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Transformations of Alkynes at a Cyclotriphosphato Ruthenium Complex

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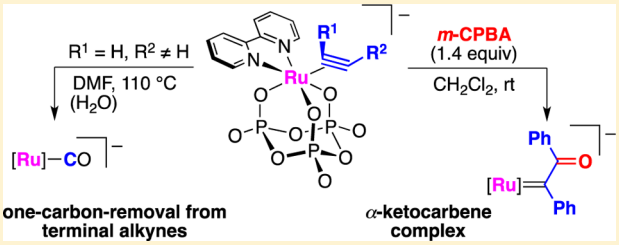
Supporting Information

ABSTRACT: Photolysis of the cyclotriphosphato complex (PPN)[Ru(P_3O_9)(η^6-C_6H_6)] (**2**) with bpy (2,2′-bipyridyl) in alcohols generated a violet solution of (PPN)[Ru(P_3O_9)(bpy)(ROH)] (**3**) with a labile alcohol ligand. Complexes **3** were readily oxidized during recrystallization to give the Ru(III) alkoxo complexes (PPN)[Ru(OR)(P_3O_9)(bpy)] (**4**). Treatment of **3** with internal alkynes led to selective formation of η^2-alkyne complexes (PPN)[Ru(P_3O_9)(bpy)(η^2-RC≡CR′)] (**7**), which did not undergo vinylidene rearrangement under heating and photoirradiation conditions in contrast to its dppe analogues. On the other hand, diphenylacetylene complex **7c** (R = R′ = Ph) gave the α-ketocarbene complex (PPN)[Ru(P_3O_9)(bpy)(=CPhCOPh)] (**8**) on reaction with *m*-CPBA. This observation provides a very rare example for the direct and controlled oxidation of a coordinated alkyne ligand. Reactions of **3** with the terminal alkynes in alcohols and in DMF afforded the alkoxycarbene complexes (PPN)[Ru(P_3O_9)(bpy){=C(OR)CH_2CR′}] (**9**) and the carbonyl complex (PPN)[Ru(P_3O_9)(CO)(bpy)] (**12**), respectively, presumably by way of vinylidene intermediates.



INTRODUCTION

Organometallic complexes with O-donor ancillary ligand sets have received much attention, because they can serve as molecular models for heterogeneous metal catalysts.[1] O-donor ligands have also been expected to endow metal centers with novel reactivities different from those of organometallic complexes with commonly used P- and N-donor ligands. In this context, molecular complexes with cyclophosphates ($P_nO_{3n}^{n-}$),[2] which are composed of *n* corner-sharing PO_4 tetrahedra and have oxygen donor atoms in a regularly cyclic arrangement, can be a potential candidate for the molecular model of the oxo surface in solid catalysts. In particular, cyclotriphosphato ($P_3O_9^{3-}$) complexes have unique structures closely related to the hydroxyapatite-supported metal catalysts that are known to be effective for aerobic oxidations of organic substrates, carbon−carbon bond-forming reactions, dehalogenation of haloarenes, and fixation of carbon dioxide into epoxide.[3] Although several molecular transition-metal complexes with $P_3O_9^{3-}$ have been isolated,[4] their reactivities still remain unexplored. Klemperer and co-workers, pioneers in this field, revealed the epoxidation of the cod (1,5-cyclooctadiene) ligand of the iridium complex [Ir(cod)(P_3O_9)]$^{2-}$ by O_2.[5] Cummins and co-workers described the facile hydrolytic cleavage of a P−O bond in $P_3O_9^{3-}$ in the presence of a cobalt complex[6a] to give the known cobalt complex with the $P_3O_{10}H_2^{3-}$ ligand [Co(P_3O_8(OH)$_2$)(tacn)] (tacn = 1,4,7-triazacyclononane).[6b]

Meanwhile, we have been engaged in synthesizing organometallic complexes on a cyclophosphato platform in recent years and found that mono- and multinuclear complexes with Pt, Ru, Nb, Ta, Rh_2, Rh_4, Pd_2, Ru_2, Ti_2, and Ti_3 cores can be obtained by using the P_3O_9 and P_4O_{12} ligands.[7] These complexes exhibit unique structural and chemical properties based on the circular array of P−O groups as an effective σ-donor set. Among those, the anionic ruthenium P_3O_9 complex (PPN)[Ru(P_3O_9)(MeOH)(dppe)] (**1**; PPN = $(Ph_3P)_2N^+$, dppe = $Ph_2PCH_2CH_2PPh_2$), which is derived from (PPN)[Ru(P_3O_9)(η^6-C_6H_6)] (**2**), can affect the vinylidene rearrangement of general internal alkynes via the 1,2-migration of alkyl, aryl, and acyl groups.[7d,8] Prior to our studies, this type of reaction has been reported only for the transformation of acylalkynes[9] and regarded to be hardly achievable with common internal alkynes.[10]

The facile photolysis of **2** to give **1** has prompted us to investigate the generation of analogous active complexes from **2** by using another bidentate ligand, 2,2′-bipyridyl (bpy), and their reactivities with organic substrates, particularly with

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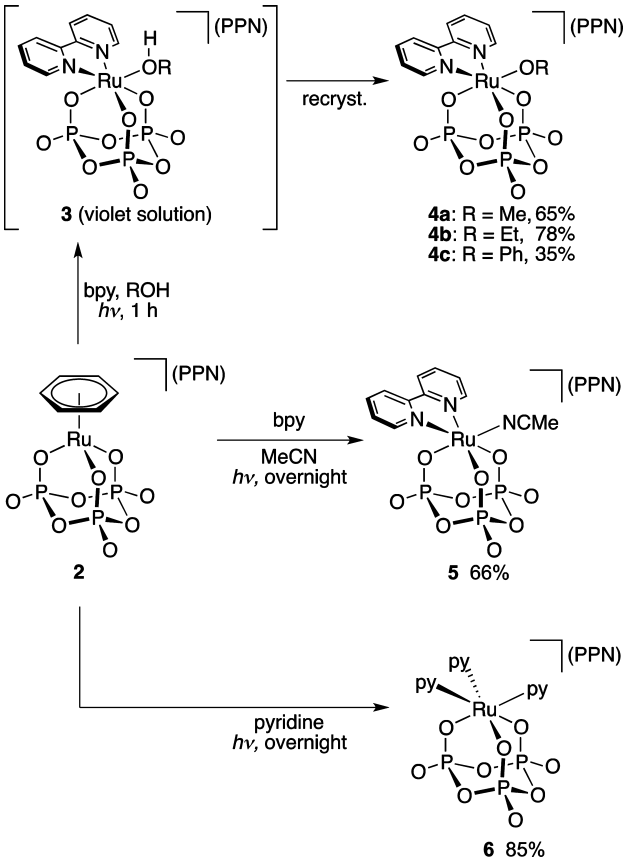
alkynes. Now, we have developed novel reactive (bpy)(alcohol) complexes (PPN)[Ru(P_3O_9)(bpy)(ROH)] (**3**) and found that **3** exhibits reactivities different from those of **1**.

RESULTS AND DISCUSSION

Synthesis of Ruthenium-P_3O_9 Complexes with bpy or Pyridine Ligands. When a solution of **2** and bpy in MeOH was irradiated with an ultra-high-pressure Hg lamp for 1 h, the color of the reaction mixture turned to violet. The $^{31}P\{^1H\}$ NMR spectrum of this solution displays one triplet at δ −17.2 ($^2J_{PP}$ = 20 Hz) and one doublet at δ −22.4 ($^2J_{PP}$ = 20 Hz), suggesting that the replacement of the benzene ligand by bpy yields the product with a *Cs* symmetry. Tentatively, this product is deduced to be the Ru(II) methanol complex (PPN)[Ru(P_3O_9)(bpy)(MeOH)] (**3a**) (Scheme 1) on the basis of the following observations, although all attempts to isolate **3a** in a pure form failed.

Scheme 1. Photolysis of 2 in Alcohols, Acetonitrile, and Pyridine



Complex **3a** was transformed into the Ru(III) complex (PPN)[Ru(P_3O_9)(OMe)(bpy)] (**4a**) during recrystallization from dichloromethane/methanol−diethyl ether under a dry-nitrogen atmosphere. This observation is in sharp contrast to the related dppe complex **1**, which can be readily isolated and shows no symptom of oxidation during usual handling. The $^{31}P\{^1H\}$ and ^1H NMR spectra of **4a** do not show any resonances, whereas its EPR spectrum shows signals with *g* values of 2.37, 2.25, and 1.87, indicating the paramagnetism of **4a** (Figure 1). The structure of **4a** has been determined by an X-ray diffraction study (Figure 2). The ruthenium center in **4a**

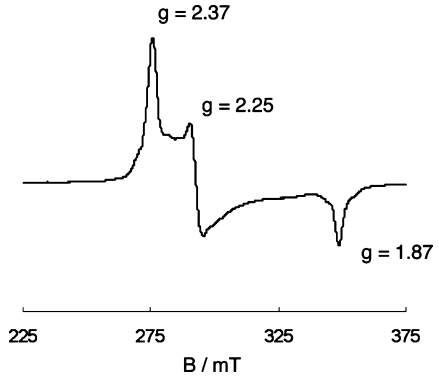


Figure 1. EPR spectra of **4a** in MeOH at −150 °C.

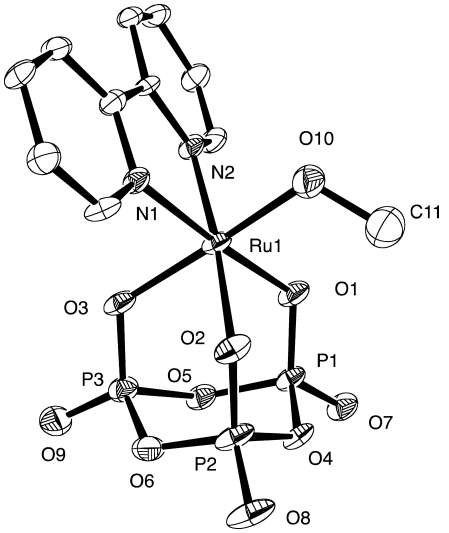


Figure 2. ORTEP drawings for the anionic part of **4a**·THF (50% thermal ellipsoids). Hydrogen atoms and solvating THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−O1, 2.106(3); Ru1−O2, 2.107(4); Ru1−O3, 2.077(4); Ru1−N1, 1.994(4); Ru1−N2, 2.002(4); Ru1−O10, 1.933(4); O1−Ru1−O2, 91.7(1); O1−Ru1−O3, 89.8(1); O2−Ru1−O3, 88.7(1); N1−Ru1−N2, 79.6(1); Ru1−O10−C11, 116.9(4).

adopts an octahedral geometry, where the three oxygen atoms of the P_3O_9 ligand occupy the facial positions, and the bpy and methoxido ligands are located at the other *fac* coordination sites. The Ru−OMe bond length of 1.933(4) Å is comparable to the values in the alkoxo Ru(III) complexes, such as [RuCl(OMe)(py)$_4$](ClO$_4$) (1.937(2) Å),[11a] [TpRuCl(OMe)(PCy$_3$)] (Tp = hydrotris(pyrazolyl)borato, Cy = cyclohexyl; 1.943(1) Å),[11b] and [Tp^{iPr}Ru(OMe)(Ph$_2$PCH$_2$P(=O)Ph$_2$-κ^1P,κ^1O)][PF$_6$] (Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borato; 1.933(3) Å).[11c] The three Ru−O(P) bond lengths (av, 2.097 Å) are longer than the Ru−OMe bond distance. The photolysis of **2** in EtOH and acetone−PhOH in the presence of bpy initially generated the violet Ru(II) species (PPN)[Ru(P_3O_9)(bpy)(ROH)] (**3**, R = Et, Ph), which was confirmed by their $^{31}P\{^1H\}$ NMR spectra analogous to that of **3a** (R = Et, δ −17.9 (t, $^2J_{PP}$ = 21 Hz), δ −23.7 (d, $^2J_{PP}$ = 21 Hz); R = Ph, δ −18.0 (t, $^2J_{PP}$ = 21 Hz), δ −24.8 (d, $^2J_{PP}$ = 21 Hz)). Similar oxidation also took place during recrystallization to give the corresponding Ru(III) complexes (PPN)[Ru(P_3O_9)(OR)(bpy)] (**4b**, R = Et; **4c**, R = Ph), and their paramagnetism and molecular structure of **4c** have been confirmed by EPR and

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X-ray analyses, respectively (Figures S1 and S2 in the Supporting Information).

Although mechanistic details of the oxidation of **3** have not been clarified, several related oxidations of Ru(II) to Ru(III) have been reported in the literature. Kirchner and Akita independently reported that treatment of [TpRuCl(dmf)(PCy$_3$)] (dmf = *N*,*N*-dimethylformamide) and [Tp^{iPr}RuCl(Ph$_2$PCH$_2$PPh$_2$)]/AgPF$_6$ with MeOH/O$_2$ afforded [TpRuCl(OMe)(PCy$_3$)] and [Tp^{iPr}Ru(OMe)(Ph$_2$PCH$_2$P(=O)Ph$_2$-κ^1P,κ^1O)][PF$_6$].[11b,c] However, even when the photolysis of **2** with bpy in MeOH was conducted under an O$_2$ atmosphere, the reaction mixture showed ^{31}P{^{1}H} signals assignable to **3a**. It would be reasonable that the high electron density at the anionic ruthenium in **3** may cause the oxidation during recrystallization. Actually, IR absorption of the CO ligand in (PPN)[Ru(P$_3$O$_9$)(CO)(bpy)] (1939 cm^{-1}; vide infra) is lower in wavenumber than that in the dppe complex (PPN)[Ru(P$_3$O$_9$)(CO)(dppe)] (1966 cm^{-1}).

The photoreaction of **2** was also applicable to other related P$_3$O$_9$ ruthenium complexes. Thus, photolysis of **2** with bpy in acetonitrile afforded the (bpy)(acetonitrile) complex (PPN)[Ru(P$_3$O$_9$)(bpy)(MeCN)] (**5**) as dark red blocks in 66% yield without oxidation to the corresponding Ru(III) species (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of **5** displays A$_2$X type signals (δ −7.5 (d, $^2J_{PP}$ = 22 Hz) and δ −8.2 (t, $^2J_{PP}$ = 22 Hz)) attributable to the P$_3$O$_9$ ligand, while the ^{1}H NMR spectrum exhibits signals ascribed to the bpy and acetonitrile ligands, indicating that **5** has a *Cs* symmetry. The molecular structure of **5** has been determined by an X-ray analysis to confirm that the coordination environment around the ruthenium center in **5** is similar to that in **4a**, except that an acetonitrile ligand binds the ruthenium center instead of the methoxido ligand (Figure 3). The Ru−NCMe (1.995(3) Å) and average Ru−O (2.134 Å) bond lengths are comparable to those in (Bu$_4$N)[Ru(P$_3$O$_9$)(MeCN)$_3$] (1.973 (av) and 2.116 (av) Å, respectively)[4f] and (Bu$_4$N)[Ru(P$_3$O$_9$)(cod)(MeCN)] (2.05(1) and 2.12 (av) Å, respectively.[4h]

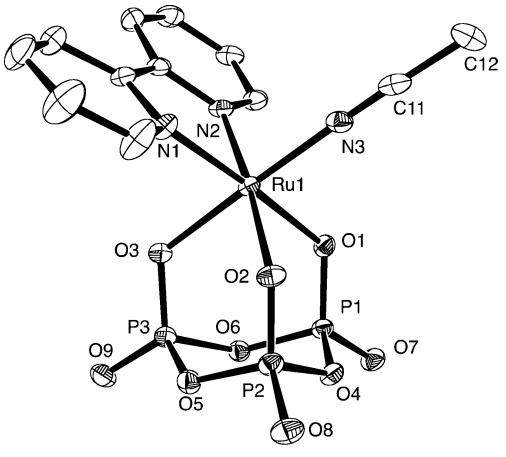
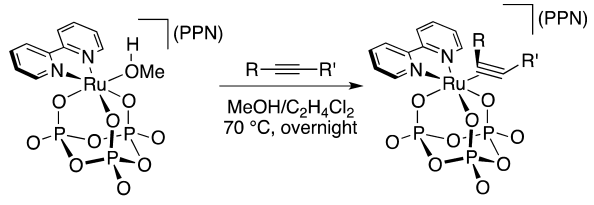


Figure 3. ORTEP drawing for the anionic part of **5**·2MeCN (50% thermal ellipsoids). Hydrogen atoms and solvating molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−O1, 2.142(2); Ru1−O2, 2.152(2); Ru1−O3, 2.107(2); Ru1−N1, 1.995(3); Ru1−N2, 2.001(3); Ru1−N3, 1.980(2); N3−C11, 1.141(4); C11−C12, 1.465(4); O1−Ru1−O2, 88.67(9); O1−Ru1−O3, 88.52(8); N1−Ru1−N2, 79.9(1); Ru1−N3−C11, 177.6(3); N3−C11−C12, 177.8(4).

Similar photolysis of **2** in pyridine resulted in the formation of (PPN)[Ru(P$_3$O$_9$)(py)$_3$] (**6**) in high yield (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of **6** shows a singlet at δ −7.5 assignable to the P$_3$O$_9$ ligand, while the ^{1}H NMR spectrum displays only one set of signals ascribed to the *o*- and *m*-protons in the three pyridine ligands at δ 8.42 (d, $^3J_{HH}$ = 5.2 Hz, 6H) and δ 7.27 (pseudo t, $^3J_{HH}$ = 7.2 Hz, 6H; the *p*-proton signal is overlapped with PPN signals), all of which are in accord with the C_3 structure.

Reaction of 3 with Internal Alkynes. To compare the reactivities of the [Ru^{II}(P$_3$O$_9$)(bpy)]$^-$ complex with its dppe analogue, the latter of which provides an active metal site for the vinylidene rearrangement of internal alkynes,[7d] reactions of internal alkynes with **3**, **5**, and **6** were examined. When the violet solution of **3a** was treated with an excess amount of DMAD (dimethyl acetylenedicarboxylate) at 70 °C overnight, the η^2-alkyne complex (PPN)[Ru(P$_3$O$_9$)(η^2-dmad)(bpy)] (**7a**) was selectively obtained in 44% isolated yield as red crystals (Scheme 2). **7a** shows an IR absorption at 1978 cm^{-1},

Scheme 2. Reaction of in Situ Generated 3a with Internal Alkynes



3a

7a: R = R' = CO$_2$Me, 44%
7b: R = R' = CO$_2$Et, 37%
7c: R = R' = Ph, 22%
7d: R = Me, R' = Ph, 33%

indicating the presence of the η^2-alkyne ligand. The ^{31}P{^{1}H} NMR spectrum of **7a** shows A$_2$X spin signals at δ −7.4 (t, $^2J_{PP}$ = 18 Hz) and δ −8.2 (d, $^2J_{HH}$ = 18 Hz) assignable to the P$_3$O$_9$ ligand, whereas the ^{1}H NMR spectrum of **7a** exhibits signals ascribed to the bpy ligand and the coordinated DMAD. The molecular structure of **7a** was further confirmed by an X-ray analysis (Figure 4a). The orientation of the alkyne unit relative to the [Ru(P$_3$O$_9$)(bpy)] moiety in **7a** is not parallel to the N1−O1 axis; the Ru−alkyne plane is twisted toward the O3−Ru1−N1 and O3−Ru1−O1 planes with the angles of 22.5 and 17.3° (Figure 4b). The symmetrically bound alkyne fragment is bent back with the angles of 21.7° and 25.1°, respectively, and the C≡C bond length at 1.216(4) Å falls in the range of those in known η^2-alkyne complexes[8c,9d,12] and is comparable to that in a related P$_3$O$_9$ complex (PPN)[Ru(P$_3$O$_9$)(η^2-MeC≡CCO$_2$Et)(dppe)] (1.169 (8)Å).[7d] The bond lengths of Ru1−C11 (2.110(3) Å) and Ru1−C12 (2.121(3) Å) in **7a** are shorter than those in (PPN)[Ru(P$_3$O$_9$)(η^2-MeC≡CCO$_2$Et)(dppe)] (2.130(6) and 2.203(6) Å). Similar reactions of **3a** with other internal alkynes afforded the corresponding η^2-alkyne complexes (PPN)[Ru(P$_3$O$_9$)(η^2-RC≡CR')(bpy)] (**7b**, R = R' = CO$_2$Et; **7c**, R = R' = Ph; **7d**, R = Me, R' = Ph), albeit in lower isolated yields (Scheme 2).

Unfortunately, the conversion of **7** into the corresponding disubstituted vinylidene complexes could not be observed either thermally or photochemically despite that the η^2-internal alkyne complexes (PPN)[Ru(P$_3$O$_9$)(η^2-RC≡CR')(dppe)] and [CpM(η^2-RC≡CR')(PP)][BAr$^F_4$] (M = Ru, Fe; Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$; PP = (PPh$_3$)$_2$, dppe) have the ability to shift into

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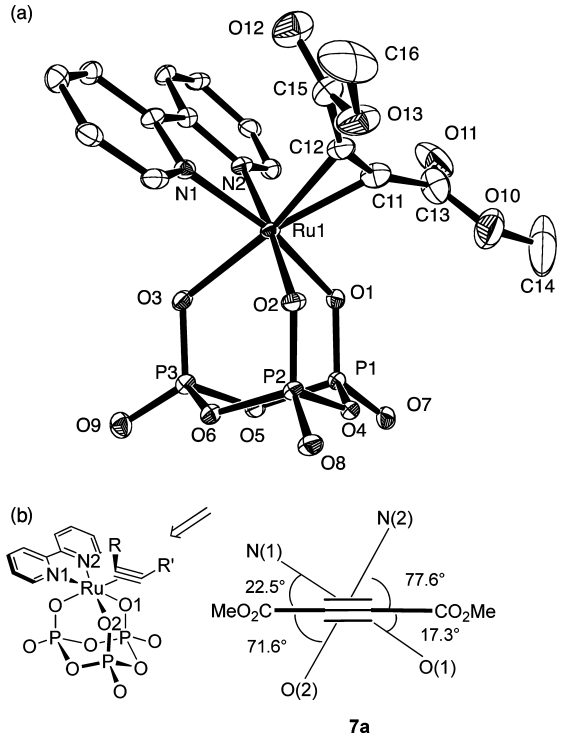
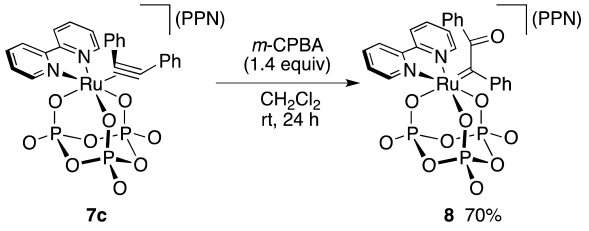


Figure 4. (a) ORTEP drawing and (b) orientation of the alkyne ligands for the anionic part of **7a**·MeOH·THF (50% thermal ellipsoids). Hydrogen atoms and solvating molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−O1, 2.129(2); Ru1−O2, 2.127(2); Ru1−O3, 2.110(2); Ru1−N1, 2.031(2); Ru1−N2, 1.994(2); Ru1−C11, 2.110(3); Ru1−C12, 2.121(3); C11−C12, 1.216(4); O1−Ru1−O2, 91.25(7); O1−Ru1−O3, 85.42(7); O2−Ru1−O3, 90.79(7); N1−Ru1−N2, 79.75(8); C11−Ru1−C12, 33.4(1), C12−C11−C13, 158.3(3); C11−C12−C15, 154.9(3).

the η^1-disubstituted vinylidene complexes (PPN)[Ru(P_3O_9)-{=C=C(R)R′}(dppe)] and [CpM{=C=C(R)R′}(PP)]-[BAr^F_4] via 1,2-migration of aryl and alkyl groups.[7d,8]

On the other hand, monooxygenation of the PhC≡CPh ligand in **7c** was observed on reaction with *m*-CPBA. Thus, when complex **7c** was allowed to react with *m*-CPBA (1.4 equiv) at room temperature, the α-ketocarbene complex (PPN)[Ru(P_3O_9)(=CPhCOPh)(bpy)] (**8**) was obtained in 70% yield (Scheme 3). The $^{13}C\{^1H\}$ NMR spectrum of **8**

Scheme 3. Oxidation of η^2-Diphenylacetylene



displays signals at δ 210.4 and δ 323.6 characteristic of a carbonyl group and a carbene ligand, respectively. The IR spectrum of **8** also shows a strong absorption at 1590 cm^{-1} due to the CO stretch vibration of the carbonyl group. The molecular structure of **8** was determined by an X-ray analysis to confirm that one of the η^2-alkyne carbons was oxygenated to form the α-ketocarbene ligand (Figure 5). Complex **8** has the

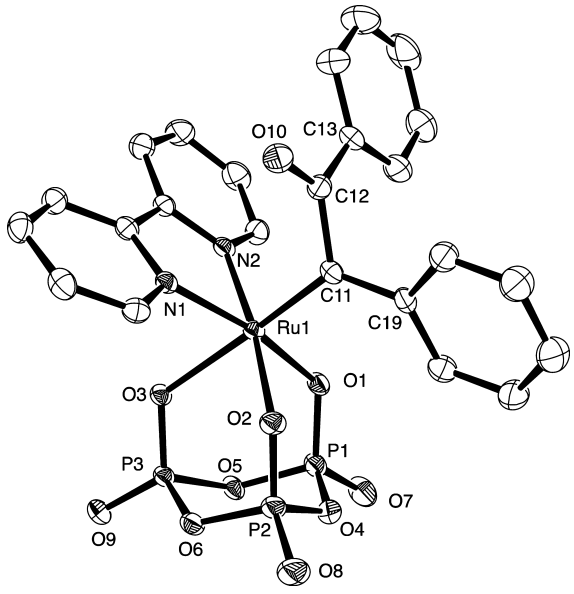


Figure 5. ORTEP drawing for the anionic part of **8**·2MeOH (50% thermal ellipsoids). Hydrogen atoms and solvating MeOH molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−O1, 2.1192(18); Ru1−O2, 2.1090(17); Ru1−O3, 2.1864(18); Ru1−N1, 2.023(3); Ru1−N2, 2.021(2); Ru1−C11, 1.891(3); O10−C12, 1.235(4); C11−C12, 1.482(3); C12−C13, 1.495(5); C11−C19, 1.472(4); O1−Ru1−O2, 90.88(7); O1−Ru1−O3, 85.86(7); O2−Ru1−O3, 87.47(7); N1−Ru1−N2, 80.01(9); Ru1−C11−C19, 128.13(15); Ru1−C11−C12, 117.8(2); C12−C11−C19, 113.9(2).

expected octahedral geometry with a Ru=C bond length (1.901(5) Å) similar to those in known α-ketocarbene[13] and α-alkoxycarbonylcarbene[14] complexes of ruthenium. The P_3O_9 ligand in **8** is not symmetrically bonded to the ruthenium. The Ru−O3 bond distance trans to the carbene ligand is longer than the Ru−O1 and Ru−O2 bond lengths, indicating the strong trans influence of the carbene ligand. Although α-ketocarbenoid species have been proposed as intermediates for oxidation of alkynes in some cases, particularly gold-catalyzed reactions,[15] most α-ketocarbene complexes have been prepared from metal fragments with α-diazocarbonyl compounds. Metal-mediated and metal-catalyzed intermolecular oxidation of alkynes often suffers from overoxidation.[16] Consequently, the present observation provides a rare example for the direct and controlled oxidation of a coordinated alkyne ligand at ruthenium to form the α-ketocarbene ligand; the only example of such a monooxygenation of diphenylacetylene and their derivatives at a transition-metal complex has been observed for the CpMn system with dimethyldioxirane as the oxidizing reagent.[17]

Nitrile complex **5** and tris(pyridine) complex **6** were inert toward alkynes, such as DMAD and HC≡CCO_2Me, even at elevated temperature, though the related bis(nitrile) complex [$RuCl_2$(MeCN)$_2$(PPr^i_3)$_2$] smoothly reacts with terminal alkynes to give the corresponding vinylidene complexes [$RuCl_2${=C=CHR}(PPr^i_3)$_2$].[18]

Reaction of 3 with Terminal Alkynes. When the terminal alkynes were used instead of internal alkynes, subsequent reactions of η^2-alkynes were observed. Thus, the reactions of the alcohol solution of **3a** and **3b** with an excess amount of a terminal alkyne, such as HC≡CCO_2Me and HC≡CPh, resulted in the formation of the methoxy- and ethoxycarbene complexes (PPN)[Ru(P_3O_9){=C(OR)CH_2R′}(bpy)] (**9a**: R

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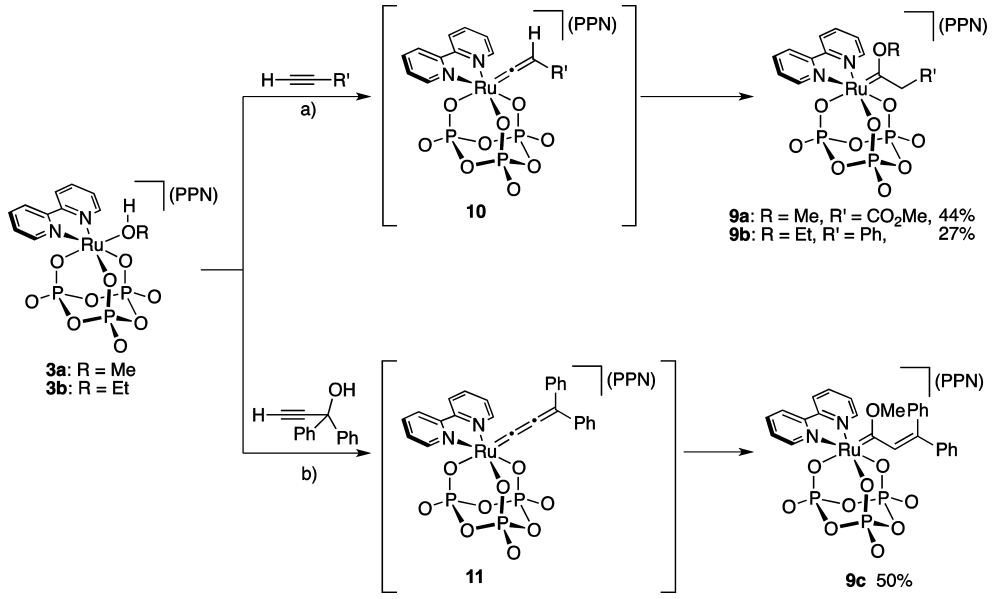
Scheme 4. Reactions of in Situ Generated 3 with Terminal Alkynes[a]



[a]Reaction conditions: (a) terminal alkynes (excess), $ROH/C_2H_4Cl_2$, 60−70 °C; (b) $HC{\equiv}CC(OH)Ph_2$ (excess), $MeOH/C_2H_4Cl_2$, 70 °C, overnight.

= Me, R′ = CO_2Me; **9b**: R = Et, R′ = Ph), respectively (Scheme 4). Their $^{31}P\{^1H\}$ NMR spectra show A_2X signals attributable to the P_3O_9 ligand, indicating the formation of complexes with a C_S symmetry. The $^{13}C\{^1H\}$ NMR spectra display downfield signals at δ 302.2 (**9a**) and δ 309.4 (**9b**) characteristic of a carbene ligand, and the ^1H NMR spectra signals assignable to the OMe and OEt groups. The molecular structure of **9a** has been confirmed by X-ray crystallography, and its ORTEP drawing is shown in Figure 6. The ruthenium atom in **9a** adopts an octahedral geometry, and the plane of the carbene fragment bisects the N−Ru−N angle. Fenske and co-workers have calculated the total energies of $[CpRu(=CH_2)(PH_3)_2]^+$ for both the vertical and the alternate horizontal geometries of the carbene ligand; they have predicted that the carbene moiety preferentially lies in the symmetry plane of the molecule.[19] The Ru1−C11 bond length of 1.855(5) Å is comparable with those in related alkoxycarbene complexes of ruthenium (1.787−2.016 Å).[20] The vinyl−carbene complex $(PPN)[Ru(P_3O_9)\{=C(OMe)CH=CPh_2\}(bpy)]$ (**9c**) was also obtained from the reaction of **3a** with $HC{\equiv}CC(OH)Ph_2$, whose structure has been clarified by an X-ray analysis (Figure S3 in the Supporting Information).

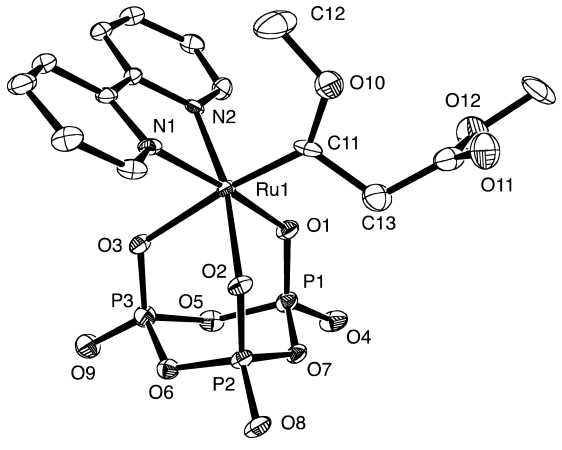


Figure 6. ORTEP drawings for the anionic part of **9a** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−O1, 2.125(2); Ru1−O2, 2.130(3); Ru1−O3, 2.216(3); Ru1−N1, 1.994(3); Ru1−N2, 2.022(3); Ru1−C11, 1.855(5); O10−C11, 1.325(6); O10−C12, 1.445(6); C11−C13, 1.544(6); O1−Ru1−O2, 91.6(1); O1−Ru1−O3, 84.8(1); O2−Ru1−O3, 86.4(1); N1−Ru1−N2, 79.9(1); Ru1−C11−O10, 138.8(3); O10−C11−C13, 104.7(4); C11−O10−C12, 119.0(4).

These Fischer-type carbene complexes **9** were presumably formed via the nucleophilic attack of an alcohol molecule on the α-carbon of the vinylidene and allenylidene ligands in the intermediary complexes $(PPN)[Ru(P_3O_9)(=C=CHR')(bpy)]$ (**10**) and $(PPN)[Ru(P_3O_9)(=C=C=CPh_2)(bpy)]$ (**11**), because it is well-known that terminal alkynes are readily converted into the corresponding vinylidenes at metal complexes.[10b,21] In addition, the α-carbon of a vinylidene ligand is electrophilic and smoothly attacked by alcohols, giving an alkoxycarbene ligand.[12f,22] We attempted to isolate the intermediary vinylidene complexes **10** in the absence of alcohols. After the photolysis of **2** with bpy in DMF, the resulting solution was treated with an excess amount of $HC{\equiv}CCO_2Me$ and HC≡CPh at 110 °C (Scheme 5). However, the carbonyl complex $(PPN)[Ru(P_3O_9)(CO)(bpy)]$ (**12**) was isolated as the final product (48−69% isolated yields) instead of the vinylidene complexes **10**. Alternatively, the carbonyl complex **12** is also synthesized by the reaction of **3a** with CO (73% isolated yield). The $^{31}P\{^1H\}$ NMR spectrum of **12** exhibits A_2X signals (δ −7.6 (d, $^2J_{PP}$ = 20 Hz) and δ −11.4 (t, $^2J_{PP}$ = 20 Hz)) assignable to the P_3O_9 ligand, and the IR spectrum shows a strong CO absorption (1939 cm^{-1}). The structure of **12** has also been established crystallographically (Figure 7).

Since **12** was not formed in the absence of the terminal alkynes, the carbon atom of the carbonyl ligand should be derived from the terminal alkynes. In addition, toluene was detected by GLC analysis of the reaction mixture with

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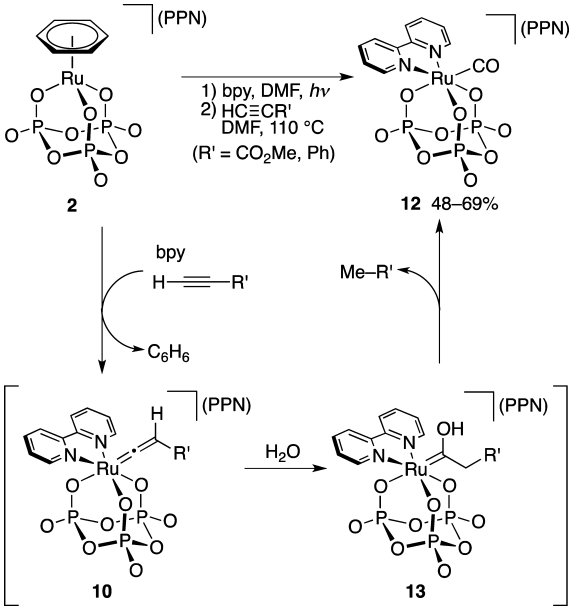
Scheme 5. Reaction of 2 with Terminal Alkynes in DMF Giving CO Complex 12



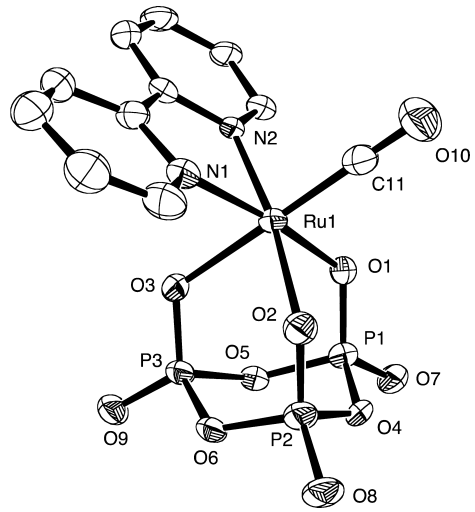


Figure 7. ORTEP drawing for the anionic part of **12**·CH_2Cl_2 (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−O1, 2.126(5); Ru1−O2, 2.125(6); Ru1−O3, 2.146(5); Ru1−N1, 2.024(7); Ru1−N2, 2.032(7); Ru1−C11, 1.813(8); O10−C11, 1.17(1); O1−Ru1−O2, 90.0(2); O1−Ru1−O3, 86.2(2); O2−Ru1−O3, 88.5(2); N1−Ru1−N2, 80.2(3); Ru1−C11−O10, 177.2(7).

phenylacetylene, albeit in low yield (10%). Considering precedent papers for neutral and cationic vinylidene complexes of ruthenium,[18,21a,23] **12** was probably generated as follows. Nucleophilic attack of an adventitious water molecule on the α-carbon of the vinylidene ligand in the intermediary **10** forms hydroxycarbene species **13**, which undergoes enol-to-keto tautomerization, leading to an acylruthenium species. This species subsequently undergoes decarbonylation to give **12**.

CONCLUSION

By utilizing the photolysis of (PPN)[Ru(P_3O_9)(η^6-C_6H_6)] (**2**) as a key reaction, we have explored new reactivities of ruthenium P_3O_9 complexes. While nitrile and tris(pyridine) complexes were found to be inert toward substitution by alkynes, photolysis of **2** with bpy in ROH (R = Me, Et, Ph) furnished violet solutions of (PPN)[Ru(P_3O_9)(bpy)(ROH)] (**3**) with a labile ROH ligand. The alcohol complexes **3** failed to be isolated, because they were converted into the Ru(III) alkoxo complexes (PPN)[Ru(P_3O_9)(OR)(bpy)] (**4**) during recrystallization. However, complexes **3** formed in situ could be further converted into the η^2-internal alkyne complexes (PPN)[Ru(P_3O_9)(η^2-RC≡CR′)(bpy)] (**7**) on reactions with internal alkynes. Unlike the reaction of the dppe complex (PPN)[Ru(P_3O_9)(η^2-RC≡CR′)(dppe)], the internal alkyne ligands were not converted into the corresponding vinylidene even under heating and photoirradiation. On the other hand, monooxygenation of an η^2-diphenylacetylene ligand took place to give the α-ketocarbene complex as the sole product, which provides a rare example of selective monooxygenation of an alkyne ligand. When terminal alkynes were allowed to interact with **3** in alcohols, the alkoxycarbene complexes (PPN)[Ru(P_3O_9){=C(OR)CH_2R′}(bpy)] (**9**) were obtained presumably via the formation of an intermediary vinylidene complex and the subsequent attack of alcohols on the α-carbon of the vinylidene ligand. Photolysis of **2** in the presence of bpy, followed by treatment with terminal alkynes in DMF, resulted in the C≡C triple bond scission of the terminal alkynes to give the carbonyl complex (PPN)[Ru(P_3O_9)(CO)(bpy)] (**12**). In addition to the reactivities observed for (PPN)[Ru(P_3O_9)(dppe)(L)] species,[7d] these results clearly demonstrated that P_3O_9 complexes can activate a wide range of alkyne molecules, including internal alkynes. Further investigation into P_3O_9 complexes of transition metals other than ruthenium is now in progress.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an atmosphere of dry dinitrogen by means of standard Schlenk techniques unless otherwise specified. Dehydrated solvents (diethyl ether, hexane, tetrahydrofuran) were purchased from a commercial source. Other solvents were dried and distilled by common procedures and degassed before use. (PPN)[Ru(P_3O_9)(η^6-C_6H_6)]·0.5CH_2Cl_2 (**2**·0.5CH_2Cl_2)[7d] was prepared according to the literature methods, while the other reagents were obtained from commercial sources and used without further purification. ^{1}H, ^{13}C{1H}, and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL ECA-500 spectrometer (^{1}H, 500 MHz; ^{31}P, 202 MHz; ^{13}C, 126 MHz). IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 II CHN analyzer. X-band EPR spectra were measured on a JEOL FE-2XG spectrometer with 100 kHz field modulation of 0.5 mT. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by ^{1}H NMR spectroscopy.

(PPN)[Ru(OMe)(P_3O_9)(bpy)]·MeOH (4a·MeOH). A mixture of **2**·0.5CH_2Cl_2 (121.4 mg, 0.122 mmol) and bpy (20.4 mg, 0.131 mmol) in methanol (4 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) for 1 h. The resulting violet solution was evaporated to dryness, and the residue was recrystallized from (dichloromethane/methanol)−diethyl ether to afford (PPN)[Ru(OMe)(P_3O_9)(bpy)]·MeOH (**4a**·MeOH) as red crystals (87.0 mg, 0.079 mmol, 65% yield). IR (KBr, cm^{-1}): 1311 (s), 1286 (s), 1113 (s), 1027 (m). EPR (MeOH, −150 °C): g = 2.37, 2.25, 1.87. Anal. Calcd for $C_{48}H_{45}N_3O_{11}P_5Ru$: C, 52.61; H, 4.14; N, 3.83. Found: C, 52.23; H, 3.83; N, 3.84. Orange needles of **4a**·THF suitable for X-ray analysis were obtained by further recrystallization from (tetrahydrofuran/methanol)−diethyl ether.

(PPN)[Ru(OEt)(P_3O_9)(bpy)]·0.5CH_2Cl_2 (4b·0.5CH_2Cl_2). This compound was synthesized in a manner similar to that described for **4a** except that the solvents for the photoreaction and recrystallization

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were ethanol and dichloromethane/methanol−diethyl ether, respectively. Red plates (78% yield). IR (KBr, cm^{-1}): 1309 (s), 1275 (s), 1113 (s), 1035 (m), 954 (s). EPR (CH_2Cl_2, −150 °C): g = 2.36, 2.24, 1.89. Anal. Calcd for $C_{48.5}H_{44}ClN_3O_{10}P_5Ru$: C, 52.00; H, 3.96; N, 3.75. Found: C, 52.36; H, 3.97; N, 3.82.

(PPN)[Ru(OPh)(P_3O_9)(bpy)]·0.5CH_2Cl_2 (4c·0.5CH_2Cl_2). This compound was synthesized in a manner similar to that described for **4a** except that the reaction with phenol (large excess) was performed in acetone. Dark red block crystals (35% yield). IR (KBr, cm^{-1}): 1310 (s), 1286 (s), 1113 (s), 950 (s). EPR (CH_2Cl_2, −150 °C): g = 2.45, 2.29, 1.84. Anal. Calcd for $C_{52.5}H_{44}ClN_3O_{10}P_5Ru$: C, 53.97; H, 3.80; N, 3.60. Found: C, 54.13; H, 3.88; N, 3.64. Red crystals of **4c**·0.5Et_2O suitable for X-ray analysis were obtained by further recrystallization from acetone−diethyl ether.

(PPN)[Ru(P_3O_9)(CO)(dppe)]. A solution of (PPN)[Ru(P_3O_9)(N_2)(dppe)][7d] (49.7 mg, 0.038 mmol) in $C_2H_4Cl_2$ was stirred at 60 °C for 1 h under atmospheric CO. The resulting pale yellow solution was evaporated to dryness, and the residue was recrystallized from (methanol/acetonitrile)−diethyl ether to afford (PPN)[Ru(P_3O_9)(CO)(dppe)]·0.5MeOH·0.5MeCN as pale yellow crystals (29.1 mg, 0.022 mmol, 57%). IR (KBr, cm^{-1}): 1966 (s, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 65.2 (s, dppe), 20.8 (s, PPN), −10.4 (d, $^2J_{PP}$ = 19 Hz, P_3O_9), −12.5 (t, $^2J_{PP}$ = 22 Hz, P_3O_9). ^1H NMR (CD_2Cl_2): δ 7.93−7.36 (m, 50H, Ar), 2.97−2.53 (m, 4H, CH_2 of dppe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 200.0 (t, $^2J_{CP}$ = 19 Hz, CO). Anal. Calcd for $C_{64.5}H_{57.5}N_{1.5}O_{10.5}P_7Ru$: C, 57.15; H, 4.18; N, 3.22. Found: C, 56.78; H, 4.31; N, 2.96.

(PPN)[Ru(P_3O_9)(bpy)(MeCN)]·2MeCN (5·2MeCN). A mixture of **2**·0.5CH_2Cl_2 (35.2 mg, 0.035 mmol) and bpy (7.1 mg, 0.045 mmol) in acetonitrile (2 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) overnight. The resultant violet solution was evaporated to dryness, and the residue was recrystallized from acetonitrile−diethyl ether to afford (PPN)[Ru(P_3O_9)(bpy)(MeCN)]·2MeCN (**5**·2MeCN) as dark red block crystals (27.0 mg, 0.023 mmol, 66%). IR (KBr, cm^{-1}): 2256 (m), 1301 (s) 1272 (s), 1131 (s), 1117 (s). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.5 (d, $^2J_{PP}$ = 22 Hz, P_3O_9), −8.2 (t, $^2J_{PP}$ = 22 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 9.23 (d, $^3J_{HH}$ = 5.5 Hz, 2H, bpy), 8.32 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 7.85 (pseudo t, $^3J_{HH}$ ∼ 7.8 Hz, 2H, bpy), 7.55−7.49 (m, 14H, *m*-H of PPN and bpy), 2.31 (s, 3H, coordinated MeCN), 2.03 (s, 6H, free MeCN). Anal. Calcd for $C_{52}H_{47}N_6O_9P_5Ru$: C, 54.03; H, 4.10; N, 7.27. Found: C, 53.70; H, 4.10; N, 7.28.

(PPN)[Ru(P_3O_9)(py)$_3$]·0.25CH_2Cl_2 (6·0.25CH_2Cl_2). A solution of **2**·0.5CH_2Cl_2 (148.5 mg, 0.149 mmol) in pyridine (5 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) overnight. The red solution was evaporated to dryness, and the residue was recrystallized from (dichloromethane/pyridine)−diethyl ether to afford orange crystals of (PPN)[Ru(P_3O_9)(py)$_3$]·0.25CH_2Cl_2 (**6**·0.25CH_2Cl_2) (143.1 mg, 0.126 mmol, 85% yield). IR (KBr, cm^{-1}): 1308 (s), 1292 (s), 1260 (m), 1152 (s), 1116 (s), 995 (s). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.5 (s, P_3O_9). Selected ^1H NMR (CD_3OD): δ 8.42 (d, $^3J_{HH}$ = 5.2 Hz, 6H, *o*-H of py), 7.74−7.71 (m, 9H, *p*-H of py and PPN), 7.27 (pseudo t, $^3J_{HH}$ ∼ 7.2 Hz, 6H, *m*-H of py). Anal. Calcd for $C_{51.25}H_{45.5}Cl_{0.5}N_4O_9P_5Ru$: C, 54.23; H, 4.04; N, 4.94. Found: C, 54.47; H, 4.33; N, 4.98.

(PPN)[Ru(P_3O_9)(η^2-$MeO_2CC{\equiv}CCO_2Me$)(bpy)]·0.5CH_2Cl_2 (7a·0.5CH_2Cl_2). A mixture of **2**·0.5CH_2Cl_2 (179.0 mg, 0.180 mmol) and bpy (39.4 mg, 0.252 mmol) in a mixed solvent of methanol (2 mL) and 1,2-dichloroethane (4 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) for 15 min. To the resulting violet solution was added dimethyl acetylenedicarboxylate (100 μL, 0.81 mmol), and the mixture was stirred at 70 °C overnight. The solution was evaporated to dryness, and the residue was dissolved in methanol. The solution was passed through a column of Sephadex LH-20 using methanol as an eluent, and the third reddish brown band was collected. Recrystallization from dichloromethane−(diethyl ether) afforded (PPN)[Ru(P_3O_9)(η^2-$MeO_2C{\equiv}CCO_2Me$)(bpy)]·0.5CH_2Cl_2 (**7a**·0.5CH_2Cl_2) as red crystals (95.9 mg, 0.079 mmol, 44% yield). IR (KBr, cm^{-1}): 1978 (m), 1713 (s), 1311 (s), 1286 (s), 1118 (s), 1038 (m), 998 (m), 952 (s). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.4 (t, $^2J_{PP}$ = 18 Hz, P_3O_9), −8.2 (d, $^2J_{PP}$ = 18 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 9.09 (d, $^3J_{HH}$ = 5.5 Hz, 2H, bpy), 8.37 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 8.08 (pseudo t, $^3J_{HH}$ ∼7.3 Hz, 2H, bpy), 7.65 (pseudo t, $^3J_{HH}$ ∼ 6.8 Hz, 2H, bpy), 3.71 (s, 6H, Me). Anal. Calcd for $C_{52.5}H_{45}ClN_3O_{13}P_5Ru$: C, 51.80; H, 3.73; N, 3.45. Found: C, 51.59; H, 3.92; N, 3.42. Brown block crystals of **7a**·THF·MeOH suitable for X-ray analysis were obtained by further recrystallization from (tetrahydrofuran/methanol)−diethyl ether.

(PPN)[Ru(P_3O_9)(η^2-$EtO_2C{\equiv}CCO_2Et$)(bpy)]·2MeOH (7b·2MeOH). This compound was synthesized from **2**, bpy, and diethyl acetylenedicarboxylate by a procedure similar to that for **7a** (5 equiv of diethyl acetylenedicarboxylate was used) in 37% yield as dark red crystals. IR (KBr, cm^{-1}): 1987 (m), 1951 (m), 1309 (s), 1286 (s), 1117 (s), 1038 (m), 998 (m). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.5 (t, $^2J_{PP}$ = 18 Hz, P_3O_9), −8.2 (d, $^2J_{PP}$ = 18 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 9.09 (d, $^3J_{HH}$ = 5.0 Hz, 2H, bpy), 8.38 (d, $^3J_{HH}$ = 7.5 Hz, 2H, bpy), 8.08 (pseudo t, $^3J_{HH}$ ∼ 7.0 Hz, 2H, bpy), 7.66−7.56 (m, 14H, bpy and *o*-H of PPN), 4.16 (q, 4H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 1.24 (t, 6H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3). Anal. Calcd for $C_{56}H_{56}N_3O_{15}P_5Ru$: C, 53.09; H, 4.46; N, 3.32. Found: C, 53.03; H, 4.26; N, 3.43.

(PPN)[Ru(P_3O_9)(η^2-PhC≡CPh)(bpy)]·0.5CH_2Cl_2 (7c·0.5CH_2Cl_2). A mixture of **2**·0.5CH_2Cl_2 (180.7 mg, 0.181 mmol) and bpy (41.4 mg, 0.265 mmol) in methanol (4 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) for 15 min. To the resulting violet solution was added diphenylacetylene (67.2 mg, 0.377 mmol), and the mixture was refluxed for 2 h. This reaction mixture was passed through a column of Sephadex LH-20 using methanol as an eluent, and the third violet band was collected. Recrystallization from (methanol/dichloromethane)−diethyl ether afforded (PPN)[Ru(P_3O_9)(η^2-PhC≡CPh)(bpy)]·0.5CH_2Cl_2 (**7c**·0.5CH_2Cl_2) as dark purple crystals (50.7 mg, 0.040 mmol, 22% yield). IR (KBr, cm^{-1}): 1993 (w), 1304 (s), 1282 (s), 1185 (m), 1126 (s), 998 (m). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −5.7 (t, $^2J_{PP}$ = 19 Hz, P_3O_9), −8.2 (d, $^2J_{PP}$ = 19 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 8.98 (d, $^3J_{HH}$ = 6.0 Hz, 2H, bpy), 8.22 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 7.79 (pseudo t, $^3J_{HH}$ ∼ 7.5 Hz, 2H, bpy), 7.31 (pseudo t, $^3J_{HH}$ ∼ 6.5 Hz, 2H, bpy), 7.21−7.14 (m, 10H, Ph). Anal. Calcd for $C_{60.5}H_{49}ClN_3O_9P_5Ru$: C, 57.97; H, 3.94; N, 3.35. Found: C, 57.76; H, 4.27; N, 3.35.

(PPN)[Ru(P_3O_9)(η^2-MeC≡CPh)(bpy)]·MeOH (7d·MeOH). This compound was synthesized from **2**, bpy, and 1-phenyl-1-propyne by a procedure similar to that for **7c** (6 equiv of 1-phenyl-1-propyne was used) in 33% yield as dark purple crystals. IR (KBr, cm^{-1}): 2021 (w), 1289 (s), 1183 (m), 1162 (m), 1123 (s), 1021 (m), 998 (m). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −6.1 (t, $^2J_{PP}$ = 19 Hz, P_3O_9), −8.2 (d, $^2J_{PP}$ = 19 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 9.20 (d, $^3J_{HH}$ = 5.0 Hz, 2H, bpy), 8.19 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 7.78 (pseudo t, $^3J_{HH}$ ∼ 7.5 Hz, 2H, bpy), 7.31 (pseudo t, $^3J_{HH}$ ∼ 6.3 Hz, 2H, bpy), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-H of C≡CPh), 7.01 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-H of C≡CPh), 6.81 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-H of C≡CPh), 2.27 (s, 3H, C≡CMe). Anal. Calcd for $C_{56}H_{50}N_3O_{10}P_5Ru$: C, 56.95; H, 4.27; N, 3.56. Found: C, 56.63; H, 4.16; N, 3.65.

(PPN)[Ru(P_3O_9)(=CPhCOPh)(bpy)]·MeOH (8·2MeOH). A mixture of **7c**·0.5CH_2Cl_2 (103.0 mg, 0.082 mmol) and *m*-CPBA (19.4 mg, 0.112 mmol) in dichloromethane (4 mL) was stirred at room temperature for 24 h. The solution was evaporated to dryness, the residue was dissolved in methanol, which was passed through a column of Sephadex LH-20 using methanol as an eluent, and the green band eluted was collected. Recrystallization from methanol−diethyl ether afforded (PPN)[Ru(P_3O_9)(=CPhCOPh)(bpy)]·MeOH (**8**·MeOH) as dark green crystals (72.0 mg, 0.057 mmol, 70% yield). IR (KBr, cm^{-1}): 1590 (s). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.6 (t, $^2J_{PP}$ = 19 Hz, P_3O_9), −11.9 (d, $^2J_{PP}$ = 19 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 8.35 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 8.10 (d, $^3J_{HH}$ = 7.4 Hz, 2H, COPh), 7.82 (br, 2H, bpy), 7.67 (t, $^3J_{HH}$ = 7.4 Hz, 1H, COPh), 7.59−7.29 (m, 36H, PPN, bpy, and COPh), 7.21 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ph), 7.07 (d, $^3J_{HH}$ = 6.9 Hz, 2H, Ph), 7.00 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ph). Selected $^{13}C\{^1H\}$ NMR (CD_3OD): δ 323.6 (Ru=C), 210.4 (CO). Anal. Calcd for $C_{61}H_{52}N_3O_{11}P_5Ru$: C, 58.19; H, 4.16; N, 3.34. Found: C, 57.84; H, 3.99; N, 3.10. Crystals of **8**·2MeOH

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suitable for X-ray crystallography were obtained by further recrystallization from (methanol/THF)−diethyl ether.

(PPN)[Ru(P_3O_9){=C(OMe)CH_2CO_2Me}(bpy)] (9a). A mixture of **2**·0.5CH_2Cl_2 (181.8 mg, 0.182 mmol) and bpy (41.2 mg, 0.264 mmol) in a mixed solvent of methanol (2 mL) and 1,2-dichloroethane (4 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) for 15 min. To the resulting violet solution was added methyl propiolate (100 μL, 1.12 mmol), and the mixture was stirred at 60 °C overnight. The reaction mixture was passed through a column of Sephadex LH-20 using methanol as an eluent, and the third brown band was collected. Recrystallization from acetonitrile−(hexane/diethyl ether) afforded (PPN)[Ru(P_3O_9){=C(OMe)CH_2CO_2Me}(bpy)] (**9a**) as brown crystals (92.1 mg, 0.080 mmol, 44% yield). IR (KBr, cm^{-1}): 1736 (s), 1306 (s), 1270 (s), 1184 (m), 1128 (s), 998 (m). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.6 (d, $^2J_{PP}$ = 20 Hz, P_3O_9), −12.2 (t, $^2J_{PP}$ = 20 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 8.44 (d, $^3J_{HH}$ = 6.5 Hz, 2H, bpy), 8.19 (d, $^3J_{HH}$ = 5.5 Hz, 2H, bpy), 7.98 (pseudo t, J ∼ 7.0 Hz, 2H, bpy), 7.35 (pseudo t, $^3J_{HH}$ ∼ 6.3 Hz, 2H, bpy), 3.86 (s, 3H, OMe), 3.64 (s, 3H, OMe), 3.30 (s, 2H, CH_2). Selected $^{13}C\{^1H\}$ NMR (CD_3OD): δ 302.2 (Ru=C), 167.0 (CO), 160.7 (bpy), 152.9 (bpy), 138.1 (bpy), 125.7 (bpy), 124.2 (bpy), 61.4 (OMe), 52.5 (CO_2Me), 49.6 (CH_2). The ^1H and ^{13}C signals for bpy and the alkoxycarbene ligands were fully assigned by $^1H-^1H$ and $^{13}C-^1H$ COSY spectra. Anal. Calcd for $C_{51}H_{46}N_3O_{12}P_5Ru$: C, 53.32; H, 4.04; N, 3.66. Found: C, 53.01; H, 4.08; N, 3.96. Dark red platelet crystals of **9a** suitable for X-ray analysis were obtained by further recrystallization from (tetrahydrofuran/methanol)−diethyl ether.

(PPN)[Ru(P_3O_9){=C(OEt)CH_2Ph}(bpy)] (9b). This compound was synthesized in a manner similar to that described for **9a** except that the reaction with ethynylbenzene was performed at 70 °C in ethanol/1,2-dichloroethane. Dark red block crystals (27% yield). IR (KBr, cm^{-1}): 1305 (s), 1281 (s), 1186 (m), 1119 (s), 1030 (m), 998 (m). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −8.0 (d, $^2J_{PP}$ = 19 Hz, P_3O_9), −12.5 (t, $^2J_{PP}$ = 19 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 8.48 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 8.29 (d, $^3J_{HH}$ = 5.5 Hz, 2H, bpy), 8.00 (pseudo t, J ∼ 7.8 Hz, 2H, bpy), 7.37 (pseudo t, $^3J_{HH}$ ∼ 6.0 Hz, 2H, bpy), 7.13−7.05 (m, 3H, *m*- and *p*- H of CH_2Ph), 6.95 (d, $^3J_{HH}$ = 6.0 Hz, 2H, *o*-H of CH_2Ph), 4.42 (q, $^3J_{HH}$ = 6.8 Hz, 2H, OCH_2), 4.10 (s, 2H, CH_2Ph), 0.93 (t, $^3J_{HH}$ = 6.8 Hz, 3H, Me). Selected $^{13}C\{^1H\}$ NMR (CD_3OD): δ 309.4 (Ru=C), 161.0, 152.9, 137.8, 125.7, 124.3 (bpy), 136.6 (*ipso*-C of CH_2Ph), 129.8, 129.3 (*o*- and *m*-C of CH_2Ph), 127.0 (*p*-C of CH_2Ph), 71.3 (OCH_2), 56.4 (CH_2Ph), 15.4 (Me). Anal. Calcd for $C_{56}H_{50}N_3O_{10}P_5Ru$: C, 56.95; H, 4.27; N, 3.56. Found: C, 57.17; H, 4.31; N, 3.86.

(PPN)[Ru(P_3O_9){=C(OMe)CH=CPh_2}(bpy)]·2MeOH (9c·2MeOH). This compound was synthesized in a manner similar to that described for **9a** except that the reaction with 1,1-diphenyl-2-propyn-1-ol was performed at 70 °C and (acetonitrile/methanol)−(hexane/diethyl ether) was used for recrystallization. Dark red block crystals (50% yield). IR (KBr, cm^{-1}): 1301 (s), 1281 (s), 1127 (s), 1033 (m), 998 (m). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.6 (d, $^2J_{PP}$ = 19 Hz, P_3O_9), −12.1 (t, $^2J_{PP}$ = 19 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 8.41 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 8.29 (d, $^3J_{HH}$ = 5.0 Hz, 2H, bpy), 8.00 (pseudo t, J ∼ 7.8 Hz, 2H, bpy), 7.44 (pseudo t, $^3J_{HH}$ ∼ 6.8 Hz, 2H, bpy), 7.33−7.21 (m, 6H, *m*- and *p*-H of CPh_2), 7.16 (d, $^3J_{HH}$ = 4.0 Hz, 4H, *o*-H of CPh_2), 6.65 (s, 1H, CH=C), 3.53 (s, 3H, OMe). Selected $^{13}C\{^1H\}$ NMR (CD_3OD): δ 303.0 (Ru=C), 62.3 (OMe). Anal. Calcd for $C_{64}H_{60}N_3O_{12}P_5Ru$: C, 58.27; H, 4.58; N, 3.19. Found: C, 58.08; H, 4.28; N, 3.38.

(PPN)[Ru(P_3O_9)(CO)(bpy)]·2CH_2Cl_2 (12·2CH_2Cl_2). *Method (a).* The reaction with ethynylbenzene is representative. A mixture of **2**·0.5CH_2Cl_2 (179.7 mg, 0.180 mmol) and bpy (39.6 mg, 0.254 mmol) in *N*,*N*-dimethylformamide (6 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) overnight. To the resulting violet solution was added ethynylbenzene (100 μL, 0.91 mmol), and the mixture was stirred at 110 °C overnight. The solution was evaporated to dryness, and the residue was recrystallized from (dichloromethane/methanol)−(diethyl eher) to afford dark red needles of (PPN)[Ru(P_3O_9)(CO)(bpy)]·2CH_2Cl_2 (**12**·2CH_2Cl_2), which were suitable for crystallographic study. The crystals gave off a part of 1,2-dichloroethane by drying in vacuo to afford a red powder, which was found to possess the empirical formula **12**·0.5CH_2Cl_2 (136.7 mg, 0.124 mmol, 69%). IR (KBr, cm^{-1}): 1939 (s, CO), 1309 (s), 1287 (s), 1129 (s), 1118 (s). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.8 (s, PPN), −7.6 (d, $^2J_{PP}$ = 20 Hz, P_3O_9), −11.4 (t, $^2J_{PP}$ = 20 Hz, P_3O_9). Selected ^1H NMR (CD_3OD): δ 8.77 (d, $^3J_{HH}$ = 5.5 Hz, 2H, bpy), 8.44 (d, $^3J_{HH}$ = 8.0 Hz, 2H, bpy), 8.17 (pseudo t, $^3J_{HH}$ ∼ 7.5 Hz, 2H, bpy), 7.72−7.65 (m, 8H, bpy and *p*-H of PPN). Anal. Calcd for $C_{47.5}H_{39}ClN_3O_{10}P_5Ru$: C, 51.71; H, 3.56; N, 3.81. Found: C, 51.76; H, 3.65; N, 3.81.

Method (b). A mixture of **2**·0.5CH_2Cl_2 (180.1 mg, 0.181 mmol) and bpy (39.8 mg, 0.255 mmol) in methanol (6 mL) was irradiated with an ultra-high-pressure Hg arc lamp (520 W) for 15 min, and the resultant violet solution was stirred under an atmosphere of carbon monoxide at 60 °C overnight. The solvent was removed in vacuo, and the residue was recrystallized from (dichloromethane/methanol)−diethyl ether to afford **12**·2CH_2Cl_2 (144.9 mg, 0.131 mmol, 73%).

X-ray Crystallographic Study. Diffraction data for **4a**·THF, **5**·2MeCN, **7a**·MeOH·THF, **9a**, and **12**·2CH_2Cl_2 were collected at −165 °C on a Rigaku RAXIS-RAPID imaging plate area detector, whereas those for **4c**·0.5Et_2O, **8**·2MeOH were collected at −150 °C on a Rigaku Mercury CCD area detector, both equipped with the graphite monochromatized Mo Kα radiation (λ = 0.71069 Å). Reflections were collected for the 2θ range of 5−55°. No significant decay was observed over the course of data collection. Intensity data were corrected for numerical absorptions (NUMABS[24] for **4a**·THF, **5**·2MeCN, **7a**·MeOH·THF, and **9a**) or empirical absorptions (ABSCOR[25] for **12**·2CH_2Cl_2; REQAB[26] for **4c**·0.5Et_2O, **8**·2MeOH, and **9c**·2MeOH) and for Lorentz and polarization effects. Corrections for secondary extinction were further applied for **9c**·2MeOH (coefficient, 29.64(13)).[27] The structure solution and refinements were carried out by using the CrystalStructure package[28] except for refinement of **8**·2MeOH, which were performed using SHELXL-97.[29] The positions of the non-hydrogen atoms were determined by the heavy atom Patterson method (PATTY[30] for **4c**·0.5Et_2O) or by the direct method (SIR97[31] for **8**·2MeOH; SIR92[32] for the others) and subsequent Fourier syntheses (DIRDIF99).[33] The goodness of fit indicators $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$ were all refined to the value of 1.000 except for that of **8**·2MeOH (1.080). The atomic scattering factors were taken from ref 34, and anomalous dispersion effects were included.[35] The values of $\Delta f'$ and $\Delta f''$ were taken from ref 36.

For **4a**·THF, a relatively large residual density was observed in this single crystal. Since the density was around the midpoint of the Ru1−O3 bond (Ru1−O3, 2.077(4)Å; Ru1−residual density, 1.004 Å; O3−residual density, 1.092 Å), it seems unlikely that any atom is present there. Consequently, the peak is probably due to the electrons of the ruthenium atom. For **4c**·0.5Et_2O, the solvating diethyl ether molecule was positioned on the center of symmetry and four carbon and one oxygen atom of the diethyl ether molecule were refined with fixed isotropic thermal parameters. For **5**·2MeCN, one of the solvating acetonitrile molecules was disordered, and hence two carbon atoms of the acetonitrile were modeled over two positions with the occupancies of 60% and 40%, each pair being refined with fixed isotropic thermal parameters. For **8**·2MeOH, one of the solvating methanol molecules was disordered to be modeled over two positions with the occupancies of 50% and 50%. The other non-hydrogen atoms were refined on F_o ($I > 3\sigma(I)$) by full-matrix least-squares techniques with anisotropic thermal parameters, while all the hydrogen atoms were placed at the calculated positions [C−H distance of 0.95 Å] with fixed isotropic parameters, except for one methyl hydrogen atom of solvating ether in **4c**·0.5Et_2O, and hydroxo hydrogen atoms of solvating alcohols in **7a**·MeOH·THF, **8**·2MeOH, and **9c**·2MeOH, while the positions of hydroxo atoms in **9c**·2MeOH were determined by Fourier syntheses. Details of the crystals and data collection parameters are summarized in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures and CIF files giving EPR spectra and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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