Syntheses and Reactions of Methyl(methoxymethyl)- and Dimethylrhodium(III) Complexes†

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Cleavage of the C–O bond of the compound $RhBr(CH_3)(CH_2OCH_3)(PMe_3)_3$ (1) with trimethylsilyl bromide provides ethylene, formed by methyl migration to a methylene entity and subsequent β-elimination. Compound 1 also reacts with silver ion, losing bromide and providing an entry into a family of well-characterized cationic compounds $[Rh(Me)(CH_2OMe)(PMe_3)_n(CH_3CN)_{4-n}][SbF_6]$ (compound 2, $n = 4$; compound 3, $n = 3$; compound 4, $n = 2$). Compounds 1, 2, and 4 are relatively stable at room temperature in methylene chloride solution, but the tris(phosphine) compound 3 decomposes, forming equal amounts of methyl vinyl ether and methyl ethyl ether, together with several rhodium compounds including compound 4 and $[RhH_2(PMe_3)_4][SbF_6]$. This decomposition is believed to result from an α-C–H activation of the methoxymethyl group. Analogous dimethylrhodium compounds 5–8 are described for comparison and are unreactive under identical conditions.

Introduction

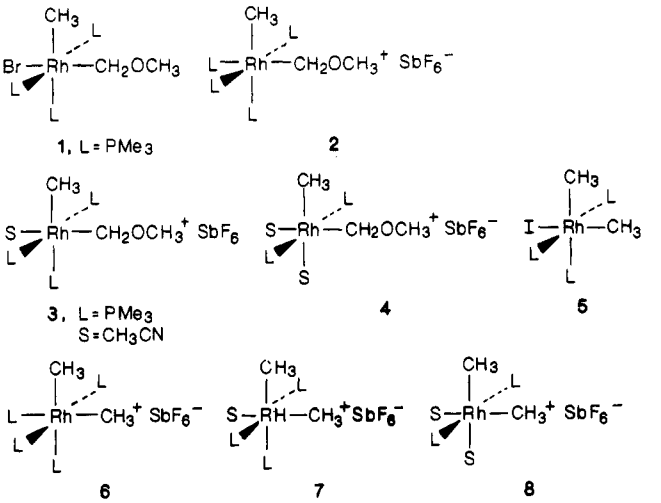
For some time we have been studying the chemistry of transition-metal compounds bearing an alkoxymethyl group. Our initial interest in alkoxymethyl complexes resulted from their similarity to the more elusive hydroxymethyl complexes and from the tendency of the alkoxymethyl group to undergo C–O bond cleavage and form a reactive methylene group.[1,2] Our studies of alkoxymethyl complexes have concentrated on methoxymethyl complexes of rhodium[3] and iridium[2], primarily because these metals support a variety of other organic groups in coordination sites adjacent to the methoxymethyl group. This provides the reactive fragment derived from the methoxymethyl group an opportunity to undergo tractible intramolecular reactions with existing organic groups.

Recent studies have shown that the metal-bound alkoxymethyl group can also participate in α-C–H bond activation reactions, as in Scheme I.[3-5] This reaction has been encountered in several methoxymethyl iridium complexes,[2d] and preliminary findings on the reactivity of the rhodium methyl methoxymethyl complex 1[3] have been communicated. This paper provides complete details of the preparation and reactivities of the rhodium methyl methoxymethyl compound 1 and its derivatives 2, 3, and 4 and elaborates on some unexpected subtleties of the chemistry of these compounds. For purposes of comparison, the related dimethylrhodium compounds 5–8 are also described.

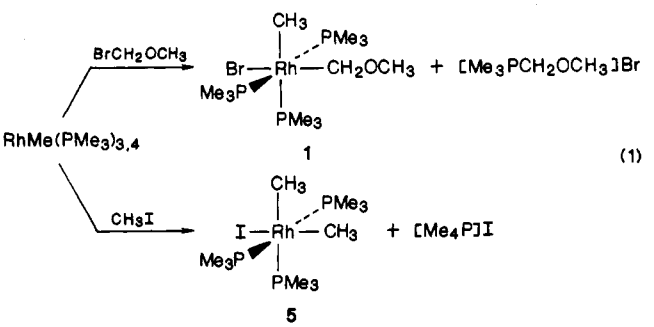
A critical aspect of α-C–H activation, evident from Scheme I, is the necessity of a vacant coordination site adjacent to the alkoxymethyl group. If there is no coordination vacancy, the simple α-C–H reaction of Scheme I cannot occur, although other α-C–H reactions, such as hydrogen atom transfer to another group ("sacrificial elimination"),[6] are still possible. Consequently, this paper concentrates on processes which open or block coordination sites of these rhodium methoxymethyl compounds and discusses the variation in their subsequent reactivities.

Results

Preparation of the Methyl Methoxymethyl Compound 1 and Dimethyl Compound 5. Compounds 1 and 5 are quite easily obtained from the reaction between commercially available alkyl halides and tris- or tetrakis-



(trimethylphosphine)methylrhodium(I) (eq 1). The methylrhodium(I) starting material is prepared by treating



(1)

† Contribution No. 3963.

(1) For example, see the following and references cited therein: (a) O'Conner, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869–1874. (b) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203–1205. (c) Labinger, J. A. *J. Organomet. Chem.* **1980**, *187*, 287–296. (d) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsey, S. G. *J. Mol. Catal.* **1981**, *13*, 43–59. (e) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141–152. (f) Cutler, A. *Ibid.* **1979**, *101*, 604–606.

(2) (a) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984–5986. (b) Thorn, D. L. *Organometallics* **1982**, *1*, 879–881. Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Ibid.* **1984**, *3*, 1223–1230. (c) Parshall, G. W.; Thorn, D. L.; Tulip, T. H. *CHEMTECH* **1982**, 571–576. (d) Thorn, D. L. *J. Mol. Catal.* **1982**, *17*, 279–288. Thorn, D. L., unpublished work. (e) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580–1586.

(3) Thorn, D. L. *Organometallics* **1985**, *4*, 192–194.

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

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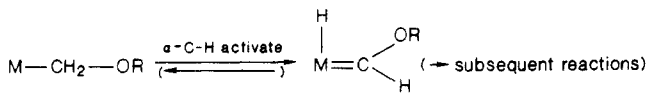
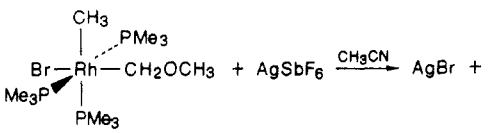
Scheme I



$[Rh(PMe_3)_4]Cl$ with methyllithium or methyl Grignard reagents.[7] Material that has been recrystallized is reportedly the tris(phosphine) complex, but crude samples approach the stoichiometry $Rh(CH_3)(PMe_3)_4$. The precise composition is unimportant; an excess of the alkyl halide reacts with the labile fourth phosphine (if any), and the quarternary salt is easily separated, providing the tris(phosphine) Rh(III) organometallic complexes in good yield.

As obtained from this reaction, compound **1** is the *mer* isomer drawn in eq 1, with the methyl group trans to a phosphine and cis to the bromide, as proven by the ^{13}C NMR spectrum of the $^{13}CH_3$-labeled compound **1**. Alternative *mer* isomers are not observed. Whether this reflects a global thermodynamic preference for the isolated isomer, or a highly stereospecific oxidative addition reaction of the bromomethyl methyl ether substrate, is not known.

Preparation of Tetrakis(phosphine), Tris(phosphine) Acetonitrile, and Bis(phosphine) Bis(acetonitrile) Methyl Methoxymethyl Compounds 2, 3, and 4, Respectively. The bromide ligand of compound **1**, being trans to a strongly donating alkyl group, is quite labile and is easily abstracted by using silver ion (eq 2a). In noncoordinating or weakly coordinating solvents no tractable organorhodium product has been identified, but if acetonitrile is used, the monosolvated compound **3** can be observed in solution and impure samples can be isolated. Again, only the *mer* isomer drawn in eq 2a has been identified, with the solvated coordination site trans to the methoxymethyl group (^{13}C NMR). Solutions of compound **3** are only stable in the presence of acetonitrile, and CD_2Cl_2 solutions decompose within hours at room temperature (see below).



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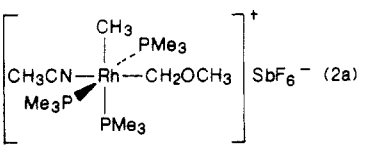

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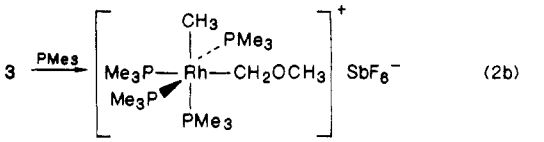
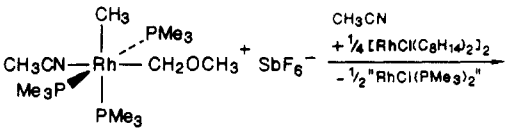
Adding trimethylphosphine to compound **3** immediately forms the tetrakis(trimethylphosphine) compound **2** (eq 2b). Solutions of compound **2** are stable in the presence of trace amounts of free PMe_3, and spectroscopically pure samples of the SbF_6 salt have been obtained from CH_2Cl_2 solution by precipitation with ether.

It is not surprising that the monosolvated tris(phosphine) compound **3** is an isolable material (albeit reactive; see below). But it was initially quite surprising when NMR spectra of decomposed solutions of compound **3** indicated the presence of a stable, doubly solvated bis(phosphine)



2

compound. Subsequent efforts to synthesize this material were successful and the doubly solvated bis(phosphine) compound **4** has been isolated, although in poor yield, from the reaction of eq 3. Here the cyclooctene Rh(I) chloro



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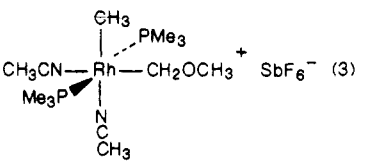

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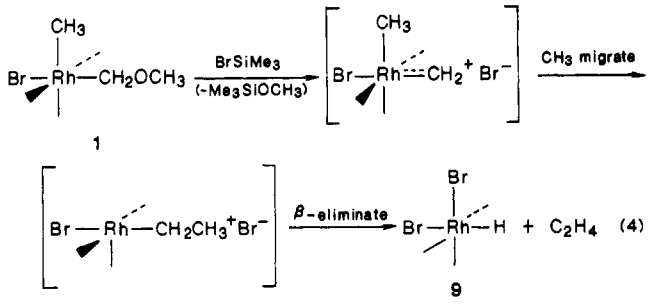
complex[8] has been used as a phosphine abstracting/scavenging reagent. The resulting chlororhodium trimethylphosphine product has not been characterized but does not appear to be a simple, nor a single, species. The cyclooctene Rh complex was used despite its obvious disadvantages and poor yields of desired compound **4**, because other phosphine scavengers that were tried ($(acac)(C_2H_4)_2Rh$, CuCl) provided intractable mixtures.

In the presence of acetonitrile, compound **4** is relatively stable, but in CD_2Cl_2 solution compound **4** slowly decomposes over a period of several days to uncharacterized products.

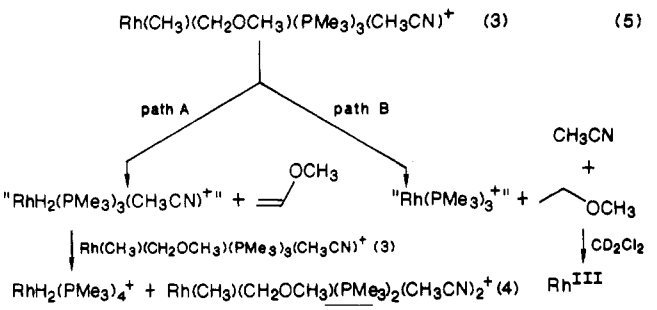
Preparation of Tetrakis(phosphine), Tris(phosphine) Acetonitrile, and Bis(phosphine) Bis(acetonitrile) Dimethyl Compounds 6, 7, and 8, Respectively. These compounds are prepared by the identical methods used to prepare compounds **2–4**. One significant difference between the dimethyl compounds **6–8** and the methyl methoxymethyl compounds **2–4** is that the dimethyl compounds are considerably more stable with no tendency to decompose at room temperature and consequently are easier to prepare and purify. The similarity of the bis(phosphine) bis(acetonitrile) dimethyl compound **8** to the bis(phosphine)bis(solvento)dimethylplatinum(IV) compounds reported by Clark and Manzer[9] and to the family of bis(phosphine)bis(solvento)dihydridorhodium[10] and -iridium(III)[11] compounds should be noted.

Reactions of 1 and 3. Originally, compound **1** was prepared to study its propensity to undergo C–O bond cleavage with subsequent reaction between the methyl group and the resulting methylene group, as an extension of our studies of the analogous iridium compound.[2a] Indeed, compound **1** reacts slowly with the silylating reagent $BrSiMe_3$ to form Me_3SiOCH_3, ethylene, and the hydridorhodium compound **9**, most likely by the mechanism of eq 4. Compound **1** also reacts with protic acids, but these appear to cleave Rh–C bonds directly and C_2 products have not been identified.

(5) May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49.
(6) See: Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104 and references therein.
(7) 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.
(8) Van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92–93.
(9) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 2749–2755.
(10) Schrock, R. R.; Osborne, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397–2407.
(11) See: Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994–7001 and references therein.



Perhaps more interesting is the chemistry that becomes accessible when the bromide ligand is removed from compound **1** in the presence of CH_3CN, initially forming compound **3**. In CD_2Cl_2 solution compound **3** is unstable and decomposes over the course of a few hours by a complicated set of reactions summarized in eq 5. Two path-



ways for the decomposition have been identified: path A forms methyl vinyl ether as the only organic product; path B forms methyl ethyl ether and acetonitrile. Methyl ethyl ether and methyl vinyl ether are formed simultaneously in approximately a 1:1 ratio, so paths A and B are equally probable. Together, methyl vinyl ether and methyl ethyl ether account for more than 85% of the organic products. Traces of unidentified organic products accumulate at long reaction times but appear to arise from secondary decomposition reactions. Further discussion of these reaction pathways and their probable mechanism, α-activation/methyl migration, is given below. Here, three peculiar features of these reaction pathways are noted.

First, the formation of methyl vinyl ether (path A) must be accompanied by an equivalent amount of a rhodium dihydride, shown in eq 5 as "$RhH_2(PMe_3)_3(CH_3CN)^+$". This material is not observed as it rapidly scavenges a phosphine to make the tetrakis(trimethylphosphine) dihydrido compound.[10] One source of phosphine is unreacted compound **3**, forming the bis(acetonitrile) bis(trimethylphosphine) compound **4**. Both compound **4** and $RhH_2(PMe_3)_4^+$ accumulate in the reaction solution, although compound **4** does itself decompose at a substantially slower rate. Thus, there are two processes that deplete compound **3**: actual decomposition (by paths A and B) and loss of phosphine to make the relatively less reactive compound **4**.

A second peculiar feature is that formation of methyl ethyl ether by path B is accompanied by net release of CH_3CN. This accumulation of CH_3CN helps stabilize unreacted compound **3**, thus inhibiting further decomposition. The rhodium product(s) of path B have not been identified but are believed to involve reaction of a nascent Rh(I) compound with the CD_2Cl_2 solvent.[7,12]

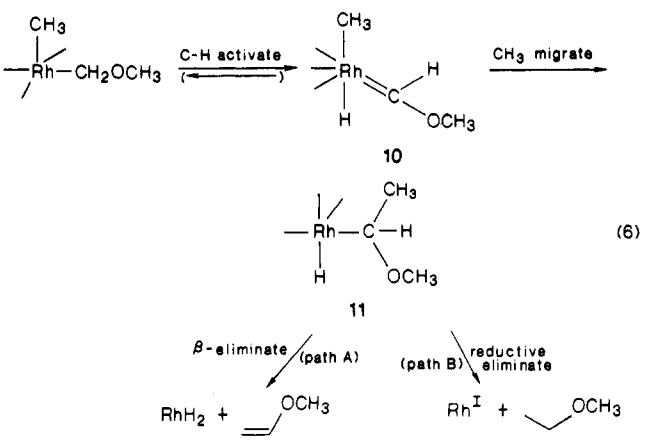
A third peculiar feature is that an olefin and a hydridorhodium compound are both formed in path A. Many hydridorhodium compounds are potent catalysts for olefin hydrogenation (see for instance ref 10), but this particular hydridorhodium compound is relatively inert, which is very fortunate as it allows the vinyl ether to survive in the reaction solution. This inertness reflects the fact that all four PMe_3 ligands are tightly bound, thus providing no opportunity for olefin hydrogenation by the conventional mechanism.

Discussion

There are two different organometallic reactions exhibited by the family of methoxymethyl compounds **1–4**. One reaction is C–O bond cleavage by oxophilic reagents (eq 4), and the other is decomposition of the coordinatively unsaturated compounds (eq 5).

C–O Bond Cleavage. The probable mechanism of the C–O bond cleavage reaction is summarized in eq 4. Following attack at the oxygen atom by the trimethylsilyl group the C–O bond is broken, leaving a reactive or transient methylene entity,[1,2a] which rapidly reacts with the neighboring methyl group to make an ethyl group. β-Elimination of ethylene and binding of bromide complete the reaction. None of the postulated intermediate species has been observed, and the best evidence for this particular mechanism is the very close similarity to the analogous iridium system,[2a] where a trapped-methylene complex was detected.[13] There are two additional differences between this rhodium chemistry and the previously reported iridium chemistry.[2a] First, β-elimination from the iridium ethyl complex does not occur at room temperature and the ethyl complex can be isolated, whereas the rhodium ethyl intermediate is not observable. And second, the C–O bond of the rhodium complex is more difficult to cleave than the C–O bond of the iridium analogue. In a competition experiment where equimolar amounts of compound **1** and its iridium analogue were treated with $BrSiMe_3$, the iridium compound reacted completely within 15 min, whereas the rhodium compound **1** required several hours for complete reaction. One possible reason for the relative difficulty in cleaving the C–O bond of the rhodium complex **1** is that Rh(III) may be less effective at stabilizing the (postulated) methylene intermediate than is Ir(III).

Mechanism of the Decomposition Reaction. Decomposition of the solvated compound **3** is thought to proceed by the mechanism of eq 6. Here the key step is



an α-C–H activation, possibly reversible, which forms a hydrido methyl methoxycarbene intermediate, **10**. The reactive methoxycarbene group couples with the adjacent methyl group to form the hydrido methoxyethyl complex

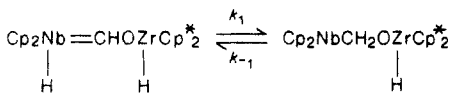
(12) Marder, T. B., to be submitted for publication. The author thanks Dr. Marder for relaying his interest in this system.

(13) (a) For other examples of methylene trapping see: Canestrari, M.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1789–1793. See also ref 1e. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708–6710.

11. Complex 11 in turn undergoes either β-elimination to make methyl vinyl ether and a dihydridorhodium complex (path A, cf. eq 5 and 6) or reductive elimination to make methyl ethyl ether (path B). The Rh(I) product of reductive elimination (path B) apparently reacts with the dichloromethane solvent, resulting in compounds to be described elsewhere.[12]

Given the complexity of the overall reaction (eq 5) and the fact that no reaction intermediates can be observed, only indirect and circumstantial evidence supporting the α-C–H activation portion of this mechanism can be provided.

First, there is ample precedent for all the proposed steps of eq 6. Reversible α-C–H activation of zirconoxymethyl compound **12** was described by Threlkel and Bercaw,[4] and other examples of α-C–H activation are very well-documented.[6,14] There is also a large body of literature on the



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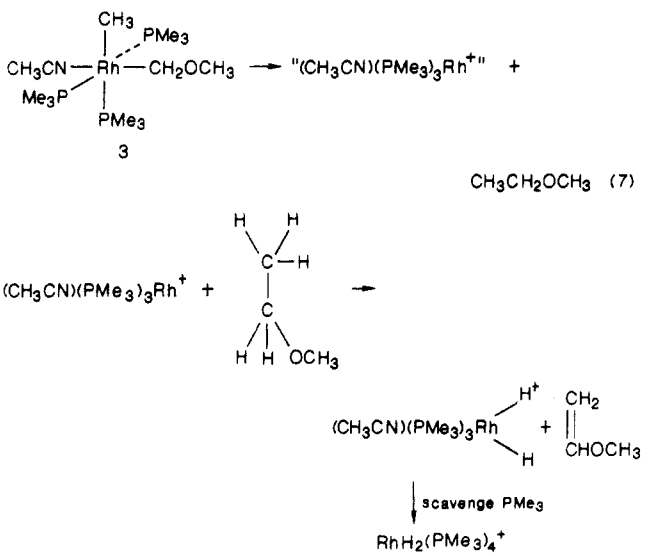
thermal decomposition of polyalkyl compounds where α-elimination is a probable component.[15] Alkoxycarbene–hydride coupling has been described in several systems;[4,16,17] alkoxycarbene–methyl coupling has been proposed in reactions of related iridium compounds[2c,d,5] and is closely related to the methylene–methyl reaction proposed for compound **1** (eq 4) and its iridium analogue,[2a] as well as other alkylidene–alkyl coupling reactions.[18–20] The final steps, β-elimination (path A) or reductive elimination (path B), are both very common organometallic reactions.

In support of the proposed α-C–H activation in this particular system, note first that a vacant coordination site is crucial, as in Scheme I. Consistent with this, the coordinatively saturated compounds **1** and **2** do not undergo any reaction until a ligand is removed, and the acetonitrile compound **3** is stabilized by free acetonitrile. A complication is that the vacant coordination site must be cis to the methoxymethyl group in order to permit α-C–H activation, so isomerization of the trans acetonitrile methoxymethyl compound **3** is an additional requirement.

In this context it is remarkable that the bis(phosphine) bis(acetonitrile) compound **4**—which has two vacant coordination sites, one already cis to the methoxymethyl group—is so much more stable than the tris(phosphine) acetonitrile compound **3**. Solutions of compound **4** persist unchanged for hours after solutions of compound **3** have significantly decomposed. The rationalization of the stability of compound **4** is that the phosphine-depleted, electron-poor rhodium center cannot undergo the α-C–H activation and/or cannot support the required methoxycarbene intermediate. This underscores an interesting conflict: While coordinative unsaturation is necessary for α-C–H activation, extreme unsaturation suppresses α-C–H activation. In this particular system, where tetrakis(phosphine), tris(phosphine), and bis(phosphine) compounds **2**, **3**, and **4** are available, it is the tris(phosphine) compound **3** which is the reactive compromise between the need for coordinative unsaturation and the need for phosphine ligands to provide electron density.

Additional support for the proposed α-C–H activation mechanism of eq 6 is found in observations that discourage other apparently reasonable alternative mechanisms. Perhaps the most attractive alternate mechanism is given in eq 7, where the key step is direct reductive elimination of methyl ethyl ether from compound **3**, followed by dehydrogenation of some of the methyl ethyl ether. But a labeling experiment provided compelling evidence against this mechanism for vinyl ether formation. The



$^{13}CH_3$ compound **3** was prepared and allowed to decompose in the presence of 1.5 equiv of unlabeled methyl ethyl ether. That vinyl ether which was formed in the decomposition was $^{13}CH_2{=}CH(OCH_3)$, and no unlabeled ether was detected. Thus, free methyl ethyl ether is not dehydrogenated under the present reaction conditions. Equation 7 requires that methyl ethyl ether be dehydrogenated to form the methyl vinyl ether, but the results of the labeling experiment confict with this requirement. It remains possible that strong cage effects are operating and that reductive elimination of methyl ethyl ether is followed by rapid dehydrogenation prior to exchange with free methyl ether,[21] but this seems unlikely.

Another possibility is that two different mechanisms are operating; perhaps methyl ethyl ether is indeed formed by direct reductive elimination (see eq 7) while methyl vinyl ether is formed by the α-C–H activation sequence (see eq 6). The available data do allow this interpretation, but with serious difficulties: The two mechanisms would have to operate at the same rate, in order to form methyl ethyl ether and methyl vinyl ether in the observed 1:1 ± 10% ratio. The 1:1 ratio is a troublesome observation in any case and perhaps suggests that some binuclear species simultaneously provides both products.[21] But the sequence of eq 6, where the putative hydrido methoxyethyl complex **11** decomposes (possibly bimolecularly[21]) to form methyl ethyl ether and methyl vinyl ether in near equal

(14) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217–1224.

(15) For examples see: Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121–1127. Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978–6989. See also: Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219–242. Schrock, R. R.; Parshall, G. W. *Ibid.* **1976**, *76*, 243–268.

(16) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335–360.

(17) Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1984**, *272*, 283–293.

(18) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43–51.

(19) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648–4650. Hayes, J. C.; Cooper, N. J. *Ibid.* **1982**, *104*, 5570–5572. Jernakoff, P.; Cooper, N. J. *Ibid.* **1984**, *106*, 3026–3027.

(20) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem.* **1983**, *95*, 49–50; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46–47.

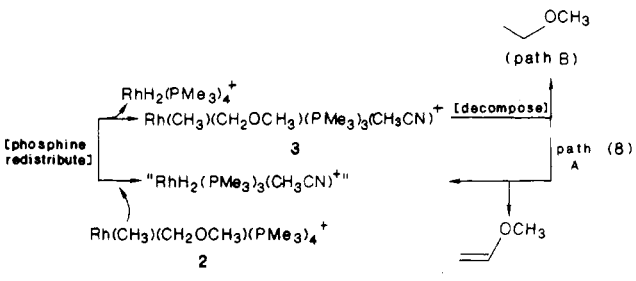
(21) The reviewers are thanked for noting these possibilities.

amounts, is a more satisfactory explanation than fortuitously equal reaction rates for two totally distinct mechanisms.

Finally, given the complete stability of all the dimethyl compounds **5–8** and the relative stability of the bis(phosphine) bis(acetonitrile) methyl methoxymethyl compound **4**, it appears that direct reductive elimination from compounds **1–8** simply is not a facile reaction. The reactivity that is observed for compound **3** is best rationalized by the α-C–H activation mechanism of eq 6. Incidentally, the stability of the dimethyl compounds demonstrates that it is only the methoxymethyl group, not the methyl group,[13-15,22] which undergoes the α-C–H activation and initiates the decomposition sequence. This in turn is consistent with the apparent difficulty of forming the rhodium-methylene intermediate in eq 4.

Further Peculiarities of the Decomposition Reaction: Phosphine Abstraction/Redistribution Catalysis. Attempts to perform more quantitative studies of the decomposition of compound **3** (eq 5) were frustrated by the complexity of the overall reacting system (particularly the tendency for CH_3CN to accumulate and inhibit further decomposition) and by the inability to obtain compound **3** in rigorously pure form. However, it is clear that in order to drive the reaction rapidly to completion, it is necessary to (1) supply enough extra PMe_3 to prevent the formation of "unreactive" bis(phosphine) compound **4** and (2) prevent the accumulation of either CH_3CN (which stabilizes **3** and suppresses further reaction) or PMe_3 (which converts **3** to unreactive tetrakis(phosphine) compound **2**). At first glance these requirements are totally incompatible.

Yet, by starting with the tetrakis(phosphine) complex **2**, both requirements actually can be met. By itself, compound **2** is stable, as it lacks the vacant coordination site necessary for α-C–H activation. But if a phosphine is abstracted from compound **2**, it becomes the unstable and reactive tris(phosphine) compound **3**. All that is really necessary is a trace of the unstable tris(phosphine) compound **3**, provided its decomposition products can also abstract a phosphine ligand from tetrakis(phosphine) starting material **2**. This would permit a pseudocatalytic cycle to operate, as outlined in eq 8. In fact, the reaction



cycle of eq 8 operates very smoothly: CD_2Cl_2 solutions of tetrakis(phosphine) compound **2**, when treated with a small amount (less than 0.1 equiv) of either impure tris(phosphine) compound **3** or pure bis(phosphine) compound **4**, decomposed completely within 4 h at room temperature, with methyl ethyl ether and methyl vinyl ether formed together in excellent yield. A solution containing only compound **2** was unchanged during this time, although it also eventually decomposed, possibly catalyzed by traces of phosphine-scavenging impurities. Probably, phosphine "abstraction" from compound **2** (and also compounds **3**, **6**, and **7**) is a dissociation process, that would establish a small but finite equilibrium concentration of free PMe_3 were it not for the presence of other species that react with PMe_3.

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Summary and Conclusions

This paper has described the chemistry of a family of methyl(methoxymethyl)rhodium compounds **1–4**, with the greatest emphasis on those reactions which ultimately allow C–C bond formation. One way this occurs is by electrophilic cleavage of the C–O bond of compound **1**, whereupon ethylene is formed by the reaction of eq 4. A second way that new C–C bonds are formed is the α-activation sequence of eq 6, which is initiated by bromide abstraction from compound **1** or by phosphine abstraction from compound **2**. In all cases a key step is coupling of methyl and methylene or carbene groups bound to the rhodium center, which has been viewed as methyl migration to electron-deficient carbon.[2a,18-20,23] An alternative viewpoint, methylene or carbene insertion into the rhodium methyl bond, cannot be disproved from the present data but is believed less likely. The methoxymethyl group is a critical component of all these reactions, as the analogous dimethylrhodium compounds **5–8** are unreactive under comparable conditions.

While the main aspects of the chemistry of these compounds have been studied and discussed, there remain any number of questions that cannot be answered at this time. Perhaps the major question is: what is preventing reductive elimination? None of the dialkyl compounds, and not even the hydrido methyl methoxycarbene intermediate **10** proposed in eq 6, appears to undergo reductive elimination at room temperature. Only the hypothetical reaction intermediate **11** of eq 6 is thought to reductively eliminate, and even that reaction is in competition with β-elimination. A number of recent studies have shown that reductive elimination is not a rapid nor universal nor simple process.[24-26] A recurring theme in reductive elimination is prior ligand dissociation or addition;[25,26] perhaps the hydrido methyl methoxycarbene intermediate **10** does not undergo reductive elimination owing to its coordinative saturation, whereas hydrido methoxyethyl intermediate **11** is able to reductively eliminate because it is coordinatively unsaturated. As both **10** and **11** are only hypothetical intermediates, however, these inferences are speculative. Certainly the isolated rhodium compounds do display ligand addition/dissociation processes, but under the mild conditions explored in this study these processes appear to facilitate α-activation rather than reductive elimination.

Experimental Section

All reactions were carried out at room temperature by using dried solvents and standard inert-atmosphere techniques. Reagents were obtained commercially (Aldrich Chemical Co. or Strem Chemicals, Inc.) and were used as supplied. *Note that alkyl halides in general, and halomethyl ethers in particular, should be treated with great caution, as they are toxic and possibly carcinogenic.* In this work they were stored and used in a drybox. NMR spectra (^1H, ^{13}C) were recorded at ambient probe temperature by using a Nicolet/GE QE-300 spectrometer. ^1H NMR data for compounds **1–8** are summarized in Table I, with chemical shifts reported in parts per million downfield from external Me_4Si. Coupling constants in parentheses in hertz. Elemental analyses

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Table I. ^{1}H NMR Data[a] for Compounds 1–8

compd	Rh–CH_3	Rh–CH_2OCH_3	Rh–CH_2OCH_3	$P(CH_3)_3$	CH_3CN
1, $RhBrMe(CH_2OCH_3)(PMe_3)_3$	0.06, t (7.7) of d (5.8) of d (1.9)	3.50, t (5.8) of d (3.9) of d (2.7)	3.13	1.39 (t, 3, of d, 0.6), 1.40 (d, 7.1)	
2, $RhMe(CH_2OCH_3)(PMe_3)_4SbF_6$	−0.04, t (7.5) of d (6.8) of d (4.6) of d (1.8)	3.45, q (5.9) of t (1.9)	3.18	1.41 (t, 3), 1.41 (d, 7), 1.43 (d, 7)	
3, $RhMe(CH_2OCH_3)(PMe_3)_3(CH_3CN)SbF_6$[b]	0.10, t (7.5) of d (5.4) of d (1.8)	3.39, q (5.8) of d (2.8)	3.13	1.35 (t, 3.1), 1.40 (d, 7.5)	1.99[b]
4, $RhMe(CH_2OCH_3)(PMe_3)_2(CH_3CN)_2SbF_6$	−0.03, t (7.4) of d (2.3)	3.66, t (5.7) of d (2.7)	3.21	1.34 (t, 3.1)	2.25
5, $RhIMe_2(PMe_3)_3$	0.07, d (8.3) of t (6.0) of d (2.4); 0.18, t (7.7) of d (5.8) of d (1.9)			1.42 (d, 6.5), 1.48 (t, 3.0)	
6, $RhMe_2(PMe_3)_4SbF_6$	−0.06, m (12 lines, splitting 2 Hz)			1.41 (t, 2.6), 1.43 (t, 6.2)	
7, $RhMe_2(PMe_3)_3(CH_3CN)SbF_6$	−0.22, q (8.0) of d (2.2); +0.08, t (7.6) of d (5.6) of d (1.8)			1.38 (t, 2.9), 1.40 (d, 6.9)	2.28 (br d, 0.8)
8, $RhMe_2(PMe_3)_2(CH_3CN)_2SbF_6$	−0.07, t (7.3) of d (2.3)			1.33 (t, 3)	2.24

[a] All compounds in CD_2Cl_2 unless otherwise noted. Chemical shifts in parts per million downfield of external Me_4Si; coupling constants in parentheses in hertz. [b] Trace of CD_3CN added to suppress decomposition.

(C, H, and [where appropriate] N) were performed by Galbraith Laboratories. Methylrhodium(I) *x*(trimethylphosphine) was prepared following Jones et al.[7] from $Rh(PMe_3)_4Cl$ and methyl Grignard reagent in THF (tetrahydrofuran) and was used directly as the crude pentane extract with no attempt at recrystallization. While recrystallized material is reportedly the tris(phosphine) complex, the crude material has the approximate composition $Rh(CH_3)(PMe_3)_4$. For ^{13}C NMR experiments the Rh–$^{13}CH_3$ labeled material was synthesized by using the Grignard reagent prepared from $^{13}CH_3I$ (Merck Isotopes, 98%).

Preparation of Bromomethyl(methoxymethyl)tris(trimethylphosphine)rhodium(III) (1). In a typical preparation, crude methyltetrakis(trimethylphosphine)rhodium(I) (0.75 g) was dissolved in 20 mL of THF and the mixture treated with 0.49 g of bromomethyl methyl ether (*Caution! toxic and carcinogenic reagent!*). The suspension was stirred 30 min and filtered. The insoluble material, mostly $PMe_3(CH_2OCH_3)Br$, was discarded, and the solution was evaporated, leaving 0.70 g (84%) of off-white solid. Anal. Calcd for $C_{12}H_{35}O_1P_3Br_1Rh_1$: C, 30.59; H, 7.49. Found: C, 30.16; H, 7.36. ^{13}C NMR (CD_2Cl_2): Rh–$^{13}CH_3$, δ 3.0, d (91) of d (19) of t (9.5); $J(^{13}C–H)$ = 128 Hz.

Methyl(methoxymethyl)tetrakis(trimethylphosphine)rhodium(III) Hexafluoroantimonate (2). Compound 3 [$Rh(CH_3)(CH_2OCH_3)(PMe_3)_3(CH_3CN)SbF_6$], 0.20 g, in 10 mL of THF was treated with 0.10 g of PMe_3 and stirred 30 min. The cloudy solution was filtered and evaporated, leaving 0.19 g yellow-white solid (90%). An analytical sample was prepared by slow diffusion of ether into a CH_2Cl_2 (dichloromethane) solution containing a drop of free PMe_3. Anal. Calcd for $C_{15}H_{44}O_1F_6P_4Rh_1Sb_1$: C, 25.63, H, 6.31. Found: C, 25.17; H, 6.44.

Methyl(methoxymethyl)tris(trimethylphosphine)(acetonitrile)rhodium(III) Hexafluoroantimonate (3). Compound 1 (0.71 g) in 10 mL of CH_3CN (acetonitrile) was treated with $AgSbF_6$ (0.52 g) and stirred 30 min. The AgBr precipitate was discarded and the filtered solution concentrated to near dryness. The residue was redissolved in ca. 10 mL of CH_2Cl_2, filtered again, concentrated, and precipitated with ether, yield 0.72 g of off-white solid (71%). This could not be recrystallized successfully, but the crude material was 85–95% pure (^1H NMR). IR (Nujol): 2282, 2318 cm^{-1} (w). ^{13}C NMR (CD_3CN): Rh–$^{13}CH_3$, δ 2.1, d (85) of d (20) of t (10).

Methyl(methoxymethyl)bis(trimethylphosphine)bis(acetonitrile)rhodium(III) Hexafluoroantimonate (4). Compound 1 (0.50 g) in 15 mL of CH_3CN was treated with 0.37 g of $AgSbF_6$ and stirred 30 min. The mixture was filtered and the solution treated with 0.19 g of $[RhCl(C_8H_{14})_2]_2$.[8] After being stirred 1 h, the mixture was filtered again and the solution evaporated to near dryness. The residue was redissolved in benzene and filtered again after 30 min. Pentane was allowed to diffuse slowly into the resulting solution, depositing a brown oil and white crystalline solid. The crystalline material was collected, yield 0.175 g (26% from starting compound 1). (The brown oil contained additional amounts of compound 4.) Anal. Calcd for $C_{13}H_{32}N_2O_1F_6P_2Rh_1Sb_1$: C, 24.67; H, 5.10; N, 4.43. Found: C, 24.39; H, 5.20; N, 4.28. ^{13}C NMR (CD_2Cl_2): Rh–$^{13}CH_3$, δ −7.8, d (33) of t (8); $J(^{13}C–H)$ = 128 Hz.

Dimethyliodotris(trimethylphosphine)rhodium(III) (5). Crude $Rh(CH_3)(PMe_3)_4$ (0.58 g) and methyl iodide (0.40 g) were mixed in 10 mL of THF and stirred 10 min. The initial solution rapidly precipitated a white solid, mostly PMe_4I (0.23 g, 77% of theoretical), and was evaporated to leave an off-white residue. This was washed with ether, leaving 0.53 g of white solid compound 5 (79%). Anal. Calcd for $C_{11}H_{33}P_3Rh_1I_1$: C, 27.07; H, 6.81. Found: C, 27.18; H, 6.84.

Dimethyltetrakis(trimethylphosphine)rhodium(III) Hexafluoroantimonate (6). Compound 7 [$RhMe_2(PMe_3)_3(CH_3CN)SbF_6$], 0.14 g in 1 mL of CH_2Cl_2, was treated with 0.03 g of PMe_3 and the solution stirred for 5 min. Addition of ether precipitated 0.13 g of white solid (88%). Anal. Calcd for $C_{14}H_{42}F_6P_4Rh_1Sb_1$: C, 24.98; H, 6.29. Found: C, 24.94; H, 6.21.

Dimethyltris(trimethylphosphine)(acetonitrile)rhodium(III) Hexafluoroantimonate (7). Compound 5 (0.44 g) was dissolved in 10 mL of CH_2Cl_2, and 1 mL of CH_3CN was added followed by 0.31 g of $AgSbF_6$. The mixture was stirred 15 min and filtered. The solution was concentrated to low volume. Addition of ether precipitated 0.46 g of white solid (80%). IR (Nujol): 2290, 2320 cm^{-1}.

Dimethylbis(trimethylphosphine)bis(acetonitrile)rhodium(III) Hexafluoroantimonate (8). Compound 5 [$RhMe_2I(PMe_3)_3$], 0.22 g, and $AgSbF_6$, 0.16 g, were dissolved in 10 mL of CH_3CN, and the mixture was filtered after being stirred 30 min. $[RhCl(C_8H_{14})_2]_2$,[8] 0.10 g, was added. After being stirred 1 h, the mixture was evaporated, extracted into benzene, and filtered. Addition of pentane precipitated 0.10 g of off-white solid (48%).

Reaction of Compound 1 with Bromotrimethylsilane. A solution of 0.04 g of compound 1 in CD_2Cl_2 was treated with 0.017 g of $BrSiMe_3$. Little reaction occurred within the first 30 min but on standing overnight, the reaction was complete, forming ethylene (>85%) (^1H NMR δ 5.42, s), the hydrido compound $RhHBr_2(PMe_3)_3$ (9) (ca. 50%), unidentified PMe_3-containing Rh compounds (ca. 50%), and Me_3SiOCH_3 (^1H NMR 0.11, 3.40). The hydridorhodium compound was not isolated in pure form. ^1H NMR of $RhHBr_2(PMe_3)_3$ (9): Rh–H, δ −16.7, t of t (17.7, 13.4); PMe_3, 1.70, d (9), 1.78, t (3.5). When the $^{13}CH_3$-labeled compound 1 was treated similarly, $H_2{}^{13}C^{12}CH_2$ was the only organic product detectable; ^{13}C NMR δ 124.3.

When a CD_2Cl_2 solution of compound 1 (0.024 g) and the analogous Ir compound $IrBr(CH_3)(CH_2OCH_3)(PMe_3)_3$ (0.028 g) was treated with 0.015 g of $BrSiMe_3$, the Ir compound reacted completely within 15 min to make the ethyl compound $IrBr_2(C_2H_5)(PMe_3)_3$, but only ca. 20% of the Rh compound 1 had reacted by this time. After an additional 4.5 h the Rh compound had reacted completely.

Decomposition of Compound 3. A solution of compound 3 (0.059 g) in 2 mL of CD_2Cl_2 was prepared. Half of this solution was placed directly in an NMR tube; the remainder of the solution was treated with 3 drops of CD_3CN before being placed in a second

NMR tube. The ^1H NMR spectra, run within 15 min of preparing the solutions, were nearly identical, showing compound **3** present in ca. 90% purity contaminated by unidentified PMe_3-containing material, but traces of decomposition products were present in the sample which had no CD_3CN. Four hours later the NMR spectrum of the sample which had been treated with CD_3CN was largely unchanged, with at least 75% of the initial amount of compound **3** remaining. But the sample which had not been treated with CD_3CN had decomposed extensively. Only small amounts of compound **3** remained (ca. 9%). Approximately equal amounts of compound **4** and $RhH_2(PMe_3)_4^+$ [hydrido NMR signal, δ −10.6 d (137 Hz) of pseudoquartets (15 Hz), superimposable on the signal of an authentic sample[10,27]] were present, each approximately 29%, together with PMe_3 signals of unidentified Rh(III) compound(s). Also present was methyl vinyl ether (ca. 29%) and methyl ethyl ether (ca. 33%). Amounts of species present were determined (±5 percentage points) by ^1H NMR integration and are reported as percentages of compound **3** originally present. ^1H NMR of methyl vinyl ether (CD_2Cl_2):[28] OCH_3, δ 3.54, s; =CH(OMe) 6.54, d of d (14.3, 6.8); $=CH_2$ 4.01, d of d (6.8, 2.2), 4.18, d of d (14.3, 2.2). ^1H NMR of methyl ethyl ether (CD_2Cl_2): OCH_3, δ 3.30, s; OCH_2, 3.42, q; CH_3, 1.71, t (7.0).

For the isotope crossover studies, $^{13}CH_3$-labeled compound **3** (0.04 g) in CD_2Cl_2 was treated with methyl ethyl ether (more than 1.5 equiv, prepared from MeI and NaOEt) and allowed to decompose. NMR analysis of the solution revealed $^{13}CH_3CH_2OMe$, unlabeled methyl ethyl ether, and $^{13}CH_2$=CH(OMe). No $^{12}CH_3{}^{13}CH_2OMe$, $^{12}CH_2{}^{13}CH(OMe)$, nor $^{12}CH_2{}^{12}CH(OMe)$ could be detected (estimated detection limits 5%). ^{13}C NMR of $^{13}CH_2{}^{12}CH(OMe)$ (CD_2Cl_2):[28] δ 86.8; $J(^{13}C-H)$ = 161, 156, 9.5 Hz. ^{13}C NMR of $^{13}CH_3{}^{12}CH_2OMe$ (CD_2Cl_2): δ 16.5; $J(^{13}C-H)$ = 129, 3 Hz.

Decomposition of Compound 2 by Phosphine Redistribution Catalysis. A solution of compound **2** (0.025 g) in CD_2Cl_2 was treated with a small amount (less than 0.002 g) of compound **4**. After 2 h the solution contained compound **2** (40% of the original amount), methyl vinyl ether and methyl ethyl ether (each 28%), and compound **3** (4%). In a repeat of this experiment the reaction went to completion within 4 h. A solution of compound **2** alone in CD_2Cl_2 did not measurably react during this time.

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Registry No. **1**, 92670-91-2; **2**, 103225-66-7; **3**, 103225-67-8; **4**, 103225-69-0; **5**, 92670-94-5; **6**, 103225-71-4; **7**, 103225-73-6; **8**, 103225-75-8; **9**, 92670-92-3; $RhMe(PMe_3)_4$, 92670-95-6; $[RhCl(C_8H_{14})_2]_2$, 12279-09-3; $BrCH_2OCH_3$, 13057-17-5; $BrSiMe_3$, 2857-97-8.

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Preparation and Reactions of Cyclopentadienylplatinum Complexes: Coupling with Coordinated Cyclooctadiene

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Cleavage of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$ with TlC_5H_5 produces $[Pt(\eta^5\text{-}C_5H_5)Ph(PPh_3)]$, but in low yield. Reaction of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ with PPh_3 in THF solution gives $[Pt(\eta^1{:}\eta^2\text{-}C_8H_{12}{\cdot}C_5H_5)Ph(PPh_3)]$ (**1**) in which the cyclopentadienyl and cyclooctadiene moieties are coupled. In ether **1** and $[Pt(\eta^5\text{-}C_5H_5)Ph(PPh_3)]$ are both formed. Treatment of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ with dppe or appe in ether solution results in displacement of cyclooctadiene, but the reaction with dppe in THF yields $[Pt(\eta^1\text{-}C_5H_5)Ph(dppe)]$ and a coupling product. The products are characterized by elemental analysis and by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

We have recently shown that $[Pd(C_6H_4N{=}NPh)(\eta^5\text{-}C_5H_5)]$ undergoes a hydrogen–deuterium exchange reaction at the cyclopentadienyl ring when treated with nucleophiles such as tertiary phosphines in suitable deuterated solvents.[1] A mechanism involving $C_5H_5^-$ dissociation was suggested by us, and support for this proposal arises from the recent isolation and structural characterization[2] of $[Re(CH_3)(NO)(PMe_3)_4]^+C_5H_5^-$. Our preliminary studies indicated that these H–D exchange phenomena are not limited to palladium complexes containing chelating ligands.[1] In order to determine whether $C_5H_5^-$ dissociation from palladium, or platinum, indeed occurs, we sought to prepare complexes of the type $[M(\eta^5\text{-}C_5H_5)RL]$ (M = Pd, Pt; L = tertiary phosphine) and to investigate their reactions with nucleophiles, the platinum complexes being more amenable to study by NMR spectroscopy.

There are a number of compounds of this form which contain chelating ligands,[3-6] but isolable compounds of the type $[M(\eta^5\text{-}C_5H_5)RL]$ are rare,[7-10] and only three such platinum compounds are known.[7] Since $[Pt(\eta^5\text{-}C_5H_5)XL]$ (X = halide) compounds are much more difficult to prepare than their palladium analogues, alternative precursors

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