of mass spectrometry are performed. Ion structure determination using mass spectrometry/mass spectrometry[14] can benefit both by providing a larger number of parent ions in a given charge state and by providing parent ions wherein the sites of protonation can be assigned with greater confidence. The latter information may prove to be useful in extracting structural information from the daughter ion spectra of multiply protonated molecules.

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Synthesis of $(PMe_3)_4Ru(Me)(OC(CH_2)Me)$ as an Equilibrium Mixture of Oxygen- and Carbon-Bound Transition-Metal Enolates. Thermal Elimination of Methane To Form an η^4-Oxatrimethylenemethane Complex

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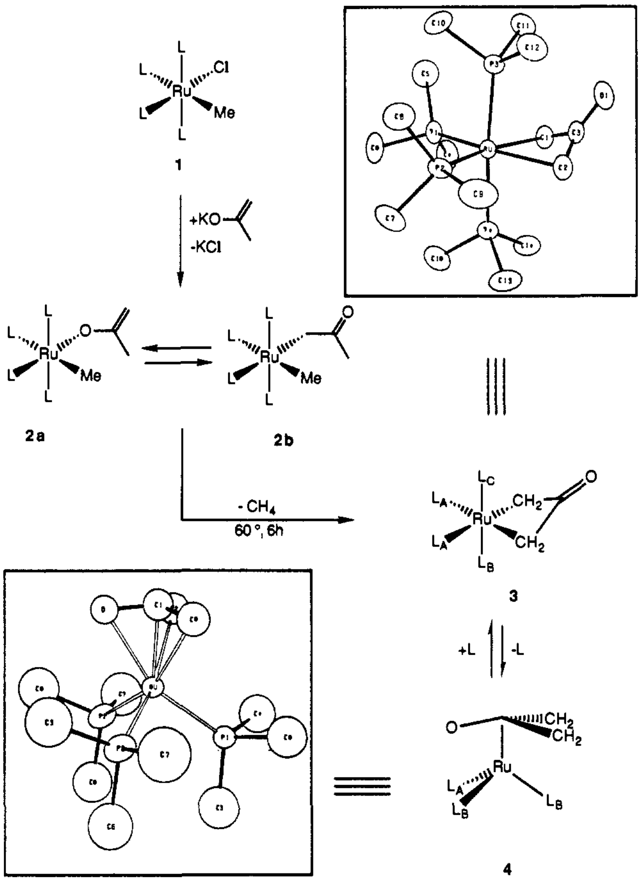
Transition-metal enolate[1] and trimethylenemethane complexes[2] have been used extensively in metal-mediated organic synthesis.[3] Many early-transition-metal enolate complexes of the O-bound form and late-transition-metal complexes of the C-bound form have been synthesized and used either stoichiometrically[1b,4] or catalytically[1a,5] in aldol reactions. Palladium complexes of trimethylenemethane have been generated in solution and used catalytically in 2 + 3 cycloaddition reactions,[2a,b] and other trimethylenemethane complexes have been isolated and structurally characterized.[2c-h] We report the synthesis of a ruthenium enolate that exists in both the C- and O-bound forms, the first direct observation of such a mixture. We also report the reaction of this equilibrium mixture to form a metallacyclobutan-3-one and its subsequent reaction to form the first isolated mononuclear oxatrimethylenemethane transition-metal complex.

Scheme I



The chemistry we have observed is summarized in Scheme I. Treatment of $(PMe_3)_4Ru(Me)Cl$ (**1**)[6] with the potassium enolate of acetone[7a] for 4 h at room temperature in toluene cleanly formed the methyl enolate complex as a 70:30 mixture (C_6D_6) of the O-bound $(PMe_3)_4Ru(Me)(OC(CH_2)Me)$ (**2a**) and C-bound $(PMe_3)_4Ru(Me)(CH_2C(O)Me)$ (**2b**) forms. This mixture was isolated in 37% yield after crystallization from ether and was characterized by conventional spectroscopic techniques, as well as microanalysis.[7b] The ^1H NMR spectrum showed two metal-bound methyl groups at δ 0.40 and −0.26 and two enolate methyl groups at δ 2.06 and 2.00. The inequivalent methylene resonances for the O-bound form appeared at δ 3.50 and 3.96, while the equivalent methylene resonances for the C-bound form appeared as a multiplet at δ 1.90. The methylene of the O-bound form was observed in the $^{13}C\{^1H\}$ NMR spectrum (DEPT) as a singlet at δ 75.68, and the CH_2 of the C-bound form appeared as a multiplet at δ 22.83.

Variable-temperature ^1H NMR spectroscopy of the isomeric mixture in THF-d_8 revealed that the O- and C-bound forms exist in equilibrium. Over the temperature range of 5–60 °C, a significant and *reversible* change in the ratio of isomers was observed. At 5 °C the ratio of O- to C-bound isomers was (2.8 ± 0.2):1, and at 60 °C the ratio was (4.4 ± 0.3):1. Cooling the sample again to 5 °C provided the same 2.8:1 mixture after 15 min. A plot of ln K vs $1/T$, containing six points in the 5–60 °C temperature range, demonstrated that in this solvent ΔH (1.5 ± 0.3 kcal/mol) is positive and favors the C-bound form, while ΔS (7.6

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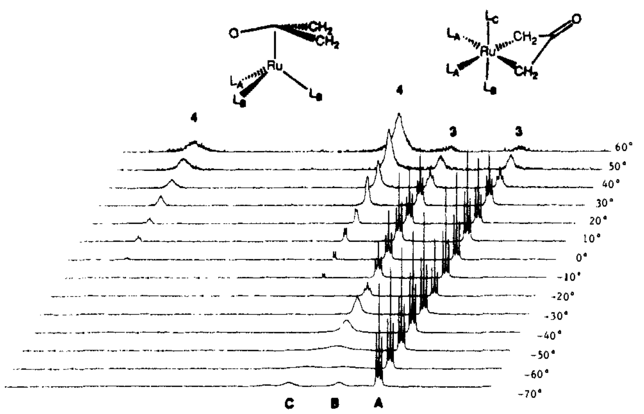

Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **4** + $PMe_3 \rightleftarrows$ **3**.

± 1.5 eu) favors the O-bound form. This is the first example of the direct observation of both O- and C-bound forms for the same enolate and metal–ligand system.

Thermolysis of the mixture of these two complexes in toluene in a sealed tube provided methane (94% by Toepler pump quantification) and the metallacyclobutan-3-one $(PMe_3)_4Ru(\eta^2\text{-}CH_2C(O)CH_2)$ (**3**) in 74% yield by ^1H NMR spectroscopy at −20 °C. Unlike many complexes possessing this ligand reported earlier,[8] complex **3** was extremely unstable, losing phosphine rapidly at room temperature. Therefore, solution spectroscopy of this complex was performed at low temperature. At −70 °C the metallacycle existed in a nearly rigid, puckered conformation, as indicated by the inequivalence of the mutually trans phosphines P_B and P_C in the $^{31}P\{^1H\}$ NMR spectrum (2:1:1 integrated ratio for the three resonances) at this temperature.

The thermolysis reaction was also conducted in benzene, and the solvent was evaporated from a frozen solution at 0 °C in order to minimize loss of PMe_3. The residue was dissolved in pentane and cooled to −40 °C to provide a single crystal of **3** which was suitable for X-ray structure analysis. The complex crystallized in the space group $P2_1/n$ and showed no unusually short intermolecular contacts. An ORTEP drawing of the molecule is shown in Scheme I. The complex possesses a pseudooctahedral geometry, and the organic ligand is bound to the metal through the two carbon atoms. The C=O bond distance was 1.261 (6) Å, while the C–C bond lengths were 1.466 (7) and 1.458 (7) Å. The metallacycle contains a large dihedral angle of 45.6 (5)°, although the metal–oxygen contact distance remains long. The dihedral angle of the ring is larger than those in the analogous (relatively flat) platinacyclobutanes[9] and titanacyclobutanes[10] and slightly smaller than the highly puckered platinacyclobutan-3-ones (48.0–53.8°).[8]

Thermolysis of the **2a**/**2b** mixture was conducted in toluene, and all the volatile materials were removed under vacuum at room temperature. Crystallization of the residue from pentane at −40 °C provided, in 38% isolated yield, a compound that contained three phosphines (A_2B pattern in the $^{31}P\{^1H\}$ NMR spectrum) rather than four. Maintenance of an 18-electron configuration in this complex would require coordination of the oxygen of the organic ligand, forming an η^4-oxadimethylenemethane complex. Such a structure is consistent with solution NMR data, which show an A_2B pattern at −20 °C in the $^{31}P\{^1H\}$ NMR spectrum, and one CH_2 and one quaternary carbon in the −20 °C $^{13}C\{^1H\}$ NMR spectrum.

Conclusive evidence for this formulation was obtained from an X-ray analysis. Crystals of **4** were obtained by sublimation of a sample of **4** in a sealed tube at 55 °C for 2 weeks. The molecule crystallized in space group P_{nma}; an ORTEP drawing is shown in Scheme I. Although the X-ray analysis was hampered by poor crystal quality (perhaps due to disorder among the CH_2 groups and the oxygen of the organic fragment), the identity and overall bonding mode of the complex are clear. The geometry at ruthenium is pseudooctahedral, with the oxadimethylenemethane ligand staggered relative to the three phosphines. The oxatrimethylenemethane ligand is bound in an η^4 fashion, and the molecule contains a mirror plane which makes the two halves of the organic ligand, as well as two of the phosphines, crystallographically equivalent. Although precise ligand bond distances and angles cannot be determined from this study, it is clear that the central carbon lies above the plane of the other three atoms, as it does in the structurally characterized trimethylenemethane complexes,[2c–e] with the Ru–C2 bond distance (1.99 (2) Å) significantly shorter than Ru–C2 (2.265 (12) Å) or Ru–O (2.224 (10) Å). A nearly planar η^4-oxatrimethylenemethane ligand that bridges two ruthenium atoms was observed previously.[11]

The interconversion of complexes **3** and **4** is reversible. The equilibration can be observed by adding 1 equiv of PMe_3 to a crystallized sample of **3** in toluene-d_8 in a sealed NMR tube and observing the $^{31}P\{^1H\}$ NMR spectra at various temperatures. A stacked plot of the $^{31}P\{^1H\}$ NMR spectra obtained between −80 and 60 °C is shown in Figure 1. At temperatures below −20 °C, only the complex containing four phosphines (**3**) was observed, while at 60 °C, **4** is the predominant species. Three broad resonances in a 2:1:1 ratio were observed at −70 °C corresponding to the nearly rigid structure of **3**. The resonances of **4** at 60 °C are also broad, perhaps due to rotation of the oxadimethylenemethane ligand[12] or to dissociation of PMe_3 groups.

The interconversion of **2a** and **2b** may occur through an η^3-enolate intermediate in which both the carbon and carbonyl oxygen atoms of the organic ligand are bound to ruthenium. This process, as well as the methane elimination that leads to **3** and **4**, is facilitated by easy dissociation of phosphine from the ruthenium center. Observation of both the C- and O-bound isomers of **2** in this system indicates that transition-metal enolates do not necessarily strongly prefer the C-bound form, as had been assumed until recently. We are presently pursuing a study of the mechanism of metal-mediated aldol reactions using enolate complexes **2a** and **2b** and are investigating the use of metallacycle **3** and oxatrimethylenemethane complex **4** in metal-mediated cycloaddition reactions.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **2a**, **2b**, **3**, and **4** and tables of acquisition parameters, intramolecular distances and angles, positional parameters, and anisotropic thermal parameters for the X-ray structure determinations of **3** and **4** (24 pages); observed and calculated structure factors for **3** and **4** (22 pages). Ordering information is given on any current masthead page.

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