(27) **8**: ^1H NMR (C_6D_6) δ 7.24 (m, Ph), 6.05 (s, 5 H), 6.02 (s, 5 H), 1.46 (s, 3 H), 1.43 (s, 3 H), 0.88 (s, 3 H), -0.14 (s, 3 H), -0.21 (s, 3 H).

(28) **9**: ^1H NMR (C_6D_6) δ 7.35 (m, Ph), 1.41 (s, 3 H), 1.09 (s, 3 H), 0.98 (s, 3 H). Anal. ($C_{11}H_{16}O_2$) C, H. Mp 80-81 °C, uncorrected; lit. mp 83-84 °C: Roger, R. *J. Chem. Soc.* **1925**, *124*, 518. Yield: 50% from **1a**.

(29) Coordinated Me_2AlCl performs a similar role in stabilizing the reactive alkylidene ligand in the Tebbe reagent $Cp_2Ti{=}CH_2{\cdot}AlMe_2Cl$. (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876.

(1) (a) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941. (b) Yoshida, T.; Matsuda, T.; Okano, T.; Otsuka, S. *Ibid* **1979**, *101*, 2027. (c) Yoshida, T.; Okano, T.; Otsuka, S. *Ibid.* **1980**, *102*, 5966. (d) Yoshida, T.; Okano, T.; Saito, K.; Otsuka, S. *Inorg. Chim. Acta* **1980**, *44*, L135. (e) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3411.

(2) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

(3) (a) Gillard, R. D.; Heaton, B. T.; Vaughan, D. *J. Chem. Soc. A* **1970**, 3126. (b) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543. (c) Chaudred, B. N.; Cole hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (d) James, B. R.; Preece, M.; Robinson, S. D. *Adv. Chem. Ser.* **1982**, *196*, 145. (e) Gotzig, R.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *285*, 99.

(4) Thorn, D. L. *Organometallics* **1982**, *1*, 197.

(5) **2**: IR (Nujol) 2068 (s, Ir-H), 3620 cm^{-1} (s, sh, O-H); ^1H NMR (pyridine-d_5) δ 1.445 (d, J = 8 Hz, 9 H, PMe_3), 1.601 (superimposed t + d, J_1 = 14, J_2 = 8 Hz, 27 H, $3PMe_3$), -1.40 (br s, 1 H, OH; disappears upon D_2O addition), -11.19 (d of q, $J_{P-H,trans}$ = 147, $J_{P-H,cis}$ = 19 Hz, 1 H, Ir H); $^{31}P\{^1H\}$ NMR (pyridine-d_5) δ -41.92 (d of d, J_1 = 20, J_2 = 16 Hz, 2 P), -47.94 (d of t, J_1 = 12, J_2 = 20 Hz, 1 P), -53.93 (d of t, J_1 = 16, J_2 = 12 Hz, 1 P). ^{31}P NMR (pyridine-d_5) δ -41.92 (m, 2 P, P trans to P), -47.94 (d of m, J = 147 Hz, 1 P, P trans to H), -53.93 (m, 1 P, P trans to OH).

0002-7863/86/1508-6387$01.50/0