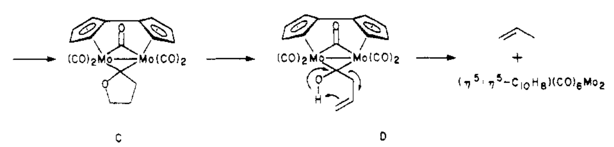
Organometallics 1985, 4, 192–194

Scheme III



Mo–Mo bond, and the carbonyl groups slightly staggered to relieve steric compression, resulting in a twisted fulvalene. The generation of such carbene complexes from 1,3-dihalopropanes and nucleophilic metals has been observed previously[7] and mechanistically discussed in terms of addition of a nucleophile (which can be another metal) to a (γ-haloacyl)metal species generating a metallaenolate $R(CO)M^-$, capable of ring closure. However, the intermediacy of a dimetallacycle of the type **2** in those cases involving bimetallic systems has not been ruled out.

Complex **3** has two hitherto unobserved features. First, it is fluxional on the NMR time scale. Thus, on heating in toluene-d_8 the fulvalene signals begin to broaden while the oxopentylidene absorptions remain sharp. Because of the thermal instability of **3** (vide infra), quantification of these dynamics was only possible by using spin saturation transfer techniques.[8] This experiment revealed the exchange (50% magnetization transfer at 25 °C) between the respective sets of α and β protons on the fulvalene and also confirmed the absence of equilibration of the trimethylene hydrogens: $\Delta G^\ddagger = 18.0 \pm 0.5$ kcal mol^{-1}. The most appealing mechanism for this dynamic behavior would involve the intermediacy of a bridging carbene (Scheme III). Isomerizations of a bridging carbene to terminal positions have recently been observed,[1b,9] but not the reverse, and, although postulated,[7b] never directly in a Fischer-type carbene.[10]

Second, and most surprising, **3** on heating to 100 °C (benzene, $t_{1/2} = 12$ h) (or on irradiation) efficiently decomposes to regenerate $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(CO)_6Mo_2$ (80%) and propene (80%)! Deuterium-labeled **3**-d_2 at carbon-3[11] gave cleanly propene-*1,1*-d_2 (NMR, m/e), **3**-d_2 labeled at carbon-4[12] furnished propene-*2,3*-d_2, and **3**-d_1 labeled at carbon-5 through a novel sequence[13] resulted in propene-*3*-d_1. Recovered starting materials from incomplete thermolyses exhibited no label scrambling. These data rule out **2**, or any related dimetallacyclopentane, as being an intermediate in this reaction. Finally, there are no noticeable deuterium isotope effects (error margin ±10%), concentration dependence, and changes due to added ligand [such as $(C_6H_5)_3P$]. Remarkably, other oxacyclopentylidenes do not yield propene on pyrolysis but rather carbene dimers or 2,3-dihydrofuran.[10,14] The free carbene also furnishes the latter, but, in addition, cyclobutanone, cyclopropane, and ethylene,[15] not found in our system.

Scheme III depicts a possible mechanistic rationale for the observed data. It is appealing (but not required) to postulate that it is the relatively ready accessibility of the bridged carbene C (possibly facilitated[16,17] by the relatively electron-donating fulvalene ligand) which allows the unraveling of the ligand to D, much like a γ-butyrolactone pyrolysis,[18] followed by a retroene reaction, such as that observed with β,γ-unsaturated acids,[19] to furnish the products. This explains the absence of similar decomposition pathways in the related $Mn_2(CO)_{10}(CH_2)_3$,[14] as well as the mononuclear systems,[7,10,14] the outcome of the deuterium labeling experiments, and the other data. Whatever the exact mechanism, it is intriguing to speculate on the potential intermediacy of the hitherto unrecognized species of the type C and/or D or their unbridged counterparts in other propene-forming reactions involving dinuclear metallacycles and even on surfaces exposed to CO and H_2.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098. The crystal structure analysis was performed by Dr. F. J. Hollander, U.C. Berkeley X-ray Crystallographic Facility. K.P.C.V. was a Camille and Henry Dreyfus Teacher–Scholar (1978–1983).

Supplementary Material Available: A listing of positional and thermal parameters and tables of bond lengths and bond and torsional angles of **3** (11 pages). Ordering information is given on any current masthead page.

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[12] From $ICH_2CD_2CH_2I$ as in Scheme I.

[13] Prepared by reacting **3** with excess $(C_6H_5)_3C^+BF_4^-$ in THF, followed by addition of $LiAlD_4$.

[14] Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 1651. We have found that $Mn_2(CO)_{10}(CH_2)_3$ also thermolyzes to 2,3-dihydrofuran.

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[19] Bigley, D. B. *J. Chem. Soc.* **1964**, 3897.

Reactions of a Methyl(methoxymethyl)rhodium(III) Complex. α-C–H and C–O Bond Cleavage and C–C Bond Formation[†]

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Summary: The complex $RhBr(CH_3)(CH_2OCH_3)(P(CH_3)_3)_3$ undergoes two different categories of reactions. If the C–O bond is cleaved, ethylene is formed by methyl group migration; if the Rh–Br bond is cleaved, methyl vinyl ether

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[†] Contribution No. 3585.

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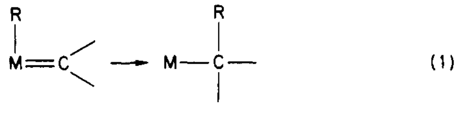
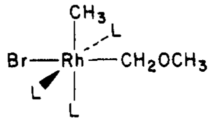
and methyl ethyl ether are formed by an α-hydrogen migration, methyl migration sequence.

Alkylidene or carbene complexes of transition metals are implicated in many organometallic reactions, including reactions where new carbon–hydrogen or carbon–carbon bonds are formed. Recently a number of mononuclear compounds[1] have been prepared that undergo the C–H or C–C bond formation reactions summarized in eq 1,[2] pre-



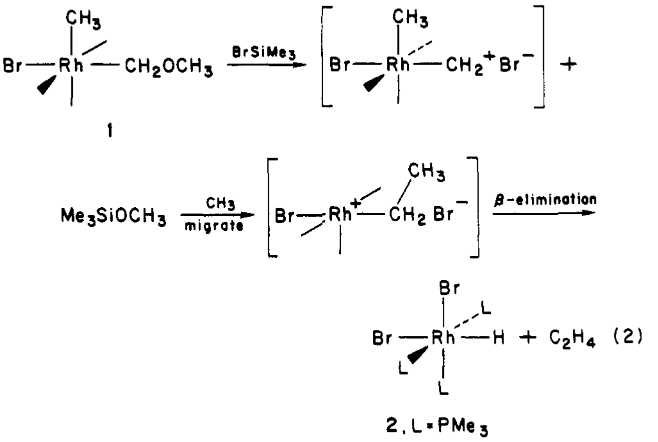
(1)

sumably by a straightforward migration reaction that may or may not be reversible.[2g] Previous work in this laboratory has focused on alkoxy- and hydroxymethyl complexes of iridium, which are converted into reactive methylene complexes by protonation, silylation, or alkylation and which undergo the migration reactions of eq 1.[2c,d,e] This approach now has been extended to comparable rhodium complexes, in particular compound 1, in which methyl group migration and α-hydrogen "decomposition" both have been observed and are described in this communication.



1, L = PMe$_3$

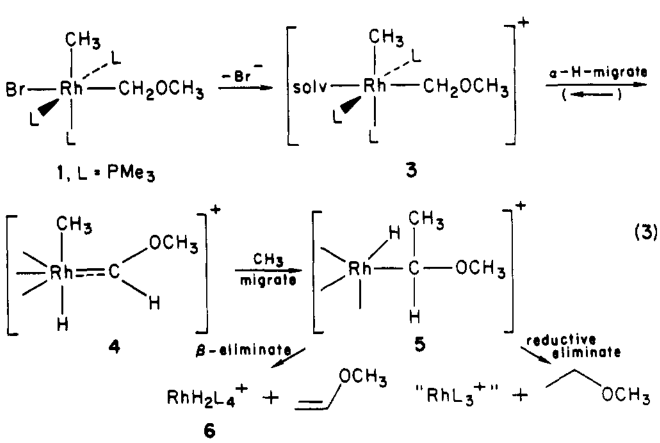
Compound 1[3,4] is prepared by reacting the methyl(tetraphosphine)rhodium(I) complex[5] with bromomethyl methyl ether.[6] In nonreactive solvents under an inert-atmosphere compound 1 is indefinitely stable at room temperature. However, when treated with the silylating agent BrSiMe$_3$,[6] compound 1 reacts, presumably by the mechanism of eq 2. The major products of the reaction



(2)

are Me$_3$SiOMe, ethylene, and the hydridorhodium complex 2.[7] None of the intermediate species of eq 2 has been observed, but this mechanism is supported by its analogy to the chemistry of the related iridium complex.[2c] The CH$_2$–O bond of complex 1 is more resistant to cleavage than that of the iridium analogue. The reaction between compound 1 and BrSiMe$_3$ requires several hours at room temperature, while the iridium analogue reacts within time of mixing.[2c,e] A possible explanation is that Rh(III) is less able to support a methylene group than is Ir(III).

More surprising is the reaction that occurs when compound 1 is treated with bromide-abstracting reagents (AgSbF$_6$ or TlBF$_4$). In acetonitrile solution the solvated cation 3 (eq 3) is formed and is reasonably stable,[8] but when compound 3 is dissolved in dichloromethane, it decomposes slowly, forming both methyl vinyl ether and methyl ethyl ether.[9] Equation 3 summarizes the proposed mechanism. The key step is α-hydrogen migration from the methoxymethyl group to the vacant (or solvated) coordination site on the metal center, forming a hydrido



(3)

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(3) ^{1}H and ^{13}C NMR spectra were measured at ambient probe temperatures using a Nicolet QE-300 instrument. Chemical shifts are reported in parts per million downfield from external Me$_4$Si. All reactions were carried out at room temperature by using standard inert-atmosphere techniques.

(4) ^{1}H NMR of 1 (CD$_2$Cl$_2$): Rh–CH$_3$, 0.07 (t (7.7 Hz) of d (5.8) of d (2.0)); P(CH$_3$)$_3$, 1.42 (d (7.5 Hz)), 1.42 (pseudo t of d (effective J(H–P) = 3 Hz, J(H–Rh) = 1 Hz)); OCH$_3$, 3.14 (s); Rh–CH$_2$, 3.52 (t (5.8) of d (3.9) of d (2.6)). ^{13}C NMR of 1-Rh^{13}CH$_3$ (CD$_2$Cl$_2$): 10.5 (d (91 Hz) of d(19) of t (9.5 Hz)); J(^{13}C–H) = 128 Hz.

(5) (a) Rh(CH$_3$)(PMe$_3$)$_4$ was prepared following Jones et al.[5b] from Rh(PMe$_3$)$_4$Cl and methyl Grignard reagent in tetrahydrofuran. ^{1}H NMR (C$_6$D$_6$): Rh–CH$_3$, 0.19 (br s, 3 H), P(CH$_3$)$_3$, 1.35 (br s, 12 H). ^{13}C NMR: Rh–^{13}CH$_3$, −8.9 (d (J(C–Rh) = 17.4 Hz)); J(H–^{13}C) = 124.5 Hz. An analytically pure sample has not been obtained as the phosphines appear to be quite labile, and purified samples reportedly have the stoichiometry Rh(CH$_3$)(PMe$_3$)$_3$.[5b] The Grignard reagent prepared from ^{13}CH$_3$I (98%, Merck) was used to synthesize the labeled compounds. (b) Jones, R. A.; Mayor Real, F.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511–518; **1981**, 126–131. Herskovitz, T. H., unpublished work.

(6) These reagents are very toxic. Commerical material (Aldrich) was used as supplied.

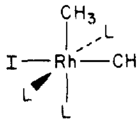
(7) ^{1}H NMR of 2 (CD$_2$Cl$_2$): Rh–H, −16.7 (t of t (17.7, 13.4 Hz)); P(CH$_3$)$_3$, 1.70 (d (9 Hz)), 1.78 (t (3.5 Hz)). An analytically pure sample has not been obtained. Ethylene is formed in at least 80% yield, and from the ^{13}C NMR spectrum of the reaction mixture using 1-^{13}CH$_3$ (98%, ref 5a) no other ^{13}C-enriched species can be detected.

(8) ^{1}H NMR of 3 (CD$_3$CN): Rh–CH$_3$, 0.06 (t (7.5 Hz) of d (5.7) of d (1.9)); P(CH$_3$)$_3$, 1.32 (t (3.3)), 1.37 (d (7.5)); OCH$_3$, 3.09 (s); Rh–CH$_2$, 3.37 (quart. (6.3) of d (3.3)). ^{13}C NMR: Rh–^{13}CH$_3$, 2.1 (d (85) of d (20) of t (10)); J(^{13}C–H) = 128 Hz.

methyl methoxycarbene complex, 4, which then undergoes methyl group migration to form complex 5. Complex 5 decomposes both by reductive elimination to form methyl ethyl ether and a Rh(I) complex[10] and by β-elimination to form methyl vinyl ether and a dihydrido rhodium(III) compound. The dihydrido compound 6 that is detected is actually the tetrakis(trimethylphosphine) complex $RhH_2(PMe_3)_4^+$,[11] which means phosphine redistribution reactions complicate the overall reaction kinetics.[12]

Although the proposed intermediate species 4 and 5 of eq 3 have not been observed, supporting evidence for this reaction mechanism comes from studies of related iridium compounds and from the effect of coordinating ligands on the reaction, which must await the full publication for adequate description.[2e] However, reasons for excluding two possible alternative mechanisms are presented briefly below.

One possible alternative to the mechanism of eq 3 is α-hydrogen migration from the methyl group followed by methoxymethyl group migration to the methylene carbon atom. But, if a methyl group can function as a source of a migrating α-hydrogen atom, the dimethylrhodium complex 7[13] should evolve ethylene when treated with halide-abstracting reagents. Complex 7 does react with halide-abstracting reagents, but no ethylene, ethane, or methane is formed and the dimethylrhodium complex can be recovered by adding halide. This implies that methyl groups do not function as α-hydrogen sources (in this coordination environment), consistent with the earlier suggestion that mononuclear Rh(III) methylene complexes are not readily accessible. The methoxymethyl group may function as an α-hydrogen source, as the resulting methoxycarbene group is relatively more stable.



7, L = PMe$_3$

A second possible alternate mechanism is the direct reductive elimination of methyl ethyl ether from compound 1, or perhaps from compound 3, with subsequent dehydrogenation of the ethyl group. However, the $^{13}CH_3$-labeled compound 1[5a] undergoes the halide abstraction reaction forming ^{13}C-labeled methyl vinyl ether,[14] and no unlabeled methyl vinyl ether, even in the presence of 1.5 equiv of unlabeled methyl ethyl ether. Therefore, the methyl vinyl ether cannot result from dehydrogenation of free methyl ethyl ether. The most plausible mechanism for vinyl ether formation remains the "α-elimination" mechanism summarized in eq 3.

Acknowledgment. I was first made aware of α-hydrogen processes in reactions of alkylmetal compounds[15] and was introduced to synthetic organometallic chemistry in general by Professor Earl Muetterties and his co-workers while at Cornell University. Without his inspiration the present work would not have been attempted.

Registry No. 1 (L = PMe$_3$), 92670-91-2; 2 (L = PMe$_3$), 92670-92-3; 3 (L = PMe$_3$), 92670-93-4; 7 (L = PMe$_3$), 92670-94-5; $Rh(CH_3)(PMe_3)_4$, 92670-95-6; $Rh(PMe_3)_4Cl$, 92670-96-7.

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[9] (a) ^1H NMR of methyl vinyl ether (CD_2Cl_2): OCH_3, 3.55 (s); $=CH(OMe)$, 6.54 (d of d (14.2, 6.9 Hz)); $=CH_2$, 4.01 (d of d (6.9, 2.2)), 4.18 (d of d (14.2, 2.2)).[9b] ^1H NMR of methyl ethyl ether (CD_2Cl_2): CH_3CH_2, 1.18 (t), 3.42 (q (7.1 Hz)); OCH_3, 3.31 (s). These products are formed simultaneously in a 1:1 ratio (±10%) and together account for at least 85% of reacted compound 3. (b) Herberhold, M.; Wiedersatz, G. O.; Kreiter, C. G. *Z. Naturforsch, B*: **1976**, *31B*, 35–38.

[10] The Rh(I) product(s) appears to react with CD_2Cl_2 forming several uncharacterized products. Marder, T. B., personal communication.

[11] Schrock, R. R.; Osborne, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397–2407. The inability of this compound to hydrogenate olefins under mild conditions allows the accumulation of methyl vinyl ether.

[12] Another methyl(methoxymethyl)rhodium compound, believed to be $Rh(CH_3)(CH_2OCH_3)(PMe_3)_2(acetonitrile)_2^+$, can be detected during the reaction but is eventually consumed. This compound does not appear to be involved in the formation of the organic products but arises, and disappears, as a result of phosphine redistribution reactions.

[13] ^1H NMR of 7 (CD_2Cl_2): Rh–CH_3, 0.08 (d (8.2 Hz) of t (6.0) of d (2.4)); 0.18 (t (7.7) of d (5.8) of d (2.0)); $P(CH_3)_3$, 1.42 (d (6.2)), 1.48 (t (3.0) of d (1 Hz)).

[14] ^{13}C NMR of $^{13}CH_2{=}CH(OMe)$ (CD_2Cl_2): 85.3; J(C–H) = 161, 156, 9.5 Hz.[9b] No $^{12}CH_2{=}CH(OMe)$ can be detected in the ^1H NMR spectrum.

[15] Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978–6989.

Synthesis and Crystal Structure of (*syn*-η^3-Pentadienyl)Mn[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$_2$ and Its Reactions To Produce Mn[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$_3^+PF_6^-$ and *cis*-Mn[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$_2$[$P(OCH_3)_3$]$_2^+PF_6^-$†

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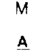
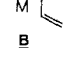
Summary: Reaction of $MnBr_2$ with 1,2-bis(dimethylphosphino)ethane (dmpe) and potassium pentadienide results in the formation of (*syn*-η^3-pentadienyl)Mn(dmpe)$_2$ (**1**). A single-crystal X-ray diffraction study of **1** has established that the *syn*-η^3-pentadienyl ligand is essentially W-shaped, with carbon atom C5 rotated slightly out of the plane made by C1, C2, C3, and C4. Reaction of **1** with $NH_4^+PF_6^-$ produces Mn(dmpe)$_3^+PF_6^-$ (**2**), the first example of a homoleptic manganese–phosphine complex. Treatment of **1** with $NH_4^+PF_6^-$ in the presence of trimethyl phosphite produces *cis*-Mn(dmpe)$_2$[$P(OCH_3)_3$]$_2^+PF_6^-$ (**3**).

In recent years, the acyclic pentadienyl group has begun to be utilized as a ligand in organotransition metal complexes.[1] One of the intriguing features of this ligand is its ability to adopt a variety of bonding modes and geometries. Recent structural reports of pentadienylmetal complexes, for example, have described three different solid-state geometries for η^3-pentadienyl ligands, W-shaped syn-η^3 (A),[1m] sickle-shaped anti-η^3 (B),[1l] and U-shaped anti-η^3 (C).[1n] The U-shaped η^5-bonding mode is also



A



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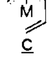

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† Dedicated to the memory of Earl Muetterties—mentor and friend.

[1] Recent reports of pentadienyl transition-metal complexes include the following: (a) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (b) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 1120. (c) Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 3737. (d) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708. (e) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Ibid.* **1983**, *2*, 1220. (f) Stahl, L.; Ernst, R. D. *Ibid.* **1983**, *2*, 1229. (g) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* **1983**, *250*, 257. (h) Seyferth, D.; Goldman, E. W.; Pornet, J. *Ibid.* **1981**, *208*, 189. (i) Paz-Sandoval, M. A.; Powell, P. *Ibid.* **1981**, *219*, 81. (j) Lehmkuhl, H.; Naydowski, C. *Ibid.* **1982**, *240*, C30. (k) Paz-Sandoval, M. A.; Powell, P. *Ibid.* **1983**, *252*, 205. (l) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026. (m) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (n) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1984**, *3*, 1422.

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