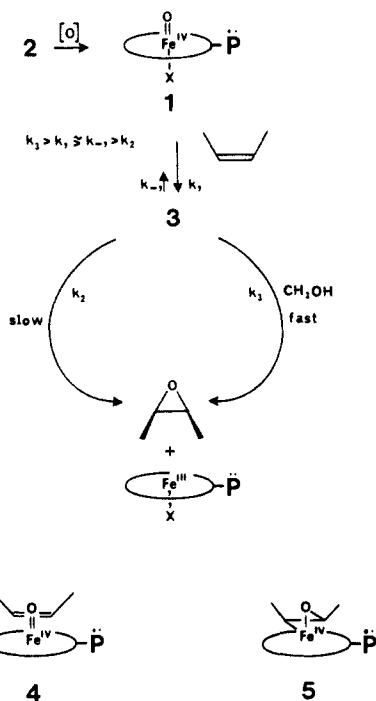**Scheme I**

after 4 h. When 50 μL of methanol containing 10 μL of styrene was added to an identical solution of **3** at −78 °C, 41% of cyclooctene oxide and *no styrene oxide* were detected after 10 min.

These results show unambiguously that an intermediate, **3**, was formed rapidly upon the addition of olefins to **1** and that the rate of its formation was sensitive to the concentration and structure of the olefin. In the absence of imidazole or methanol, **3** decomposed slowly to Fe^{III}TMP and epoxide. The isolation of styrene oxide upon addition of styrene to **3** suggests that the formation of **3** was *reversible* under these conditions, consistent with the recent kinetic analysis of Collman et al.[2m,n] The very rapid evolution of epoxide in the presence of methanol or imidazole and the production of *only* cyclooctene oxide when **3** was quenched with methanol–styrene indicates that the conversion of **3** to cyclooctene oxide was faster in the presence of methanol than its reversion to **1**. Accordingly, *the formation of 3 must be rate-limiting as well as product-determining in the presence of methanol*. The similarity of the Hammett plots for the formation of **3** in the absence of methanol and the formation of Fe(III)TMP in the presence of methanol confirms this interpretation.

A mechanism for oxygen transfer from **1** to olefins via an intermediate **3** consist with these observations is presented in Scheme I. The negative Hammett ρ^+ is consistent with an initial electron-transfer process[5] between **1** and the substrate as proposed by Ortiz de Montellano[6] and by Watanabe[7] for cyclochrome P-450. Two likely possibilities for the structure of the intermediate **3** are an olefin π-complex (**4**) and an oxametallacycle (**5**).[2m,n,8] The dark green color of **3**, the characteristic visible spectrum,[9] and the weak EPR spectrum indicate a porphyrin radical similar

to **1**.[10] That the reductive quenching of **3** with iodide decreased the amount of product indicates that the product epoxide was not fully formed at this stage. The profound effect of added imidazole or methanol on the rate of conversion of **3** to Fe^{III}TMP and epoxide suggests an important role for axial coordination of the iron on the kinetics of epoxide release.[11] A detailed examination of **3** and its reactions is under way.

Acknowledgment. Support for this research by the National Institutes of Health (GM 25923) is gratefully acknowledged. We thank Professor T. G. Traylor for an insightful discussion regarding the trapping of **3**.

Note Added in Proof. The ¹H NMR spectrum of **3** was typical of a porphyrin cation radical but lacking the high-field resonance of **1**.

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Methylene–Carbonyl Coupling: Formation of Bridging η³-Ketene and η⁴-Oxaallyl Complexes

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Formation of C–C bonds via insertion of CO into M–CH₂ is a fundamental reaction type of potential relevant to both stoichiometric[1] and catalytic[2] transformations mediated by transition metals. In previous examples involving formation of ketene ligands, further reaction of these ketenes has been limited to elimination of methyl acetate and related organics.[1d,f,g] It has, therefore, been assumed that CO insertion into M–CH₂ leads only to C₂-oxygenated products. We wish to report the synthesis and characterization of two unique ruthenium complexes, the first, which contains both a methylene ligand and an O-bound ketene ligand, and the second, which is generated by carbon monoxide induced coupling to these ligands to form a bridging η⁴-oxaallyl moiety.

Treatment of Ru₃(CO)₁₀(dppm)³ (**1**) with 2–3 equiv of ethereal diazomethane in refluxing toluene for 10 min provides a mixture of unreacted **1** (25–30%), the ligand cleavage product Ru₃-(CO)₉[μ-P(C₆H₅)CH₂P(C₆H₅)(C₆H₄)]⁴ (5–10%), and a new complex characterized as Ru₃(CO)₇(μ₃,η³-C(O)CH₂)(μ-CH₂)-(dppm) (**2**). Evaporation, TLC separation, and crystallization from pentane–acetone gave 2·CH₃COCH₃ in 30% yield as red-orange crystals.[5]

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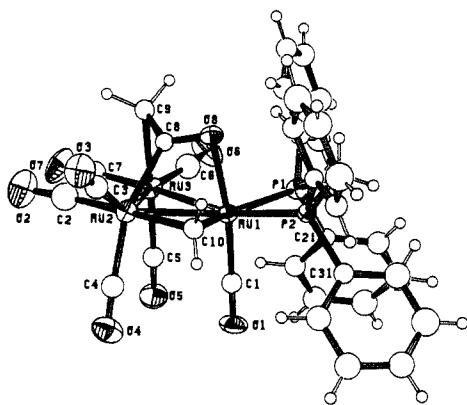
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Figure 1. ORTEP diagram of Ru₃(CO)₇(η^3-(C,C,O),μ^3-COCH₂)(μ-CH₂)(dppm) (**2**). Important bond distances (Å) and angles (deg): Ru(1)–Ru(2) = 2.707 (2), Ru(2)–Ru(3) = 2.744 (2), Ru(1)–Ru(3) = 2.894 (2), C(9)–Ru(3) = 2.30 (2), C(8)–Ru(2) = 2.13 (2), O(8)–Ru(1) = 2.11 (1), Ru(1)–C(10) = 2.07 (2), Ru(2)–C(10) = 2.13 (2); Ru-(1)–C(10)–Ru(2) = 80.2 (6).

The molecular structure of **2** is shown in Figure 1.[6] The metal–metal distances, though irregular, all fall within the range found for other Ru–Ru single bonds.[7] Each of the three atoms in the C–C–O unit is bound to a different metal atom; this is the first structurally characterized example of a ketene ligand O-bonded to a platinum group metal.[8] The bridging C–C–O moiety has a C–C distance of 1.43 (2) Å and a C–O distance of 1.30 (2) Å, which are both significantly increased over the corresponding values for free ketenes.[9] The C(9)–C(8)–O(8) angle of 119 (2)° indicates there is a great deal of distortion form ketene itself and that this coordinated CH₂CO group is best viewed as a metallo-substituted acyl or enolate moiety. The bridging methylene group is closely comparable with that in the previously reported Ru₃(CO)₇(μ-CH₂)(μ_3-η^2-CH₂=C=C-i-Pr)(μ-PPh₂).[10]

The ¹H NMR spectrum of **2** shows the ketene methylene signals at δ 2.63 and 1.77, but the bridging methylene signals are obscured by the phenyl proton multiplets. However, **2** prepared from ¹³CH₂N₂ shows ¹³C NMR signals at δ 153.4 and 36.9 (1:1 ratio, each coupled to two protons). The former signal is not unexpected for a bridging methylene;[11] the latter is typical of ketene methylenes.[12] The ketene carbonyl appears at δ 202.7. The IR of **2** shows a band at 1569 cm⁻¹, which falls within the range of C–O
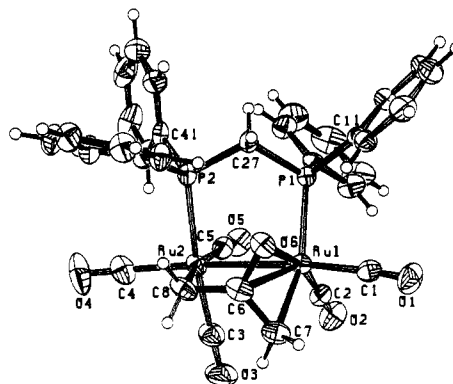

Figure 2. ORTEP diagram of Ru₂(CO)₅(η^4-C,C,C,O),μ-CH₂C(O)-CH₂)(dppm) (**3**). Important bond distances (Å): Ru(1)–Ru(2) = 2.892 (1), Ru(1)–C(6) = 2.233 (6), Ru(1)–C(7) = 2.201 (6), Ru(1)–O(6) = 2.158 (3), Ru(2)–C(8) = 2.221 (6), C(6)–O(6) = 1.317 (7), C(6)–C(7) = 1.436 (8), C(6)–C(8) = 1.447 (8).

stretching frequencies observed for metalloketenes,[13] η^2-acyls,[14] and η^2-CO groups.[15]

Complex **2** reacts readily with CO (15 psig) at room temperature to form a *dinuclear* complex (**3**) with the remaining ruthenium appearing as Ru₃(CO)₁₂ (54%).[16] Complex **3**, isolated in 60% yield after recrystallization from dichloromethane–pentane, has been characterized as Ru₂(CO)₅(μ,η^4-CH₂C(O)CH₂)(dppm).[17]

The molecular structure of **3** is depicted in Figure 2.[18] The Ru–Ru bond length is longer than that which is typical of bridged Ru₂ dimers,[19] most likely due to steric congestion. The oxaallyl ligand has three atoms π-bonded to Ru(1) and one methylene carbon σ-bonded to Ru(2). The ligand is nearly planar, C(6) is only 0.07 Å above the C(7), C(8), O(6) plane, and the bond angle [O(6)–C(6)–C(7)=112 (1)°] is close to that of an sp² hybridized carbon. This oxaallyl moiety is isoelectronic with trimethylenemethane; however, we are not aware of an example in which the latter is coordinated in a binuclear fashion.

NMR spectral data for **3** help define the oxaallyl ligand. The ¹H NMR spectrum shows signals at δ 2.9 (2 H), 2.3 (1 H), 2.1 (1 H). The ¹³C NMR of Ru₂(CO)₅(μ,η^4-*CH₂C(O)*CH₂)(dppm) (**3**) shows signals at δ 30.5 and 10.4 typical of methylenes adjacent to carbonyls.[20] If ¹³CO is added to unlabeled **2** the resulting **3** shows ¹³C enrichment in all the CO ligands but not at the oxaallyl C(O) site.

Reaction of **2** with H₂ does not proceed even under 80 psi and 110 °C. The marked contrast between this observation and the

(5) Anal. Calcd for Ru₃(CO)₇(μ_3,η^3-C(O)CH₂)(μ-CH₂)(dppm)·CH₃COCH₃: C, 45.64; H, 3.20. Found: C, 45.82; H, 3.42. Field desorption mass spectrum (¹⁰²Ru), m/z 944 (M⁺); IR (C₆H₁₂) ν_{CO} 2060 (s), 2032 (vs), 2002 (s), 1992 (w), 1974 (m), 1948 (vw), 1937 (vw), 1569 (m) cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 1.7 (s, 1 H), 2.6 (s, 1 H)), 4.2–4.7 (m, 2 H), 7–8 (m, 22 H); ¹³C NMR (90 MHz, CDCl₃, −60 °C) of Ru₃(*CO)₇(μ_3,η^3-*C(O)-*CH₂)(μ-*CH₂)(dppm), δ 36.9 (*CH₂CO), 153.4 (μ-*CH₂), 193.7 (CO), 196.1 (CO), 200.2 (CO), 202.7 (CH₂CO), 206.0 (CO), 207.4 (CO), 208.8 (CO); ³¹P NMR (101.2 MHZ, CD₂Cl₂–CH₂Cl₂) δ −5.76 (d), 0.59 (d, J_{PP} = 37 Hz).

(6) Ru₃(CO)₇(μ_3,η^3-C(O)CH₂)(μ-CH₂)(dppm)·CH₃COCH₃ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 12.700 (3) Å, b = 13.904 (3) Å, c = 12.085 (3) Å, α = 105.07 (2)°, β = 98.14 (2)°, γ = 84.45 (2)°, V = 2035.8 (9) Å³, and ρ_{calc} = 1.722 g/cm³ for Z = 2. Diffraction data (Mo Kα 3.0 ≤ 2θ ≤ 46.0°) were collected on a Syntex P2₁ diffractometer and were numerically corrected for absorption. The structure was solved by direct methods (MULTAN) and difference Fourier syntheses. The ruthenium, phosphorus, and independent oxygen atoms were refined with anisotropic thermal parameters; the remaining atoms were isotropically refined. Hydrogen atoms were fixed in "idealized" positions. Final agreement factors were R = 0.060 and R_w = 0.064.

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(16) Ru₃(CO)₁₂ was characterized by its IR spectrum. Furthermore, if the conversion of **1** to **2** is carried out using ¹³CO, Ru₃(*CO)₁₂ is observed in the ¹³C NMR spectrum.

(17) Anal. Calcd for Ru₂(CO)₅(μ,η^4-CH₂C(O)CH₂)(dppm): C, 50.51; H, 3.32. Found: C, 50.42; H, 3.29. Field desorption mass spectrum (¹⁰²Ru), m/z 786 (M⁺); IR (C₆H₁₂) ν_{CO} 2048 (vs), 2002 (vs), 1993 (s), 1976 (s), 1939 (m) cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 2.1 (m, 1 H), 2.3 (t, J_{HP} = 3 Hz, 1 H), 2.9 (m, 2 H), 3.7 (m, 1 H), 4.2 (m, 1 H), 7–7.8 (m, 20 H); ¹³C NMR (90 MHz, CDCl₃, −60 °C) of Ru₂(*CO)₅(μ,η^4-*CH₂C(O)*CH₂)(dppm), δ 10.4 (CH₂C(O)CH₂), 30.5 (CH₂C(O)CH₂), 192.1 (CO), 193.0 (CO), 197.5 (CO), 202.7 (CO), 207.5 (CO); ³¹P NMR (101.2 MHz, CD₂Cl₂–CH₂Cl₂) δ 28.09 (s), 28.11 (s).

(18) Ru₂(CO)₅(μ,η^4-CH₂C(O)CH₂)(dppm) crystallizes in the monoclinic space group $P2_1/c$ with a = 16.23 (1) Å, b = 11.47 (1) Å, c = 17.32 (1) Å, β = 93.01 (6); V = 3219 (2) Å³, and ρ_{cald} = 1.615 g/cm³ for Z = 4. Diffraction data (Mo Kα 2.0 ≤ 2θ ≤46.0°) were collected on an Enraf-Nonius CAD4 diffractometer and were numerically corrected for absorption. The structure was solved by Patterson and difference Fourier syntheses. All non-hydrogen atom positions were refined anisotropically. Hydrogen atoms were fixed in idealized positions. Final agreement factors were R = 0.030 and R_w = 0.035.

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facile reaction of **2** with CO suggests that the reaction with CO is associative, resulting in cleavage of a Ru–Ru bond. This could be the trigger for coupling of the ketene and methylene moieties at Ru(2) (reductive elimination) to form the oxallyl moiety. However, possible mechanistic complexities are indicated by the changes in the bonding mode of the dppm ligand; viz., it is bridging in **1** chelating in **2**, and, again, bridging in **3**.

This work provides an example of a three-carbon unit constructed from two methylene fragments and a carbonyl via an intermediate ketene complex. Suprisingly, this is the first example of an isolable η^3-enolate (part of the η^4-oxaallyl), though such species have been proposed as intermediates in aldol addition reactions.[21] Complex **3** does not react with H_2 under modest conditions (25 °C, 50 psig), but current investigations with more forcing conditions are underway.

Supplementary Material Available: Table I, positional and thermal parameters for $Ru_3(CO)_7(\mu_3,\eta^3\text{-}C(O)CH_2)(\mu\text{-}CH_2)$-(dppm), and Table II, positional and thermal parameters for $Ru_2(CO)_5(\mu,\eta^4\text{-}CH_2C(O)CH_2)(dppm)$ (6 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Stable Ruthenium(IV)–Oxo Complexes That Contain Tertiary Phosphine Ligands

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The chemistry of high-valent ruthenium–oxo complexes has received much attention recently due to the potential applications of these complexes as oxidation catalysts and as oxygen atom transfer agents.[1-3] In contrast, tertiary phosphine ligands have been primarily utilized in the syntheses of low-valent organometallic complexes, including those that have been used as both homogeneous and heterogeneous catalysts.[4] Through the combination of these two dissimilar types of chemistry, we wish to report the first successful syntheses and characterizations of ruthenium(IV)–oxo complexes that contain tertiary phosphine ligands in a position cis to the oxo ligand. In the syntheses of these phosphine–ruthenium(IV)–oxo complexes, oxidation of the tertiary phosphine ligand by the ruthenium(IV)–oxo moiety is avoided by initial generation of the ruthenium(II)–aquo–phosphine species,

followed by cerium(IV) oxidation to the phosphine–ruthenium-(IV)–oxo species. In this manner, no free tertiary phosphine ligand is exposed to a ruthenium(IV)–oxo complex, which would result in rapid phosphine oxidation.[5] In addition, the coordinated phosphine ligands do not undergo any intramolecular or intermolecular oxidation upon formation of the ruthenium(IV)–oxo species. Notably, the reactivity of these complexes as oxidants toward organic substrates is substantially affected by simple variation of the substitutents on the *cis*-phosphine ligand.

The general synthesis of *cis*-[(bpy)$_2$Ru^{IV}(O)(PR$_3$)]$^{2+}$ (PR$_3$ = tertiary phosphine; bpy = 2,2′-bipyridine) can be described through the synthesis of *cis*-[(bpy)$_2$Ru^{IV}(O)(PEt$_3$)]$^{2+}$ (**1**). *cis*-(bpy)$_2$Ru^{II}Cl$_2$ is combined with 1 equiv of triethylphosphine in an ethanol/water mixture, resulting in the formation of *cis*-[(bpy)$_2$Ru^{II}Cl(PEt$_3$)]$^+$ (**2**). Treatment of **2** with 1 equiv of silver perchlorate in an acetone/water mixture yields the *cis*-aquo–phosphine species, *cis*-[(bpy)$_2$Ru^{II}(OH)$_2$(PEt$_3$)]$^{2+}$ (**3**). The oxidation of **3** with cerium(IV) then affords the desired Ru(IV)–oxo complex, **1**. UV–visible spectra of complexes **1** and **3** are consistent with similar [L$_5$Ru^{II}—OH$_2$]$^{2+}$ and [L$_5$Ru^{IV}=O]$^{2+}$ complexes (Figure 1).[1c] Also, elemental analyses of complexes **1, 2,** and **3** as perchlorate salts gave satisfactory results.[6]

The presence of a Ru^{IV}=O moiety in complex **1** was established by infrared spectroscopy. The IR spectra of complexes **1** and **3** appear very similar except for two obvious differences. First, the broad O–H stretching band present in the Ru(II)–aquo species at ca. 3500–3300 cm^{-1} (typical of coordinated water) is missing in dry samples of the Ru(IV)–oxo complex. Second, an intense peak at 790 cm^{-1} is evident only in the spectrum of the *cis*-[(bpy)$_2$Ru^{IV}(O)(PEt$_3$)]$^{2+}$ complex; this peak was assigned to the Ru^{IV}=O stretch.[7] Other terminal oxo stretching frequencies for a variety of oxidation states of ruthenium, including Ru(IV), occur in the region 785–890 cm^{-1}.[8-10]

The cis configuration of the oxo and triethylphosphine ligands in the paramagnetic complex, **1**, was suggested by NMR experiments on the diamagnetic precursor, complex **3**. The decoupled and proton-coupled carbon-13 NMR spectra of complex **3** are consistent with a C_1 symmetry for this complex, which confirms a cis orientation of aquo and phosphine ligands. This cis orientation is consistent with most bis(bipyridine) transition-metal complexes, where the steric bulk of bipyridine prevents trans orientation of ligands except in several unusual cases.[11] Because the oxidation to the Ru(IV)–oxo complex is very rapid and conducted under mild conditions, we anticipate that the sterically favored cis configuration of **3** will be retained in the generation of complex **1**.

Electrochemical measurements of complexes **1** and **3** are consistent with the above structural assignments.[12] Cyclic voltam-

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(7) The peak assignment for the Ru=O stretch was confirmed by an isotopic labeling study. Upon labeling the oxo ligand with O^{18}, the peak is shifted by 40 cm^{-1} and appears at 750 cm^{-1}. This is the expected shift based on a Hooke's Law approximation; for further discussion, see: Conley, R. T. "Infrared Spectroscopy", 2nd ed.; Allyn and Bacon: Boston, 1972; p 18.

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