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.

Acknowledgment. This work was supported by the NSF Grant CHE84-07233. Instruments supported by grants NSF CHE79-16100 and NIH GM-27029 were utilized for NMR and mass spectra, respectively.

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*-$[(bpy)_2Ru^{IV}(O)(PR_3)]^{2+}$ (PR_3 = tertiary phosphine; bpy = 2,2′-bipyridine) can be described through the synthesis of *cis*-$[(bpy)_2Ru^{IV}(O)(PEt_3)]^{2+}$ (**1**). *cis*-$(bpy)_2Ru^{II}Cl_2$ is combined with 1 equiv of triethylphosphine in an ethanol/water mixture, resulting in the formation of *cis*-$[(bpy)_2Ru^{II}Cl(PEt_3)]^+$ (**2**). Treatment of **2** with 1 equiv of silver perchlorate in an acetone/water mixture yields the *cis*-aquo–phosphine species, *cis*-$[(bpy)_2Ru^{II}(OH)_2(PEt)_3]^{2+}$ (**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 $[L_5Ru^{II}{-}OH_2]^{2+}$ and $[L_5Ru^{IV}{=}O]^{2+}$ 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*-$[(bpy)_2Ru^{IV}(O)(PEt_3)]^{2+}$ 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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(6) Anal. Calcd for **1**, $[(bpy)_2Ru^{IV}(O)(PEt_3)](ClO_4)_2\cdot H_2O$ ($C_{26}H_{33}N_4O_{10}PCl_2Ru$): C, 40.84; H, 4.35. Found: C, 40.99; H, 4.35. Calcd for **2**, $[(bpy)_2Ru^{II}(Cl)(PEt_3)](ClO_4)$ ($C_{26}H_{31}N_4O_4PCl_2Ru$): C, 46.85; H, 4.69. Found: C, 46.68; H, 4.78. Calcd for **3**, $[(bpy)_2Ru^{II}(OH_2)(PEt_3)](ClO_4)_2\cdot H_2O$ ($C_{26}H_{35}N_4O_{10}PCl_2Ru$): C, 40.74; H, 4.60. Found: C, 40.38; H, 4.50.

(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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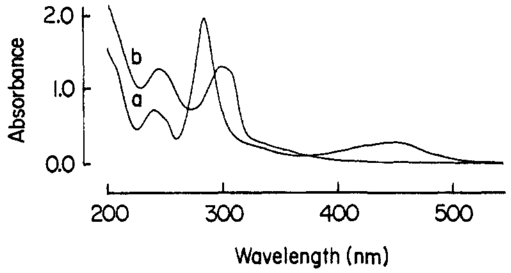
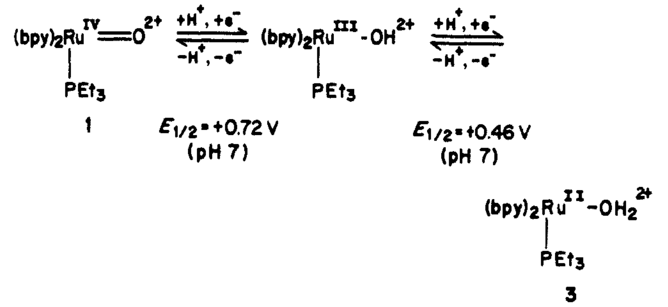


Figure 1. Electronic spectra of (a) $(bpy)_2Ru^{II}(OH_2)(PEt_3)^{2+}$ (4.0×10^{-5} M in H_2O; 1-cm quartz cells) and (b) $(bpy)_2Ru^{IV}(O)(PEt_3)^{2+}$ (8.0×10^{-5} M in H_2O; 1-cm quartz cells).

mograms of **1** and **3** taken in aqueous solution at solution pH values of 1–7 proved to be identical, indicative of the interconversion of $Ru^{IV}{=}O$ to $Ru^{II}–OH_2$ through two one-electron, one-proton redox steps:



The redox potentials for the Ru(IV)/Ru(III) and the Ru(III)/Ru(II) couples of complex **1** display potential shifts of 59 mV per pH unit, consistent with one-electron, one-proton transfers. In further cyclic voltammetric studies, when benzyl alcohol was added to an aqueous solution of the $[(bpy)_2Ru(IV)(O)(PEt_3)]^{2+}$ complex, the electrochemical potential for the onset of alcohol oxidation was less positive by 600 mV and appeared at the redox potential of the Ru(IV)/Ru(III) couple of the complex, as evidenced by an enhanced peak current of the anodic wave. This well-behaved, chemically reversible oxidation chemistry of the $[(bpy)_2Ru^{IV}(O)(PEt_3)]^{+2}$ complex is significant, for it suggests the possibility of utilizing such complexes as electron-transfer agents in catalytic organic substrate oxidation applications.

The reactivity of $[(bpy)_2Ru^{IV}(O)(PR_3)]^{2+}$ complexes with organic substrates is very sensitive to the nature of the phosphine ligand. Through spectroscopic monitoring, we have determined that the Ru(IV)–oxo complexes serve as reagents in the oxidation of organic substrates. Upon addition of alcohol to an aqueous solution of a *cis*-phosphine–ruthenium(IV)–oxo complex, spectral changes are observed in which the spectrum of the Ru(IV)–oxo species is converted to the spectrum of the corresponding Ru(II)–aquo species. Notably, there is a marked difference in the rate of alcohol oxidation depending on the phosphine ligand employed. With $[(bpy)_2Ru^{IV}(O)(PPh_3)]^{2+}$ as the catalyst, the oxidation of benzyl alcohol has a second-order rate constant of 1.9×10^{-2} M^{-1} s^{-1}, while the reaction involving $[(bpy)_2Ru^{IV}(O)(PEt_3)]^{2+}$ has a second-order rate constant of 1.1×10^{-3} M^{-1} s^{-1}. In general, we have determined that $[(bpy)_2Ru^{IV}(O)(PEt_3)]^{2+}$ oxidizes a variety of organic and inorganic substrates, including isopropyl alcohol to acetone, propionaldehyde to propionic acid, and triphenylphosphine to triphenylphosphine oxide.

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(12) Electrochemical measurements were made using a glassy carbon electrode vs. saturated sodium chloride calomel electrode (SSCE) in aqueous buffer solutions. $E_{1/2}$ values are equal to $(E_{p,a} + E_{p,c})/2$.

Sequential Michael-Michael-Aldol Additions for Easy, One-Pot, 2 + 2 + 2 Construction of Polyfunctionalized Cyclohexanols

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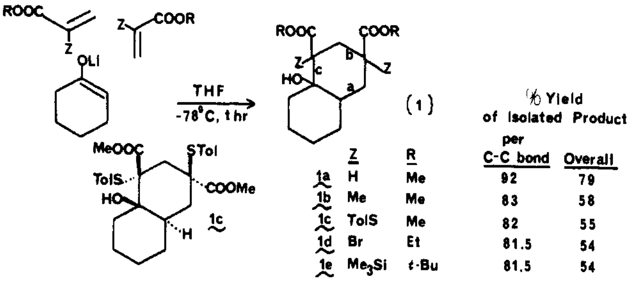
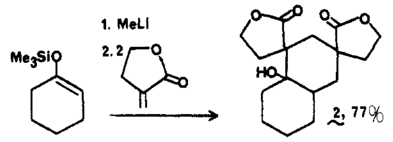
Polymerization of acrylates is an important industrial process.[1] Ketone enolate-initiated polymerization of acrylates, however, is interrupted after only two acrylate units have reacted with one ketone enolate unit (eq 1).[2] This novel process represents sequential, one-pot, three-component,[3] Michael–Michael–aldol additions leading to a very efficient, general, 2 + 2 + 2 synthesis of polyfunctionalized cyclohexanols. We report here on several aspects of this simple and synthetically useful procedure.



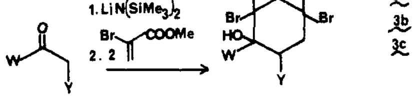
(1)

	Z	R	% Yield of Isolated Product per C-C bond	Overall
1a	H	Me	92	79
1b	Me	Me	83	58
1c	TolS	Me	82	55
1d	Br	Et	81.5	54
1e	Me_3Si	*t*-Bu	81.5	54

Approximate thermodynamic considerations indicate quite clearly that the overall process represented in eq 1 is very favorable indeed. The average yield for each of the three C–C bonds formed in eq 1 is 82.5–92%. Although methyl acrylate itself gave the best results, various α-substituted acrylates led very effectively to adducts **1b–e**. An X-ray study of adduct **1c**, the only diastereomer formed, revealed its relative stereochemistry to be as shown. Even a cyclic acrylate (i.e., α-methylene γ-butyrolactone) led very efficiently to bis-spiro adduct **2** with an average yield of almost 92% per new C–C bond (eq 2). Acrylonitrile and phenyl vinyl sulfone were not effective in place of an acrylate ester. Besides cyclohexanone lithium enolate, the lithium enolates formed by deprotonation of other representative ketones such as cycloheptanone, 3-pentanone, and *p*-methoxyacetophenone were used in some cases on gram scale very successfully (eq 3).



2, 77% (2)



3a $\overline{WY}$ = $(CH_2)_5$ 73%
3b W = Et Y = Me 69%
3c W = p-MeOPh 50%
Y = H (3)

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