Syntheses and Reactions of a Cationic Hydrido(hydroxymethyl)iridium Complex. The Crystal and Molecular Structure of Hydrido(hydroxymethyl)tetrakis(trimethylphosphine)iridium(III) Hexafluorophosphate, $[IrH(CH_2OH)(PMe_3)_4][PF_6]$[†,‡]

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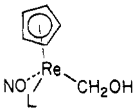
The hydrido(hydroxymethyl)iridium(III) complex $[IrH(CH_2OH)(PMe_3)_4]^+$ has been prepared by two routes: the reduction of the corresponding cationic hydridoformyl complex and O–Si bond cleavage of the silyl ether complex $[IrH(CH_2OSiMe_3)(PMe_3)_4]^+$. This silyl ether complex has been prepared by addition of ICH_2OSiMe_3 to the hydridoiridium(I) complex $IrH(PMe_3)_4$. The hydrido hydroxymethyl complex decomposes to $[IrH_2(PMe_3)_4]^+$ and formaldehyde in the presence of strong base and reacts with strong acid to form water and the methyl complex $[Ir(CH_3)I(PMe_3)_4]^+$. The latter reaction is believed to occur by hydrogen migration to a transient methylene species. The crystal and molecular structure at −100 °C of $[IrH(CH_2OH)(PMe_3)_4][PF_6]$ has been determined: space group C_{2h}^5—$P2_1/c$ (No. 14), $a = 9.237$ (2) Å, $b = 21.067$ (3) Å, $c = 13.156$ (2) Å, $\beta = 104.30$ (1)°, $V = 2481$ (1) Å^3, $Z = 4$. The final conventional and weighted agreement indices on F_o for 4417 reflections with $F_o^2 > 3\sigma(F_o^2)$ are 0.029 and 0.031, respectively. The cation has pseudooctahedral geometry with a stereochemically active hydride ligand. The C–O bond length, 1.471 (7) Å, suggests a contribution from an incipient iridium–methylene dication.

Introduction

Metal-bound hydroxymethyl fragments are often proposed as important intermediates in the reduction of carbon monoxide.[1] However, only recently have transition-metal hydroxymethyl complexes become available, and studies of their reactivities are vital if the role of the hydroxymethyl fragment in CO hydrogenation is to be understood.

Unsubstituted hydroxymethyl complexes that have been reported are the cyclopentadienylrhenium(I) compounds 1,[2-4] the osmium and iron complexes 2[5] and 3,[6] and the hydridoiridium compound 4a.[7] Hydroxymethyl complexes of Cr(III) have been studied but apparently have not been isolated and completely characterized.[8,9] In addition, elegant syntheses have been reported for C-substituted hydroxymethyl compounds;[10-12] also, numerous alkoxymethyl compounds[13,14] have been prepared and utilized as a source of carbenoid species since the initial report by Jolly and Pettit.[13]



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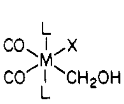

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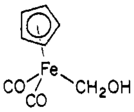

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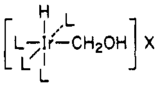

4, L=PMe$_3$; a, X=PF$_6$
b, X=I

The iridium hydrido hydroxymethyl complex 4a was first obtained by the reduction of the hydrido formyl compound 5 (Scheme I).[7] Subsequently, we have been studying the hydrido hydroxymethyl complexes 4a,b and have found them to undergo a number of interesting reactions. Unfortunately, our previously reported synthesis of compound 4a[7] is cumbersome, and the yield is poor; therefore we report a more convenient method for the preparation of compounds 4a,b. We also describe the crystal and molecular structure of compound 4a as determined by X-ray diffraction, its base-induced decomposition to $[IrH_2(PMe_3)_4]^+$ (6, Scheme I) and formaldehyde, and the reaction of 4b and related compounds

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[†] We and our colleagues at Du Pont wish to honor the memory of Professor Rowland Pettit; we have lost a valued friend.

[‡] Contribution No. 3133.

(1) (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *23*, 1–38. (b) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447–474. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. (d) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (e) Henrici-Olive, G.; Olive, S. *Angew. Chem.* **1976**, *88*, 144–150; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136–141.

(2) Nesmeyanov, A. N.; Anisimov, K. N.; Kolabova, N. E.; Krasnoslobodskaya, L. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 860–865; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Trans.*) **1970**, 807–811.

(3) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811–2815; *J. Organomet. Chem.* **1979**, *173*, C9–C12.

(4) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsey, S. G. *J. Mol. Catal.* **1981**, *13*, 43–59. Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927–1933. Casey, C. P.; Andrews, M. A.; McAlister, D. R. *Ibid.* **1979**, *101*, 3371–3373. Casey, C. P.; Andrews, M. A.; Rinz, J. E. *Ibid.* **1979**, *101*, 741–743.

(5) (a) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335–360. Headford, C. E. L.; Roper, W. R. *Ibid.* **1980**, *198*, C7–C10. Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505. (b) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353–362.

(6) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275–1277.

(7) Thorn, D. L. *Organometallics* **1982**, *1*, 197–204; *J. Am. Chem. Soc.* **1980**, *102*, 7109–7110.

(8) Espenson, J. H.; Bakoc, A. *J. Am. Chem. Soc.* **1980**, *102*, 2488–2489; **1981**, *103*, 2721–2728, 2728–2733 and references therein.

(9) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434–2443. Schmidt, W. O.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117–1123.

(10) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5608–5609. Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *Ibid.* **1978**, *100*, 6766–6768.

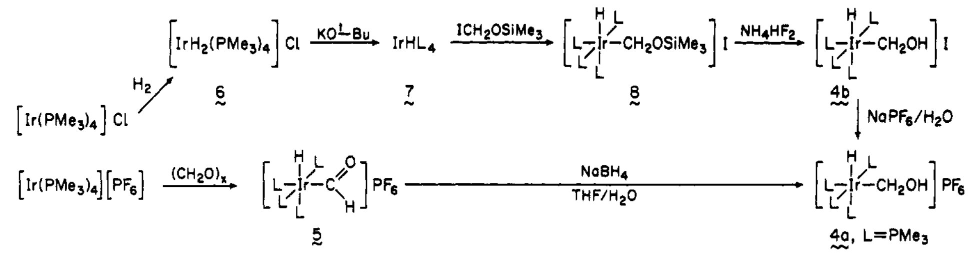
(11) Wayland, B. B.; Woods, B. A.; Minde, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634–635.

(12) Blackmore, T.; Bruce, M. I.; Davidson, P. J.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3153.

(13) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044–5045. O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869–1874 and references therein.

(14) Chou, C.-K.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271–7278.

Scheme I

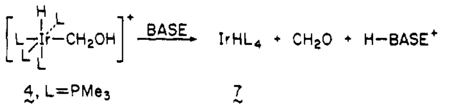


with electrophilic reagents to form methyliridium compounds.

Results

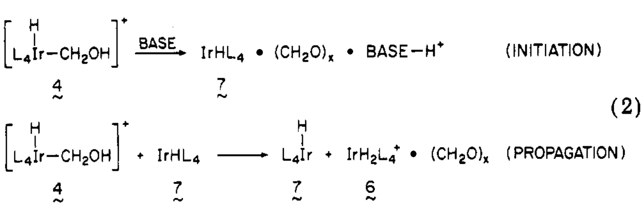
Scheme I summarizes two routes for the synthesis of compounds **4a,b** from the Ir(I) starting materials [Ir$(PMe_3)_4]Cl$[15] or $[Ir(PMe_3)_4][PF_6]$.[7] The bottom route, the previously reported reduction of the formyl complex **5**, is low yielding and requires a lengthy workup procedure. The top route, while requiring more steps than the reduction reaction, provides compounds **4a,b** in better and more reliable yield. The crucial step of this route is the addition of the reagent, iodomethyl trimethylsilyl ether,[16] to the hydridotetrakis(trimethylphosphine)iridium(I) complex (**7**), resulting in the formation of the hydrido (trimethylsiloxy)methyl complex **8**. (Excess iodomethyl silyl ether must be avoided to prevent further reaction with compound **8**; see below.) Subsequent conversion of the CH_2OSiMe_3 group of compound **8** to the hydroxymethyl group of compound **4b** is conveniently effected by ammonium bifluoride in refluxing tetrahydrofuran (THF).

In the course of our studies we discovered that compounds **4a,b** react with base (eq 1), resulting in the release



(1)

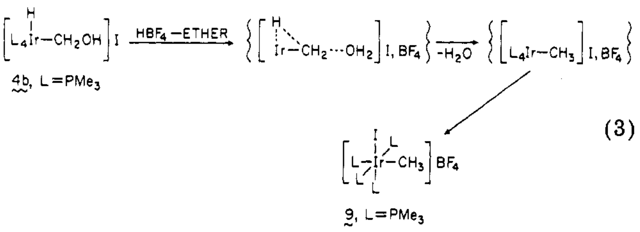
of formaldehyde and formation of the hydridoiridium compound $IrH(PMe_3)_4$ (**7**). The formaldehyde has been detected by its reaction with separately added $[Ir(PMe_3)_4]^+$ to yield a hydrido formyl complex (see Experimental Section). A base stronger than pyridine is necessary, as compound **4** is indefinitely stable in pyridine at room temperature. Potassium *tert*-butoxide is a convenient base; another basic reagent which will cause the reaction of eq 1 is $IrH(PMe_3)_4$ (**7**) itself. This allows a chain reaction for the decomposition of compound **4** to free formaldehyde and the dihydrido cation **6**, illustrated in eq 2,



(2)

in which $IrH(PMe_3)_4$ serves as the chain carrier. Therefore, care must be taken in the preparation and handling of **4**, as even trace amounts of strong base can initiate the decomposition reaction.

Compound **4b** also reacts immediately with HBF_4 etherate in methylene chloride to form the methyl compound $[Ir(CH_3)I(PMe_3)_4][BF_4]$ (**9**) and water. The mechanism we consider most likely is outlined in eq 3. Excess



(3)

HBF_4 must be avoided, as it reacts further with the methyl compound **9** to form $[HPMe_3][BF_4]$ and as-yet-unidentified iridium-containing products. Compound **4a** also reacts with HBF_4 etherate, but the reaction is more complicated and the products have not been identified.

Discussion

Compounds **4** and **8** are further examples of remarkably stable (trimethylphosphine)iridium(III) hydrido alkyl complexes.[7,17] We have not observed reductive elimination of methanol from **4** (or methyl trimethylsilyl ether from **8**), although we have not explored a wide range of conditions, owing to the other competing reactions these compounds undergo.

The base-induced decomposition (eq 1, 2) has been mentioned elsewhere.[18] The most surprising aspect of this reaction is that the hydrido complex $IrH(PMe_3)_4$[7] (**7**) does not react further with formaldehyde to make a hydrido formyl complex, whereas the analogous methyl complex $Ir(CH_3)(PMe_3)_4$ does react with formaldehyde to yield a hydrido formyl complex. Apparently, the trimethylphosphine ligands are too tightly bound, in the hydrido complex **7**, to permit formation of an η^2-formaldehyde adduct (presumably a necessary prelude to formation of a hydrido formyl complex[5,7]). That the phosphine ligands of $IrH(PMe_3)_4$ (**7**) are less labile than those of $Ir(CH_3)(PMe_3)_4$ is consistent with our observation that ethylene (at atmospheric pressure) displaces PMe_3 from the methyliridium compound[19] but does not react with the hydridoiridium compound **7**. We have been able to isolate the stable hydrido ethylene complex $IrH(C_2H_4)(PMe_3)_3$ by using a different synthetic procedure[20] and find that it reacts readily with PMe_3 to yield $IrH(PMe_3)_4$ (**7**) and free ethylene.

This reaction (eq 1, 2) accounts for a number of our observations concerning compounds **4a,b**. We believe that

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[15] Herskovitz, T. *Inorg. Synth.* **1982**, *21*, 99–102. Herskovitz, T.; Guggenberger, L. *J. Am. Chem. Soc.* **1976**, *98*, 1615–1616. English, A. D.; Herskovitz, T. *Ibid.* **1977**, *99*, 1648–1649.

[16] Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056–1060.

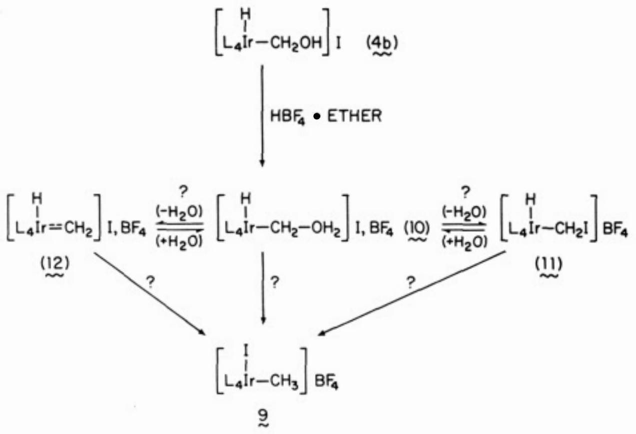
[17] Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773–3774. Other stable cis-hydrido methyl complexes have been reported by: Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263. Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139–145. Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421–5422. Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35. Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1963**, 6017–6027. See also ref 5a.

[18] Thorn, D. L. *J. Molec. Catal.*, in press.

[19] Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984–5986.

[20] Thorn, D. L.; Tulip, T. H., to be submitted for publication.

Scheme II



the low yield of **4a** in the reduction reaction (Scheme I, bottom route) is the result of partial decomposition in the alkaline reduction medium; in several instances the dihydrido complex **6** was the only isolated product. Also, attempts to prepare the hydroxymethyl complex **4b** from the siloxymethyl complex **8** using highly basic, "naked fluoride" reagents were invariably unsuccessful. The reagent we have chosen for this reaction, NH_4HF_2, is acidic, yet too weak to cause the further reaction of eq 3.

The reaction of eq 3, the formation of a methyl complex when compound **4b** is treated with HBF_4–ether, is the first example of which we are aware in which a stable methyl group has been prepared by migration of a hydrido hydrogen atom to an adjacent carbon-bound methylene precursor. There exist several examples in which hydrido methylene complexes are implicated in α-elimination reactions of methyl groups,[21,22] and a beautiful study by Shaw and colleagues has established the reversible addition of hydrogen to an Ir(I) "carbene" complex.[23] Of course, the reaction of diazomethane with transition-metal hydrido compounds is known to yield methyl complexes.[24] Also, examples of migration of hydrido hydrogen atoms to adjacent oxycarbene ligands[5,25] and of methyl groups to alkylidene or carbene ligands[19,25–28] are known.

Several aspects of this reaction are of interest. Almost certainly, the action of the acid is to protonate the oxygen atom of the hydroxymethyl complex and to form the dicationic complex **10** (Scheme II). Possibly, complex **10** is a metastable complex that could be isolated (cf. $Ir(CH_2\text{-pyridine})(CH_3)Br(PMe_3)_3{}^{+}$ [19]), but we presently have no evidence for its existence. Other dicationic complexes can be prepared; for example, $[IrH(PMe_3)_5]^{2+}$ has been isolated.[20] Substitution of I^- for H_2O in **10**, resulting in the formation of the iodomethyl complex **11** (eq 4),[5a,16,29] appears to be a plausible reaction and has been observed for an osmium hydrido hydroxymethyl complex,[5a] but again we have no evidence for its occurrence. Hydrido hydrogen atom migration may occur subsequent to or in concert with the formation of complex **10**, as implied in eq 3, or the iodomethyl complex **11** or a discrete methylene complex **12** may be the reactive species (Scheme II). Low-temperature studies (in progress) may provide additional insight into the actual mechanism for the formation of **9**.

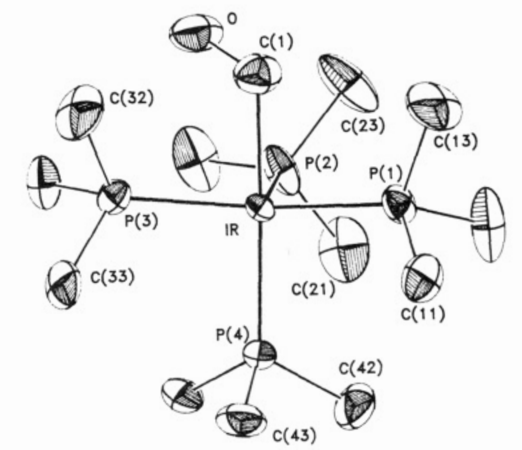
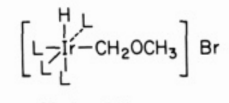
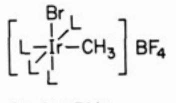


Figure 1. A perspective view of the iridium coordination sphere of $[IrH(CH_2OH)(PMe_3)_4][PF_6]$ (**4a**). The vibrational ellipsoids are drawn at the 50% probability level. Only atoms of the major isomer are included.

There is no reason to believe that the $IrCH_2$–OH group is uniquely susceptible to protonation, and in fact the (trimethylsiloxy)methyl compound **8** forms the methyl compound **9** when treated with HBF_4–ether. Also, the related methoxymethyl complex **13**[30] reacts with HBF_4–ether to form the methyl complex **14**. In addition, the



13, L=PMe3



14, L=PMe3

C–O bond of compounds **4**, **8**, and **13** is cleaved by other alkylating or silylating reagents, including iodo- and bromotrimethylsilane and iodomethyl trimethylsilyl ether; for this reason, compound **8** should not be exposed to an excess of ICH_2OSiMe_3.

One reaction observed by other researchers is intermolecular transfer of an α-hydrogen atom, eq 4.[4,31,32] A

$$M\text{—}CH_2OR \xrightarrow{\text{ACID}} [M\text{═}CH_2]^{+} \xrightarrow{M\text{—}CH_2OR} M\text{—}CH_3 + [M\text{═}CHOR]^{+} \qquad (4)$$

consequence of this reaction is that the yield of the methyl complex cannot exceed 50%. The reaction of the iridium hydrido hydroxymethyl complex **4b** with acid, eq 3, gives

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(21) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121–1127; *J. Chem. Soc., Chem. Commun.* **1974**, 761.

(22) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *101*, 6978–6989.

(23) Empsall, D. H.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589–590.

(24) Herrmann, W. A. *Angew. Chem.* **1978**, *90*, 855–867; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–812 and references therein.

(25) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650–2659.

(26) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43–51. We thank Professor Schrock for bringing this work to our attention.

(27) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648–4650.

(28) Caulton, K. G. *J. Mol. Catal.* **1981**, *13*, 71–82. Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596–5598.

(29) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1981**, 698–699. Davison, A.; Krussel, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7–C10. Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910–1918. Feser, F.; Werner, H. *Angew. Chem.* **1980**, *92*, 960–961; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 940–941.

(30) Thorn, D. L. *Organometallics* **1982**, *1*, 879–881.

(31) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wang, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141–152. Wong, W.-K.; Tam, W.; Gladysz, J. A. *Ibid.* **1979**, *101*, 5440–5442.

(32) Cutler, A. *J. Am. Chem. Soc.* **1979**, *101*, 604–606.

Table I. Selected Bond Distances (Å) and Angles (deg) and Estimated Standard Deviations

		Bond Distances	
Ir-P(1)	2.313 (1)	Ir-P(2)	2.362 (1)
Ir-P(3)	2.335 (1)	Ir-P(4)	2.355 (1)
Ir-C(1)	2.134 (5)	C(1)-O	1.471 (7)
P(1)-C(11,2,3)	1.810, 18, 01 (5,6,6)	P-F(1-6)	1.568-95 (4)
P(2)-C(21,2,3)	1.889, 763, 757 (8,7,7)	C(1)-O′	1.53 (2)
P(3)-C(31,2,3)	1.813, 1, 8 (5)	P(2)-C(21,2,3)′	2.10, 1.74, 1.77 (2)
P(4)-C(41,2,3)	1.809, 26, 19 (5,6,5)	P-F(2-5)′	1.40-71 (2)
O· · ·F(2)	2.985 (6)	O′· · ·F(3)′	2.51 (3)
		Bond Angles	
P(1)-Ir-P(2)	98.90 (4)	P(2)-Ir-P(3)	102.42 (4)
P(1)-Ir-P(3)	155.86 (4)	P(2)-Ir-P(4)	96.24 (3)
P(1)-Ir-P(4)	94.36 (4)	P(2)-Ir-C(1)	84.2 (2)
P(1)-Ir-C(1)	87.0 (2)	P(3)-Ir-P(4)	94.45 (4)
P(4)-Ir-C(1)	178.5 (2)	P(3)-Ir-C(1)	84.1 (2)
Ir-C(1)-O	110.3 (3)	F(1-5)-P-F(2-6)	86.7-94.3, 176.5-178.4 (3)
Ir-P(1)-C(11,2,3)	113.7-123.1 (2)	Ir-C(1)-O′	113.1 (8)
Ir-P(2)-C(21,2,3)	114.7-121.6 (2)	Ir-P(2)-C(21,2,3)′	107.5-124.2 (8)
Ir-P(3)-C(31,2,3)	114.1-123.0 (2)	C(21,2)′-P(2)-C(22,3)′	94-104 (1)
Ir-P(4)-C(41,2,3)	116.8-119.0 (2)	F(2-5)′-P-F(1,2′-5′,6)	69-112, 169 (1)
C(11,2)-P(1)-C(12,3)	99.9-100.8 (3)		
C(21,2)-P(2)-C(22,3)	96.2-105.7 (4)		
C(31,2)-P(3)-C(32,3)	98.3-101.7 (3)		
C(41,2)-P(4)-C(42,3)	98.6-101.5 (3)		

the methyl complex **9** in good yield, free of other products (see Experimental Section). Likewise, the reaction of compound **13** with acid gives the methyl compound **14** with no observable byproducts. An intramolecular mechanism for the formation of **9** and **14** is the most plausible, as assumed in eq 3 and Scheme II.

Description of the Structure of *cis*-[IrH(CH$_2$OH)(PMe$_3$)$_4$][PF$_6$] (4a). This compound is the first hydroxymethyl compound to be structurally characterized. The crystal structure of **4a** consists of the packing of four well-separated ion pairs. Selected bond distances and angles are listed in Table I and non-hydrogen atom positions in Table II. Non-hydrogen atom thermal parameters (Table III) and idealized hydrogen atom positions (Table IV) are also available as supplementary material, as is a listing of the observed and calculated structure factor amplitudes. Table V summarizes the crystallographic data. Figure 1 contains a representation of the iridium coordination sphere and includes the atom labels used in the text and tables. Figure 2 shows the same view of the coordination sphere but contains the minor disordered atoms, O′ and C(21)′–C(23)′. Figure 3 depicts the disordered PF$_6$ anion, and a perspective view of the unit cell is shown in Figure 4. Figures 2–4 are available as supplementary material.

In the crystal chosen for study the PF$_6$, CH$_2$OH, and Me$_3$P(2) groups are disordered. Our model for the disorder includes extra atoms F(2)′–F(5)′, O′, and C(21)′–C(23)′, each with an occupancy factor of 0.20. The occupancy factors of the corresponding unprimed atoms are decreased accordingly. These disorders are correlated because of a weak OH–F hydrogen bond (O–F(2) = 2.985 (6) Å; O′–F(3)′ = 2.51 (3) Å) and the intermeshing of the CH$_2$OH and P(2) methyl groups. The presence of two distinct isomeric forms in the solid state indicated by this disorder is consistent with our observation of two O–H and Ir–H stretching frequencies in the IR spectrum of complex **4a**.[7] We hesitate to ascribe any significance to the metrical parameters of the minor isomer but believe the values for the major isomer (unprimed atoms) are reliable.

The iridium cation, Figure 1, adopts the expected cis, octahedral geometry with the hydrido hydrogen atom occupying a well-defined coordination site. Despite the presence of a difference Fourier peak corresponding to the hydrido hydrogen atom, attempts to refine its location have failed, and this atom has not been included in the final refinement. The hydroxy hydrogen atom also been omitted. Ir–P bond distances are unexceptional[17,19] and show variations consistent with the expected pattern of trans influences. There is a general tendency for some angular distortions of neighboring ligands toward the sterically undemanding hydrido hydrogen atom. Particularly important structural features are the Ir–C(1) bond distance and the C(1)–O bond distance (2.134 (5) and 1.471 (7) Å, respectively; see Table I). The C(1)–O separation is comparable to that reported for Cp(CO)(PPh$_3$)FeCH$_2$O(menthyl) (1.474 (9) Å[14]), which is the only other structurally characterized alkoxymethyl complex. We regard the C(1)–O bond distance as significantly increased over the value expected for ordinary alcohols or ethers and believe it indicates some contribution from a "carbene" or "metallacarbonium" resonance structure, **15**.[14] However, the Ir–C separation is not significantly decreased by this resonance contribution, and the Ir–C(1) bond distance is comparable to values for other PMe$_3$Ir^{III} alkyl complexes (e.g., 2.123 (5) Å,[19] 2.127 (6) Å[17]).

$$[\mathrm{Ir{-}CH_2OH}]^{+} \longleftrightarrow [\mathrm{Ir{=}CH_2^{+\,+}\ O\bar{H}}]$$

15

Summary and Conclusions

Use of the reagent ICH$_2$OSiMe$_3$ permits facile syntheses of M–CH$_2$OSiMe$_3$ complexes (M = Mn,[16] Ir), which (for M = Ir) can be converted into a stable M–CH$_2$OH complex. This may become the preferred method for the synthesis of other hydroxymethyl compounds. We find that the hydroxymethyl complexes **4a,b** readily decompose in the presence of base and that the hydrido hydroxymethyl (and alkoxymethyl complexes in general[19]) are sensitive to acid. The structure of complex **4a** reveals a C(1)–O bond distance somewhat greater than that of simple alcohols or ethers, which we believe indicates a weakening of this bond and is consistent with facile C(1)–O bond cleavage when treated with acid.

Table II. Positional Parameters of $[IrH(CH_2OH)(PMe_3)_4][PF_6]$, 4a

ATOM	X	Y	Z	ATOM	X	Y	Z
IR	0.42928(2)	0.16192(1)	0.23996(1)	O′	0.119(3)	0.219(1)	0.226(2)
P(1)	0.2552(2)	0.11951(7)	0.0990(1)	C(1)	0.2798(7)	0.2400(3)	0.2326(5)
P(2)	0.3252(2)	0.12635(9)	0.3767(1)	C(11)	0.3321(7)	0.0977(3)	-0.0099(5)
P(3)	0.6100(2)	0.23421(6)	0.3259(1)	C(12)	0.1480(8)	0.0484(4)	0.1086(6)
P(4)	0.5994(1)	0.07753(6)	0.2501(1)	C(13)	0.1064(9)	0.1718(4)	0.0348(6)
P	-0.0019(2)	0.39518(7)	0.1812(1)	C(21)	0.3227(11)	0.0373(4)	0.3926(7)
F(1)	0.1755(4)	0.3937(2)	0.2017(4)	C(22)	0.4067(10)	0.1455(5)	0.5089(6)
F(2)	0.0165(6)	0.3433(2)	0.2689(4)	C(23)	0.1321(8)	0.1376(6)	0.3593(7)
F(3)	-0.0137(6)	0.3410(2)	0.0952(4)	C(31)	0.6647(7)	0.2426(3)	0.4674(5)
F(4)	-0.0127(6)	0.4476(2)	0.0926(4)	C(32)	0.5717(9)	0.3157(3)	0.2842(6)
F(5)	0.0199(6)	0.4501(2)	0.2663(4)	C(33)	0.7924(6)	0.2265(3)	0.2980(6)
F(6)	-0.1768(4)	0.3962(2)	0.1578(4)	C(41)	0.7317(6)	0.0649(3)	0.3750(5)
F(2)′	-0.059(3)	0.395(1)	0.295(2)	C(42)	0.5273(9)	-0.0029(3)	0.2210(7)
F(3)′	-0.023(3)	0.321(1)	0.182(2)	C(43)	0.7222(7)	0.0804(3)	0.1613(5)
F(4)′	0.018(3)	0.394(1)	0.080(2)	C(21)′	0.262(3)	0.207(1)	0.449(2)
F(5)′	0.000(3)	0.467(1)	0.195(2)	C(22)′	0.428(3)	0.093(1)	0.494(2)
O	0.2983(6)	0.2685(3)	0.3371(4)	C(23)′	0.150(3)	0.088(1)	0.354(2)

Treatment of the hydrido hydroxymethyl complex **4b** (and the other hydrido alkoxymethyl complexes **8**,**13**) with acid results in the immediate formation of the methyl complex **9**. This reaction (eq 3) provides an excellent example of one proposed step in CO reduction, the acidification of a hydroxymethyl fragment to give metal-bound methylene and water, followed by reaction of the methylene moiety with hydrogen.[1,33] In fact, compound **4a** can be obtained by borohydride or borane reduction of CO, and the present iridium system is a very good model indeed for several steps which may be important in the Fischer–Tropsch process.[18,34]

Experimental Section

Experimental procedures are described in the earlier work.[7] Iodotrimethylsilane, bromotrimethylsilane, bromomethyl methyl ether, tetrafluoroboric acid–diethyl ether, and potassium *tert*-butoxide were obtained from Aldrich Chemical Co. and were used as supplied. Paraformaldehyde was also obtained from Aldrich; purification was accomplished by washing with tetrahydrofuran (THF) and diethyl ether. Technical grade ammonium bifluoride $[NH_4HF_2]$ was obtained from Fisher. *Note that α-halo ether compounds are extremely toxic.* ^1H NMR chemical shifts are reported in parts per million downfield from external Me_4Si or from internal $OSiMe_3$ (if present). Infrared (IR) data are reported in units of inverse centimeters for solid samples in Nujol. All reactions were carried out at room temperature in an atmosphere of dinitrogen unless otherwise noted.

Hydridotetrakis(trimethylphosphine)iridium(I), $IrH(PMe_3)_4$ (7). Bubbling dihydrogen through a suspension of

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(33) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181–6182.

(34) Parshall, G. W.; Thorn, D. L.; Tulip, T. H. *CHEMTECH* **1982**, 571–576.

Table V. Summary of X-ray Diffraction Data

complex	$\{IrH(CH_2OH)[P(CH_3)_3]_4\}\{PF_6\}$
formula	$C_{13}H_{40}F_6IrOP_5$
fw	673.52
a, Å	9.237 (2)
b, Å	21.067 (3)
c, Å	13.156 (2)
β, deg	104.30 (1)
V, Å^3	2481 (1)
z	4
ρ_{calcd}, g cm^{-3}	1.803
space group	C^5_{2h}–$P2_1/c$ (No. 14)
cryst dimens, mm	0.15 × 0.30 × 0.32
temp, °C	−100
radiatn	Mo Kα (0.710 69 Å) from graphite monochromator
μ, cm^{-1}	60.62
transmissn factors	0.502, 0.998; average 0.872
2θ limits, deg	4.0–55.0
total no. of observns	6185
unique data, $F_o{}^2 > 3\sigma(F_o{}^2)$	4417
final no. of variables	267
R	0.029
R_w	0.031
error in observn of unit wt	1.54 electrons

$[Ir(PMe_3)_4]Cl$[15] in THF resulted in its conversion to the dihydride $[IrH_2(PMe_3)_4]Cl$ in ca. 80% yield.[35] A suspension of $[IrH_2(PMe_3)_4]Cl$ (0.61 g) in 10 mL of THF was treated with 0.20 g of potassium *tert*-butoxide. The mixture rapidly became a cloudy yellow solution which was filtered and evaporated after being stirred 30 min. The residue was extracted into pentane. Evaporation of the pentane extract left compound 7 as a yellow oil or paste, estimated yield 80%. The compound is too soluble in inert solvents to be recrystallized, but the crude reaction product is sufficiently pure for most purposes. The compound is extremely sensitive to oxygen and moisture: ^1H NMR (C_6D_6) δ −13.6 (quintet, IrH, J = 6 Hz), 1.55 (br s, $P(CH_3)_3$).

Iodomethyl Trimethylsilyl Ether, ICH_2OSiMe_3.[16] Paraformaldehyde (0.33 g) was added to iodotrimethylsilane (2.00 g) and dissolved within ca. 10 min at room temperature. After being stirred an additional 20 min the resulting cloudy solution, consisting primarily of ICH_2OSiMe_3,[16,36] was refrigerated and the reagent used directly as needed. The compound decomposed when distillation was attempted or after being stored for ca. 3 days at −20 °C. The compound decomposed even more rapidly when slightly damp paraformaldehyde was used.

Hydrido((trimethylsiloxy)methyl)tetrakis(trimethylphosphine)iridium(III) Iodide, $[IrH(CH_2OSiMe_3)(PMe_3)_4]I$ (8). A solution of ICH_2OSiMe_3 (0.176 g) in 2 mL of ether was added slowly to a stirred solution of 0.38 g of $IrH(PMe_3)_4$ (7) in 10 mL of ether. The resulting white suspension was stirred an additional 5 min and filtered, yielding 0.45 g (81%) of compound 8. An analytically pure sample was obtained by recrystallization from acetonitrile by the vapor diffusion of ether: dec pt 185 °C; mp >195 °C; IR 2045 (s, Ir–H) cm^{-1}; ^1H NMR (CD_3CN) δ −13.5 (d (J = 126 Hz) of t (J = 20 Hz) of d (J = 14 Hz), Ir–H), 0.0 (reference, s, $OSi(CH_3)_3$), 1.40 (d (J = 9 Hz) of d (J(H hydride) = 1 Hz)), 1.56 (d, J = 8 Hz), 1.56 (t, J(eff) = 3.6 Hz) ($P(CH_3)_3$), 4.10 (t (J = 7.7 Hz) of d (J = 6.0 Hz) of d (J = 1.8 Hz) of d (J(H hydride) = 0.6 Hz), $IrCH_2O$). Anal. Calcd: C, 26.41; H, 6.65. Found: C, 26.59; H, 6.77.

Hydrido(hydroxymethyl)tetrakis(trimethylphosphine)iridium(III) Iodide, $[IrH(CH_2OH)(PMe_3)_4]I$ (4b). Ammonium bifluoride (0.05 g) was added to a suspension of compound 8 (0.24 g) in 10 mL of THF, and the mixture was boiled gently for 1 h. After cooling, the suspension was filtered to yield 0.18 g (82%) of compound **4b**. An analytically pure sample was obtained by recrystallization from acetonitrile by the vapor diffusion of ether: IR 3350 (m, br), 2028 (s), cm^{-1}; ^1H NMR (CD_2Cl_2) δ −13.4 (d (J = 124 Hz) of t (J = 22 Hz) of d (J = 16 Hz), IrH), 1.55 (d (J = 8 Hz) of d (J(H hydride) = 1 Hz), 1.71 (d, J = 8 Hz), 1.74 (t, J(eff) = 3.6 Hz) ($P(CH_3)_3$), 4.20 (t (J = 8.2 Hz) of d (J = 5.5 Hz) of d (J = 1.5 Hz) of m, $IrCH_2O$). Anal. Calcd: C, 23.82; H, 6.15. Found: C, 23.75; H, 6.25. A signal for the OH proton was not observed in CD_2Cl_2 but occurs at δ 4.3 (br) in pyridine-d_5. Compound **4b** is unstable in methylene chloride and appreciably decomposes to uncharacterized products within 24 h. Adding excess $NaPF_6$ to an aqueous solution of compound **4b** caused the hexafluorophosphate salt **4a**[7] to precipitate.

Methyliodotetrakis(trimethylphosphine)iridium(III) Tetrafluoroborate, $[Ir(CH_3)I(PMe_3)_4][BF_4]$ (9). A solution of compound **4b** (0.071 g) in CD_2Cl_2 was treated with 0.018 g of HBF_4 diethyl etherate. The resulting cloudy solution was filtered; the ^1H NMR spectrum showed only signals of compound **9**: δ 0.84 (quartet (J = 6.8 Hz) of d (J = 4.2 Hz), $IrCH_3$), 1.73 (d, J = 9 Hz), 1.85 (d, J = 8 Hz), 1.88 (t, J(eff) = 3.4 Hz) ($P(CH_3)_3$), together with diethyl ether and excess HBF_4–(ether)$_n$–$(H_2O)n$ at δ 9.9 (s). Similar reactions of compounds **8** and **13** with HBF_4 diethyl etherate yielded the corresponding methyl compounds **9** and **14** (>95% by ^1H NMR analysis).

Base-Induced Decomposition of Compound 4b. Compound **4b** (0.20 g) in pyridine-d_5 (0.8 mL) was treated with a solution of compound **7** (0.02 g) in pyridine-d_5 (0.8 mL). The pale yellow color of compound **7** bleached within 1 min. The ^1H NMR spectrum of the resulting solution revealed $[IrH_2(PMe_3)_4]^+$[35] as the only detectible product: δ −13.1 (d (J = 100 Hz) of pseudo t (J = 21 Hz), IrH), 1.32 (d, J = 7 Hz), 1.36 (t, J(eff) = 3.5 Hz) ($P(CH_3)_3$).

In a separate experiment, 0.13 g of compound **4b**, 0.13 g of $[Ir(PMe_3)_4][PF_6]$,[7] 0.033 g of $NaPF_6$, and 0.002 g of potassium *tert*-butoxide were added sequentially to 10 mL of THF. The resulting orange suspension became white after the mixture was stirred 15 min. After being stirred an additional hour, the mixture was filtered, yielding 0.07 g of $[IrH_2(PMe_3)_4]I$; the solution was evaporated and the residue redissolved in pyridine-d_5. The dominant species in solution (^1H NMR) was again $[IrH_2(PMe_3)_4]^+$, but there was ca. 15% of the hydrido formyl complex $IrH(CHO)I(PMe_3)_3$. This formyl complex was prepared separately by adding paraformaldehyde to a suspension of $[Ir(PMe_3)_4]I$ in THF:[7,20] ^1H NMR of $IrH(CHO)I(PMe_3)_3(C_6D_6)$ δ −10.4 (d (J = 137.5 Hz) of t (J = 20 Hz), IrH), 1.41 (d (J = 8 Hz) of d (J(H hydride) = 1 Hz), 1.59 (t, J(eff) = 3.7 Hz) ($P(CH_3)_3$), 14.9 (t (J = 6.8 Hz) of d (J = 4.1 Hz) of d (J = 0.7 Hz), IrCHO); IR 2580 (m), 2022 (s), 1620 (s), 1600 (s) cm^{-1}; dec pt 140 °C. Anal. Calcd: C, 20.80; H, 5.06. Found: C, 21.08; H, 4.99.

X-ray Data Collection and Structure Solution and Refinement. For structural studies, the compound *cis*-$[IrH(CH_2OH)(PMe_3)_4][PF_6]$ (**4a**) was prepared by the reduction of the formyl compound **5** (Scheme I, bottom route).[7] Crystals of this compound suitable for diffraction studies were obtained by cooling a methanol–diethyl ether solution to −30 °C. The crystal chosen was encapsulated in a glass capillary under an atmosphere of N_2. Preliminary photographic investigations indicated the crystal system, space group, and approximate cell dimensions. These and other crystallographic data are summarized in Table V. The crystal was then placed on a Syntex P3 diffractometer and shown to be suitable for diffraction on the basis of ω scans which showed the peak width at half-height to be ca. 0.20° at −100 °C. The cell parameters were then refined on the basis of 50 computer-centered reflections chosen from diverse regions of reciprocal space.

Intensity data were collected by using the ω scan technique (variable scan range, 4.0–10.0° min^{-1}; total background time equals scan time). The intensities of four standard reflections were measured every 200 reflections. No significant deviations in the intensities of these standards were observed. The intensities of several reflections were measured at 10° increments about the diffractor vector. Empirical corrections for absorption thereby derived were subsequently applied. The data were processed by using counting statistics and a p value of 0.02 to derive standard deviations.[37]

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[35] Herskovitz, T., unpublished work. We deeply appreciate Dr. Herskovitz's helpful suggestions and continuing interest in this work.

[36] Voronkov, M. G.; Komarov, V. G.; Albanov, A. I.; Korataeva, I. M.; Dubinskaya, E. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1391–1392.

[37] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.

1586 *Organometallics* **1982,** *1,* 1586–1590

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of programs supplied by the Enraf-Nonius Corp.[38] The iridium atom was located by using an origin-removed Patterson synthesis. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinements. In the least-squares refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are, respectively, the observed and calculated structure amplitudes and where $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from the compilations of Cromer and Waber.[39a] Anomalous dispersion terms used were those of Cromer.[39b] After convergence of refinements containing the non-hydrogen atoms, a difference Fourier synthesis revealed residual electron density arising from disorder of the oxygen atom, the "equatorial" fluorine atoms F(2–5), and the carbon atoms about P(2). In a series of refinements, the populations of the minor positions were found to be approximately 0.20. This value was fixed in subsequent refinements to convergence in which atoms occupying both major and minor positions were included. The atoms occupying the major positions were allowed to vibrate anisotropically while those at the minor positions were included as isotropic bodies. The positions of the majority of hydrogen atoms were then determined in a difference Fourier synthesis. The positions of the major carbon-bound hydrogen atoms were then idealized with a C–H distance of 0.95 Å, and these atoms included as fixed contributions ($B_H = 4.0$).[40] The hydroxy hydrogen atom was not located. Although a peak corresponding to the hydrido hydrogen atom was located in the expected area, attempted refinement of this atom was unsuccessful and no contribution from this atom was included. The hydrogen atoms associated with the minor C and O positions were not included. Least-squares refinement converged to values of $R = 0.029$ and $R_w = 0.031$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$. A number of peaks on the order of 1.0 e/Å^{-3} remain in a final difference Fourier synthesis and are associated with the metal atom.

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Registry No. 4a, 79568-57-3; **4b,** 83435-10-3; **6,** 83380-24-9; **6**·Cl, 83380-23-8; **6**·I, 83380-25-0; **7,** 83380-16-9; **8,** 83380-17-0; **9,** 83380-19-2; **13,** 83380-20-5; **14,** 83380-22-7; $[Ir(PMe_3)_4]Cl$, 60314-48-9; ICH_2OSiMe_3, 83380-15-8; $NaPF_6$, 21324-39-0; HBF_4, 16872-11-0; $[Ir(PMe_3)_4][PF_6]$, 75593-00-9; $IrH(CHO)I(PMe_3)_3$, 83380-26-1; $[Ir(PMe_3)_4]I$, 83380-27-2; paraformaldehyde, 30525-89-4; iodotrimethylsilane, 16029-98-4; ammonium bifluoride, 1341-49-7; Potassium *tert*-butoxide, 865-47-4.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters (Table III) and the idealized hydrogen atom positions (Table IV), a listing of the observed and calculated structure amplitudes, views of the disordered cation and anion (Figures 2 and 3), and a stereodrawing of the unit cell (Figure 4) (26 pages). Ordering information is given on any current masthead page.

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[38] Frenz, B. A. "The Enraf-Nonius CAD4 SDP--A Realtime System for Concurrent X-ray Data Collection and Crystal Structure Determinations", in "Computing in Crystallography"; Schenk, H., Olthof-Hazelhamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

[39] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

[40] See paragraph at end of paper regarding supplementary material.

Formation and Cleavage of Carbon–Carbon and Tungsten–Carbon Bonds Involving Bis(η-cyclopentadienyl)tungsten Compounds[†]

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Cocondensation of spiro[2,4]hepta-4,6-diene with tungsten atoms gives $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)_2]$, **1**. One-electron oxidation of **1** with $AgPF_6$ gives $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)_2]PF_6$ which readily reduces to **1**. Treatment of **1** with $[Ph_3C]PF_6$ or of $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)_2]PF_6$ with Ph_3C gives $[W(\eta\text{-}C_5H_4CH_2\text{-}\mathit{trans}\text{-}\eta\text{-}CH{=}CHCH_2\text{-}\eta\text{-}C_5H_4)H]PF_6$ via a carbon–carbon bond formation reaction. $[W(\eta\text{-}C_5H_4CH_2\text{-}\mathit{trans}\text{-}\eta\text{-}CH{=}CHCH_2\text{-}\eta\text{-}C_5H_4)H]PF_6$ is readily deprotonated with aqueous base forming $[W(\eta\text{-}C_5H_4CH_2\text{-}\mathit{trans}\text{-}\eta\text{-}CH{=}CHCH_2\text{-}\eta\text{-}C_5H_4)]$. Treatment of $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)_2]$ with $PhICl_2$ cleaves both tungsten–carbon bonds forming the tetrachloro derivative $[W(\eta\text{-}C_5H_4CH_2CH_2Cl)_2Cl_2]$. This is readily reduced back to $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)_2]$ by sodium amalgam. **1** reacts with 1 equiv of benzoic acid forming $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)(\eta\text{-}EtC_5H_4)OCOPh]$ which upon treatment with trimethyliodosilane gives $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)(\eta\text{-}EtC_5H_4)I]$. This compound reacts with PMe_3 in acetone giving first $[\overline{W(\eta\text{-}C_5H_4CH_2C}H(PMe_3)(\eta\text{-}EtC_5H_4)H]PF_6$ and then $[\overline{W(\eta\text{-}C_5H_4CH_2C}H_2)(\eta\text{-}EtC_5H_4)PMe_3]PF_6$. A mechanism involving a 1,2-hydrogen shift equilibrium is proposed to account for this sequence of reactions.

Introduction

The bis(η-cyclopentadienyl)tungsten moiety has proved to be a versatile system for the study of the role of a transition-metal center in basic reactions with simple hydrocarbon systems. For example, the study of bis(η-cyclopentadienyl)tungsten derivatives has led to the acceptance of reversible 1,2-hydrogen shifts in metal alkyls as a general phenomenon.[1] Tungstenocene is one of the

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[†] Dedicated to Rolly Pettit.

[1] Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979,** 1121.