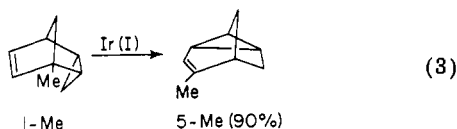


<sup>a</sup> The asterisk means, when D is present, R = H, and the double asterisk means when R = CH<sub>3</sub>, D = H.

prepared compound 1 with a methyl group substituted at the bridgehead position, 1-Me.<sup>6</sup> On reaction with Ir(I) under the same conditions as used in the above reactions, a 90% yield of 5-Me was obtained (eq 3). Methyl ana-



logues of 3 and 4 are conspicuously absent which will be addressed below. This result was quite surprising but when put together with the earlier results provides evidence for the postulated scheme that is shown in Scheme I. In this scheme using 1-Me, there are two intermediates labeled as 1B and 1B' that would be differentiated by the presence of the methyl group. It is reasonable to suggest that the methyl group would provide added stability to 1B' and would therefore favor path b. The methyl group also provides additional evidence for the idea that the bridge carbon is migrating.

The role of iridium has not been firmly established in that none of the intermediates shown in the scheme have been isolated. However, compound 1 is unreactive to the reaction conditions without Ir(I) present. It is postulated to form the iridacyclobutane complex from circumstantial evidence. First of all, these results are different from reaction of (Ph<sub>3</sub>P)<sub>2</sub>IrClCO with the exo analogue of 1. In the exo system that has been labeled with deuterium, the reaction path follows a scheme that has been previously elaborated by Katz.<sup>4</sup> In his postulate, Katz suggests that the metal (Rh) forms an intermediate complex in which the metal is in an endo position. Presumably, if the iridium in the system reported herein went by the same intermediate, the same result on labeling would be apparent. It is not.

Further, we feel that the iridium is an iradacycle rather than a  $\pi$ -allyl complex as a result of the deuterium distribution. When the iridacycle cleaves to the cationic intermediate 1A and 1A' an  $\alpha$  deuterium isotope effect

would favor the cleavage to form 1A' which gives the distribution observed. The isotope effect would have a magnitude of 1.20 which is consistent with a  $sp^3 \rightarrow sp^2$  transformation.<sup>8</sup> An alternative iridium complex would be a ( $\pi$ -allyl) metal hydride. Subsequent bridge migration would produce 4 and 5, but the ratio of products would not be consistent with the isotopic distribution observed. This transformation  $sp^2 \rightarrow sp^3$  would favor the formation of 1A over 1A', which is the opposite of what is observed.

**Conclusion.** The Ir(I)-catalyzed reaction of *endo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene to form tricyclo[3.2.1.0<sup>2,7</sup>]oct-3-ene has been shown to proceed via a carbocyclic rearrangement. This conclusion is based on the evidence garnered from both deuterium- and methyl-labeled substrates.

**Registry No.** 1-d, 86766-39-4; 1-Me, 86766-40-7; 3-d, 86766-41-8; 4, 86784-83-0; 5, 86766-42-9; 5-Me, 86766-43-0; (Ph<sub>3</sub>P)<sub>2</sub>IrClCO, 14871-41-1.

(8) Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* 1958, 80, 2326.

### Isolation and Chemical Properties of Ruthenium and Iron Hydroxymethyl Complexes ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>2</sub>CH<sub>2</sub>OH<sup>†</sup>

Y. C. Lin,\* D. Milstein, and S. S. Wreford

Central Research and Development Department,  
Experimental Station

E. I. du Pont de Nemours and Company  
Wilmington, Delaware 19898

Received May 31, 1983

**Summary:** The hydroxymethyl complexes ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>2</sub>(CH<sub>2</sub>OH) (M = Ru, Fe) were isolated from the reduction of the tricarbonyl cations ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>3</sub><sup>+</sup> with 4 equiv of NaBH<sub>3</sub>CN. They decompose catalytically to ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(CO)<sub>2</sub>H or [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> and formaldehyde when treated with phosphorus ligands. They react with CH<sub>3</sub>OH, CH<sub>3</sub>C(O)Cl/C<sub>5</sub>H<sub>5</sub>N, and (CH<sub>3</sub>)<sub>3</sub>SiCl/C<sub>5</sub>H<sub>5</sub>N to form methoxymethyl, (acyloxy)methyl, and (trimethylsiloxy)methyl complexes. Only the (trimethylsiloxy)methyl complexes can be hydrolyzed to regenerate the hydroxymethyl precursors. No CO insertion reactions were observed for any of these products at pressures up to 4000 psi at 80 °C.

We have prepared the hydroxymethyl compounds CpM(CO)<sub>2</sub>CH<sub>2</sub>OH (M = Ru (1), Fe (2)); Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) by reducing CpM(CO)<sub>3</sub><sup>+</sup> with NaBH<sub>3</sub>CN in MeOH. Although few hydroxymethyl compounds have been isolated and little is known about their chemistry, they are proposed intermediates in the direct conversion of syn gas to ethylene glycol<sup>1</sup> and the hydroformylation of formaldehyde to glycolaldehyde,<sup>2</sup> an ethylene glycol precursor.

Unsubstituted hydroxymethyl complexes have been isolated from the reactions of hydride donors with CpRe(NO)(CO)<sub>2</sub><sup>3</sup> and ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Os(CO)<sub>3</sub><sup>4</sup> acidolysis of

(6) Compound 1-Me was prepared from the reaction of methyl cyclopentadiene (Aldrich) and cyclopropene.<sup>7</sup> Along with the 1-methyl-*endo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene, we obtained the 6-methyl analogue. The overall yield was 10% with the ratio of products being 4.6, respectively. The sample was separated and collected by preparative GC-20% SE30 in Chromosorb W.

(7) Closs, G. L.; Krantz, K. D. *J. Org. Chem.* 1966, 31, 638.

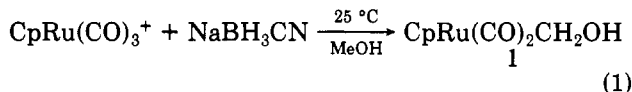
<sup>†</sup> Contribution no. 3252.

(1) (a) Masters, C. *Adv. Organomet. Chem.* 1979, 17, 61. (b) Dombeck, B. D. *J. Am. Chem. Soc.* 1979, 101, 6466; 1980, 102, 6857; 1981, 103, 6508. (c) Knifton, J. F. *J. Catal.* 1982, 76, 101.

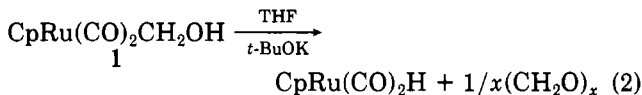
(2) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* 1979, 172, C27.

$\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{O})$ ,<sup>5</sup> and hydrolysis of  $[\text{IrH}(\text{CH}_2\text{OSiMe}_3)(\text{PMe}_3)_4]$ .<sup>6</sup> Complexes containing  $\alpha$ -hydroxyalkyl or aryl groups have been prepared from the reactions of metal hydrides with aldehydes.<sup>7</sup> These derivatives are inert and do not undergo the insertion reactions proposed for the catalytic intermediates. A reactive hydroxymethyl complex  $\text{Fe}(\text{CO})_2[\text{P}(\text{OMe})_3]_2(\text{CH}_2\text{OH})\text{Cl}$  has been characterized in situ but not isolated.<sup>8</sup> Cutler and co-workers have reported that reduction of  $\text{CpFe}(\text{CO})_3^+$  with  $\text{NaBH}_3\text{CN}$  in methanol produced  $\text{CpFe}(\text{CO})_2\text{CH}_2\text{OH}$ , based on trapping experiments.<sup>9</sup> We have found conditions that allow isolation of this compound and its ruthenium analogue.

A methanol suspension of  $[\text{CpRu}(\text{CO})_3][\text{PF}_6]$ <sup>10</sup> reacts with 4 equiv of  $\text{NaBH}_3\text{CN}$ , giving a clear solution. Evaporating the solvent immediately, extracting into hot hexane, and recrystallizing from hexane gives **1** in 45–55% yields.

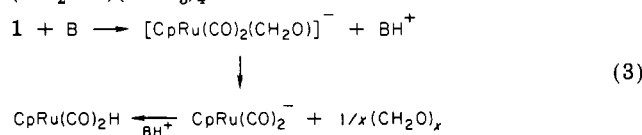


The yield is very sensitive to the reaction time and ratio of  $\text{NaBH}_3\text{CN}/\text{Ru}$ . The elemental analysis and NMR, IR, and mass spectral data<sup>11</sup> are consistent with the proposed formulation. The iron analogue **2** was isolated similarly in 35–45% yield from  $[\text{CpFe}(\text{CO})_3][\text{BF}_4]$ . A satisfactory elemental analysis was not obtained because of contamination by  $[\text{CpFe}(\text{CO})_2]_2$ ; however, the spectral data<sup>12</sup> are correct. Pure solid **1** and **2** are indefinitely stable. Solutions of **2** decompose slowly to  $[\text{CpFe}(\text{CO})_2]_2$  at room temperature; complex **1** is stable in solution below 60 °C. The hydroxymethyl complexes **1** and **2** are decomposed by bases. For example, at room temperature *t*-BuOK in THF instantaneously induces **1** to eliminate formaldehyde,

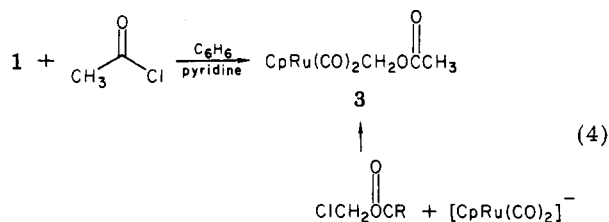


which was detected by its reaction with  $[\text{Ir}(\text{PMe}_3)_4][\text{PF}_6]$  to form  $[\text{Ir}(\text{H})(\text{CHO})(\text{PMe}_3)_4][\text{PF}_6]$ .<sup>13</sup> Complex **2** reacts

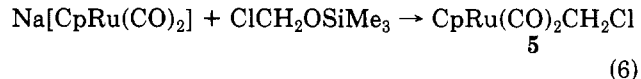
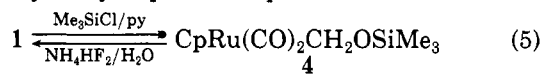
similarly forming  $[\text{CpFe}(\text{CO})_2]_2$ , the decomposition product of  $\text{CpFe}(\text{CO})_2\text{H}$ . Even the very weak Brønsted bases,  $\text{PMe}_3$  or  $\text{P}(\text{OMe})_3$ , catalyze this decomposition. Apparently, **1** and **2** are strong acids<sup>14</sup> and their conjugate bases readily eliminate formaldehyde. Similar stoichiometric, base-promoted decompositions have been observed for  $\text{HfIr}(\text{CH}_2\text{OH})(\text{PMe}_3)_4^+$ .<sup>6</sup>



When **1** reacts with acetyl chloride and pyridine or acetic anhydride, an ester complex **3**<sup>15</sup> is obtained (eq 4). Ester



complex **3** and others can also be prepared from  $\text{Na}[\text{CpRu}(\text{CO})_2]$ . We were unable to hydrolyze **3** or the corresponding pivaloyl ester to **1** under neutral, acidic, or basic conditions. The methoxymethyl complex  $\text{CpM}(\text{CO})_2\text{CH}_2\text{OMe}$  was slowly formed when **1** or **2** reacts with  $\text{MeOH}$ . This is consistent with Cutler's isolation of the Fe derivative from the reaction of  $\text{CpFe}(\text{CO})_3^+$  and  $\text{NaBH}_3\text{CN}$  when an immediate workup is not performed.<sup>9</sup> The trimethylsiloxy derivative **4**<sup>15</sup> has been prepared from **1** and can be hydrolyzed to **1** by reaction with aqueous fluoride ion. Interestingly, attempts to prepare this derivative by eq 6 under a variety of conditions failed; only the trimethylsiloxy displacement product **5**<sup>17</sup> was isolated.<sup>18</sup>



We have not been able to carbonylate **1**, its derivatives, or **2**. Monitoring the reaction of **1** or **2**, with CO by IR in a high-pressure cell, indicated no reaction occurred under the most extreme conditions that we tried (4000 psi, 80 °C). This lack of reactivity is likely a consequence of the ligand environment rather than a property of the hydroxymethyl ligand, since  $\text{CpFe}(\text{CO})_2\text{CH}_3$  reacts with CO only at 2000 psi and 125 °C<sup>19</sup> and the Ru analogue is even

(3) (a) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9; *J. Am. Chem. Soc.* **1982**, *104*, 2811. (b) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *Ibid.* **1979**, *101*, 741. (c) Casey, C. P.; Andrews, M. A.; McAllister, D. R. *Ibid.* **1979**, *101*, 3371. (d) Casey, C. P.; Andrews, M. A.; McAllister, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927. (e) Casey, C. P.; Andrews, M. A.; McAllister, D. R.; Jones, W. D.; Harsey, S. G. *J. Mol. Catal.* **1981**, *13*, 43.

(4) May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49. A report on the synthesis of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{OH})$  has recently appeared: Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430.

(5) (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7. (c) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *Ibid.* **1982**, *231*, 335.

(6) Thorn, D. L. *Organometallics* **1982**, *1*, 197. Thorn, D. L.; Tulip, T. H. *Ibid.* **1982**, *1*, 1580.

(7) (a) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5608. (b) Wayland, B. B.; Woods, B. A.; Minda, V. A. *J. Chem. Soc., Chem. Commun.* **1982**, 634.

(8) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353.

(9) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

(10) Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231.

(11) Anal. Calcd: C, 37.95; H, 3.18. Found: C, 37.83; H, 3.21. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, ppm): 5.46 (s, Cp) 5.22 (d, *J*<sub>H-H</sub> = 6.6 Hz, CH<sub>2</sub>), 3.18 (br t, *J*<sub>H-H</sub> = 6.6 Hz, OH<sup>14</sup>). IR (Nujol, cm<sup>-1</sup>): 3280 (br,  $\nu_{\text{OH}}$ ), 2104 (vs), 1964 (vs,  $\nu_{\text{CO}}$ ). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 202.1 (CO), 89.6 (Cp), 46.6 (CH<sub>2</sub>, *J*<sub>C-H</sub> = 152 Hz). Mass spectrum (90 °C): *M*<sup>+</sup> 253.9589, calcd 253.9511.

(12) <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, ppm): 5.16 (d, *J*<sub>H-H</sub> = 6.8 Hz, CH<sub>2</sub>), 4.94 (s, Cp), 0.91 (br, t, *J*<sub>H-H</sub> = 6.8 Hz, OH<sup>14</sup>). IR (Nujol, cm<sup>-1</sup>): 3210 (br,  $\nu_{\text{OH}}$ ), 1995 (vs), 1940 (vs,  $\nu_{\text{CO}}$ ). Mass spectrum (90 °C): *M*<sup>+</sup> 207.9813, calcd 207.9822.

(13) Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109.

(14) One reviewer made the following comment: "it is surprising that -OH (<sup>1</sup>H NMR) coupling is observed (implies slow exchange) This curious feature has been observed with nearly every hydroxyalkyl complex in the literature". We have found that both chemical shift and coupling in the -OH group are temperature and concentration dependent. D<sub>2</sub>O in acetone solution exchanges with the -OH group with loss of coupling.

(15) Anal. Calcd: C, 40.68; H, 3.41. Found: C, 40.66; H, 3.38. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 5.49 (s, CH<sub>2</sub>), 4.67 (s, Cp), 1.75 (s, CH<sub>3</sub>). IR (hexane, cm<sup>-1</sup>): 2018 (vs), 1978 (vs,  $\nu_{\text{M-CO}}$ ), 1740 (s,  $\nu_{\text{ester-CO}}$ ). Mass spectrum (120 °C): (*M* - CO)<sup>+</sup> 267.9701, calcd 267.9667, parent peak not observed at 120 °C.

(16) Anal. Calcd: C, 40.60; H, 4.96. Found: C, 40.82; H, 4.78. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 5.23 (s, CH<sub>2</sub>), 4.69 (s, Cp), 0.18 (s, CH<sub>3</sub>). IR (hexane, cm<sup>-1</sup>): 2024, 1966 ( $\nu_{\text{CO}}$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 202.2 (CO), 89.1 (Cp), 44.2 (CH<sub>2</sub>, *J*<sub>C-H</sub> = 151 Hz), -0.51 (CH<sub>3</sub>, *J*<sub>C-H</sub> = 112 Hz). Mass spectrum (120 °C): (*M* - CO)<sup>+</sup> 297.9977, calcd 297.9957, parent peak is not observed at 120 °C.

(17) Anal. Calcd: C, 35.38; H, 2.58. Found: C, 35.26; H, 2.60. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 4.98 (s, CH<sub>2</sub>), 4.64 (s, Cp). IR (hexane, cm<sup>-1</sup>): 2030, 1973 ( $\nu_{\text{CO}}$ ).

(18) Comment by reviewer: "the result in eq 6 might be explained by reaction of **4** with  $\text{NaCl}$ ".

(19) Coffield, T. H.; Kozikowski, J.; Closson, R. D. *Chem. Soc., Spec. Publ.* **1959**, *13*, 126.

less reactive.<sup>20</sup> Also, Berke<sup>8</sup> has shown that  $\text{Fe}(\text{CO})_2(\text{P}(\text{OMe})_3)_2\text{Cl}(\text{CH}_2\text{OH})$  readily inserts CO under mild conditions.

**Acknowledgment.** We would like to thank Drs. D. M. T. Chan and D. Thorn for very helpful discussions and E. A. Conaway and B. C. West for their technical assistance.

**Registry No.** 1, 86748-03-0; 2, 86748-04-1; 3, 86748-05-2; 4, 86748-06-3; 5, 80492-22-4;  $\text{CpRu}(\text{CO})_2\text{CH}_2\text{OMe}$ , 80492-23-5;  $[\text{CpRu}(\text{CO})_3][\text{PF}_6]$ , 31741-71-6;  $[\text{CpFe}(\text{CO})_3][\text{BF}_4]$ , 12244-69-8;  $[\text{CpFe}(\text{CO})_2]_2$ , 12154-95-9;  $[\text{Ir}(\text{H})(\text{CHO})(\text{PMe}_3)_4][\text{PF}_6]$ , 75592-93-7;  $\text{CpRu}(\text{CO})_2\text{H}$ , 57349-59-4;  $\text{Na}[\text{CpRu}(\text{CO})_2]$ , 42802-20-0;  $\text{NaBH}_3\text{CN}$ , 25895-60-7;  $\text{MeOH}$ , 67-56-1;  $\text{Me}_3\text{SiCl}$ , 75-77-4; formaldehyde, 50-00-0; acetyl chloride, 75-36-5; acetic anhydride, 108-24-7.

(20) Wojcicki, A. *Adv. Organomet. Chem.*, 1973, 11, 87.

## Preparation of Tungsten(V) Alkyl Complexes and Hydride Complexes of the Type $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{H}_x]_y$

S. J. Holmes and R. R. Schrock\*

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received May 4, 1983

**Summary:** Alkylation of  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_4]_2$  with dimethylzinc yields paramagnetic  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Me}_2\text{Cl}_2$  (1). In contrast, diamagnetic, purple  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})(\text{CCMe}_3)\text{Cl}_2$  (2) is formed from  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_4]_2$  and diisopentylzinc. Hydrogenation of  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Me}_4$  (prepared from 1 and  $\text{LiMe}$ ) at 1000 psi yielded brown  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{H}_4]_2$  (~20%) and blue  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{H}_3]_3$  (~50%) in which all hydride ligands are equivalent on the  $^1\text{H}$  NMR time scale at 25 °C. Hydrogenation of  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})(\text{CCMe}_3)\text{Me}_2$  (prepared from 2 and  $\text{LiMe}$ ) yields a similar mixture in a lower (~30%) overall yield. Hydrogenation of all complexes containing halides, however, so far has not yielded any pure product of the type  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_x\text{H}_y]_z$ .

Tantalum hydride complexes of the type  $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2\text{H}]_2$  (R = Me or Et) have been prepared by treating  $\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})(\text{propylene})\text{Cl}_2$  or  $\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$  with molecular hydrogen.<sup>1</sup> In contrast to this type of dimeric hydrido complex arose from the fact that it reacts readily with carbon monoxide to give a compound containing a side-on bonded formyl fragment.  $\text{Ta}_2(\eta^5\text{-C}_5\text{Me}_4\text{R})_2\text{Cl}_4(\mu\text{-H})(\mu\text{-CHO})$ ,<sup>2,3</sup> one of the very few

examples of formation of a formyl complex from a transition-metal<sup>4</sup> (or actinide<sup>5</sup>) hydrido complex and carbon monoxide. Extending monocyclopentadienyl chemistry to presumably less oxophilic tungsten has been problematic due to the fact that high oxidation state tungsten monocyclopentadienyl complexes are unknown. The recently discovered synthesis of  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_4]_2$ <sup>6</sup> now allows us to examine for tungsten some of the approaches and chemistry that were successful for tantalum.

$[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_4]_2$  can be alkylated by dimethylzinc to give yellow, paramagnetic  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Me}_2\text{Cl}_2$ <sup>7</sup> (1). However, if  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_4]_2$  is treated with 1 equiv of  $\text{Zn}(\text{CH}_2\text{CMe}_3)_2/\text{W}$  in toluene at 0 °C, the product is diamagnetic, purple  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})(\text{CCMe}_3)\text{Cl}_2$ <sup>8</sup> (2). Addition of methyllithium in ether to 1 at -78 °C yields yellow-orange, paramagnetic  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Me}_4$  (3)<sup>12</sup> while 2 reacts with methyllithium to give  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})(\text{CCMe}_3)\text{Me}_2$  (4), a distillable red oil.  $^1\text{H}$  NMR spectra for  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_4]_2$ , 1, and 3 can be observed but the signals are extremely broad. Odd-electron alkyl complexes are unusual since the metal-carbon bond is generally thought to be much more susceptible to homolytic cleavage than in an even-electron complex.<sup>13</sup>

Hydrogenation of 1 or 2 at 30-1000 psi produced no isolable hydrido complexes, although irreproducible signals ascribable to hydrides occasionally could be observed in the  $^1\text{H}$  NMR spectra and IR spectra of the products. However, hydrogenation of 3 at 1000 psi and 0 °C in pentane yields a pentane-soluble brown crystalline complex<sup>14</sup> (5) in ~20% yield and a relatively insoluble microcrystalline blue-black complex<sup>15</sup> (6) in ~50% yield. The  $^1\text{H}$  NMR spectrum of 5 exhibits a hydride peak of relative area of approximately 4 at -0.8 ppm with  $J_{\text{HW}} = 40$  Hz. The area of the satellite peaks (~25%) suggest that 5 is dimeric. This postulate was confirmed by a field-desorption mass spectrum showing a parent ion pattern that agreed with that calculated for the formulation  $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{H}_4]_2$ . The  $^1\text{H}$  NMR spectrum of the blue

(2) Belmonte, P. A.; Cloke, F. G. N.; Schrock, R. R. *J. Am. Chem. Soc.* 1983, 105, 2643.

(3) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* 1982, 21, 226.

(4) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* 1981, 700.

(5) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* 1981, 103, 6959.

(6) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* 1982, 104, 6808.

(7) Solvent =  $\text{CH}_2\text{Cl}_2$ ; 2  $\text{Et}_4\text{NCl}/\text{W}$ , 2  $\text{ZnMe}_2$ ; -78 °C; yield 40%. Anal. Calcd for  $\text{WC}_{15}\text{H}_{25}\text{Cl}_2$ : C, 38.97; H, 5.85. Found: C, 38.63; H, 5.84.

(8) Yield: 60%. Anal. Calcd for  $\text{WC}_{18}\text{H}_{30}\text{Cl}_2$ : C, 43.11; H, 5.99. Found: C, 42.60; H, 6.23;  $\delta(\text{C}_\alpha)$  317. So far we have not been able to prepare analogous  $\eta^5\text{-C}_5\text{Me}_5$  or  $\eta^5\text{-C}_5\text{Me}_4\text{Et}$  complexes by treating  $\text{W}(\text{CCMe}_3)(\text{dimethoxyethane})\text{Cl}_3$ <sup>9</sup> with Li, Na, or Tl cyclopentadienyl reagents. We suspect that a neopentyl group is significantly more prone toward loss of an  $\alpha$  hydrogen atom in an odd-electron complex<sup>10</sup> than in an even-electron complex<sup>11</sup> and significantly more so than a methyl group.

If only 0.5 equiv of  $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$  is employed, a yellow, paramagnetic species is obtained which we believe must be a neopentyl complex, most likely  $\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ .

(9) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* 1982, 1, 1645.

(10) Hayes, J. C.; Pearson, G. D. N.; Copper, N. J. *J. Am. Chem. Soc.* 1981, 103, 4648.

(11) Schrock, R. R. *Acc. Chem. Res.* 1979, 12, 98.

(12) Anal. Calcd for  $\text{WC}_{17}\text{H}_{33}$ : C, 48.46; H, 7.84. Found: C, 48.25; H, 7.74.

(13) (a) Manzer, L. E. *J. Am. Chem. Soc.* 1978, 100, 8068. (b) Brintzinger, H. H. *Ibid.* 1967, 89, 6871. (c) Bercaw, J. E.; Brintzinger, H. H. *Ibid.* 1969, 91, 7301. (d) Elson, I. H.; Kochi, J. K. *Ibid.* 1975, 97, 1262. (e) Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G. W.; Tebbe, F. N. *Ibid.* 1975, 97, 7374.

(14)  $\nu_{\text{MH}} = 1910$  (m), 1890 (m)  $\text{cm}^{-1}$ .

(15)  $\nu_{\text{MH}} = 1910$  (m), 1890 (m), 1860 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{WC}_{13}\text{H}_{24}$ : C, 42.90; H, 6.59. Found: C, 43.17; H, 7.10.

(1) Belmonte, P. A.; Schrock, R. R.; Day, C. S. *J. Am. Chem. Soc.* 1982, 104, 3082.