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Alkyne Addition Reactions on Pentaammineosmium(II): The Formation of π-Enol and π-Vinyl Ether Complexes

W. Dean Harman, John C. Dobson, and Henry Taube*

Department of Chemistry, Stanford University Stanford, California 94305

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The hydration of unactivated alkynes represents an important method of functionalizing this plentiful hydrocarbon resource and has found considerable synthetic use.[1] Transition metals are widely used to catalyze this process as well as the analogous reaction in which alcohols are added across the triple bond.[2] Though π-vinyl ether[3] and π-vinyl alcohol[3,4] complexes are undoubtedly intermediates in these reactions, to our knowledge there have been no reports of such species resulting from an η^2-coordinated alkyne. In an early paper on the reactivity of η^2-alkyne complexes of platinum(II), Chisholm and Clark suggested that addition of methanol occurred across the alkyne bond to produce a vinyl ether intermediate, but this suggestion was later withdrawn.[5] Here we report that the alkyne complex $[Os(NH_3)_5(\eta^2\text{-}CH_3CCCH_3)]^{2+}$ reacts quantitatively with methanol or water to form π-vinyl ether and π-vinyl alcohol complexes, respectively.

Reduction of the precursor $Os(NH_3)_5(OTf)_3$ (OTf = $CF_3SO_3^-$) in the presence of 2-butyne results in a complex, **1**, which is readily characterized as $[Os(NH_3)_5(\eta^2\text{-}CH_3CCCH_3)](OTf)_2$.[6] Though the thermal instability of this material has precluded a successful microanalysis,[7] convincing evidence for this assignment is provided by IR, ^{1}H NMR, and cyclic voltammetric data.[8]

When a methanol solution of the alkyne product **1** is allowed to stand overnight, a new material,[9] **2a**, is isolated which is characterized as the π-vinyl ether containing cation $[Os(NH_3)_5(\eta^2\text{-}cis\text{-}CH_3CH{=}C(OCH_3)(CH_3))]^{2+}$. In addition to ammine resonances, ^{1}H NMR data reveal peaks with chemical shifts and splitting patterns similar to those reported for the free ligand *cis*-2-methoxy-2-butene,[10] and electrochemical measurements provide an $E_{1/2}$ (0.53 V) similar to that reported for other olefin–pentaammineosmium(II) complexes.

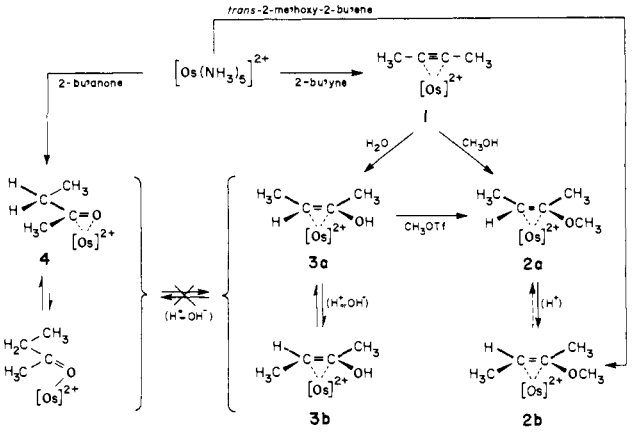

Figure 1. Chemistry associated with π-vinyl alcohol and ether complexes of pentaammineosmium(II).

An aqueous solution of the alkyne product **1** after 8 h yields a new material,[11] **3a**, whose ^{1}H NMR closely resembles that of the vinyl ether **2a**, less the methoxy resonance. In its place is a resonance at 5.00 ppm which is ascribed to the hydroxy proton of the enol cation $[Os(NH_3)_5(\eta^2\text{-}cis\text{-}CH_3CH{=}C(OH)(CH_3))]^{2+}$. Cyclic voltammetric data are consistent with a π-olefin complex showing $E_{1/2}$ = 0.37 V.[12] The infrared spectrum of **3a** as a glaze on a NaCl salt plate features a high frequency absorption at 3475 cm^{-1} which is absent in the IR of a sample of **2a** prepared in similar fashion. This feature is assigned to the enol ν(O–H). The reaction of **1** with water is significantly catalyzed by acid; in a 1 M solution of DOTf the half-life for hydration in aqueous solution is reduced from hours to seconds or less.[13] In the presence of base, an aqueous solution of **1** appears unaltered after 1 h.

Over a period of several days, ^{1}H NMR spectra of an acetone-d_6 solution of **3a** reveal that this complex is unstable with respect to its stereoisomer $[Os(NH_3)_5(\eta^2\text{-}trans\text{-}CH_3CH{=}C(OH)(CH_3))]^{2+}$ (**3b**).[14] The resonances ascribed to the trans isomer are similar to those of the cis form with the exception of the vinyl proton, which manifests a multiplet rather than a pure quartet. A similar discrepancy is found in the comparison of stereoisomers for the free ligand 2-methoxy-2-butene.[10] In acetone, methanol, or water, an equilibrium is reached between **3a** and **3b** in which the trans form (**3b**) is slightly favored ($K_{eq} \cong 1.5$). The addition of either base or acid significantly catalyzes this isomerization.[15]

The ligand *trans*-2-methoxy-2-butene was prepared from *trans*-2-butene following a modification of the procedure reported by Stang et al.[16] By the use of established synthetic procedures,[17] pentaammineosmium(II) was generated in the presence of this alkene resulting in the diamagnetic complex, **2b**. Microanalytical

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(5) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 2557.
(6) (All reactions under anaerobic conditions.) Synthesis of $[Os(NH_3)_5(\eta^2\text{-}CH_3CCCH_3)](OTf)_2$: A solution of $Os(NH_3)_5(OTf)_3$ (800 mg), *N,N*-(DMA) (1.0 mL), 1,2-dimethoxyethane (DME) (10 mL), and 2-butyne (1.0 mL) is stirred with activated magnesium (1 g, turnings; surface cleaned with I_2) for 35 min. The solution is filtered and treated with ether (200 mL). The resulting ppt is collected, washed with ether, and dried under vacuum.
(7) The solid **1** has a half-life of approximately 1 week at 25 °C in the absence of oxygen.
(8) Recorded under anaerobic conditions: ^{1}H NMR (acetone-d_6) 4.82 (b, 3 H), 3.70 (b, 12 H), 2.07 (s, 6 H); CV (acetone; NaOTf) $E_{1/2}$ = −0.10 V, NHE; IR (acetone glaze on NaCl salt plate) ν(C≡C) = 1943 cm^{-1}.
(9) Synthesis of **2a**: 200 mg of **1** are dissolved in 2 mL of MeOH for a period of 18 h. The addition of ether to this solution results in a ppt which is collected and washed with ether. The crude product is purified on column of SP Sephadex C-25 resin by eluting with 0.2 M NaCl and is isolated as the BPh_4 salt. ^{1}H NMR (acetone-d_6, BPh_4^- salt) 1.32 (d, 3 H, CCH_3), 1.63 (s, 3 H, CCH_3), 3.73 (q, 1 H, CH), 3.50 (s, 3 H, OCH_3), 3.69 (b, 12 H), 4.80 (b, 3 H), (BPh_4^-: 6.77 (8 H), 6.92 (16 H), 7.33 (16 H)); ^{13}C NMR (acetone-d_6; OTf^- salt; proton decoupled) 14.4, 58.6, 92.7, 39.9, 15.6 ppm; OTf 121.7 (q); CV (acetone; TBAH) $E_{1/2}$ = 0.53 V, NHE. Anal. Calcd for $C_{53}H_{65}OsON_5B_2$: C, 63.66; H, 6.55; N, 7.00. Found: C, 63.81; H, 6.48; N, 7.09.
(10) Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 1459.
(11) Synthesis of **3a**: 250 mg of **1** are dissolved in water for 8 h. The crude product is purified on column of SP Sephadex C-25 resin by eluting with 0.2 M NaCl and is isolated as the BPh_4 salt. ^{1}H NMR (acetone-d_6, BPh_4^- salt) 1.27 (d, 3 H, C-CH_3), 1.67 (s, 3 H, C-CH_3), 3.51 (q, 1 H, CH), 5.00 (s, 1 H, OH), 3.72 (b, 12 H), 4.73 (b, 3 H), (BPh_4^-: 6.77 (8 H), 6.92 (16 H), 7.33 (16 H)); CV (acetone, TBAH) $E_{1/2}$ = 0.37 V, NHE; IR (acetonitrile glaze on a NaCl salt plate) 3475 cm^{-1}. Anal. Calcd for $C_{52}H_{63}OsON_5B_2$: C, 63.35; H, 6.44; N, 7.10. Found: C, 62.82; H, 6.31; N, 7.04.
(12) Repeated cycling reveals the partial decomposition of the osmium(III) species; a new species appears with $E_{1/2}$ = 0.49 V, NHE.
(13) After 5 min in a 1 M DOTf/D_2O solution, ^{1}H NMR reveals complete conversion of **1** to a mixture of **2a** and **2b**. Deuterium exchange has occurred at the C1 position.
(14) Characterization of **3b**: ^{1}H NMR (acetone-d_6, BPh_4^- salt) 1.31 (d, 3 H, CCH_3), 1.63 (s, 3 H, C-CH_3), 3.26 (m, 1 H, CH), 5.03 (s, 1 H, OH), 3.72 (b, 12 H), 4.69 (b, 3 H), (BPh_4^-: 6.77 (8 H), 6.92 (16 H), 7.33 (16 H)); CV (acetone, TBAH) $E_{1/2}$ = 0.37 V, NHE.
(15) The addition of Proton Sponge in acetone or NaOMe in MeOH significantly increases the rate of isomerization of **3a**. (In water, both H^+ or OH^- catalyze this process.)
(16) *N*-bromosuccinamide was substituted for *N*-bromoacetamide. NMR of *trans*-2-methoxy-2-butene (CD_3CN) 1.46 (d of q, 3 H), 1.76 (m, 3 H), 3.51 (s, 3 H), 4.42 (q of q, 1 H); GS-MS m/z = 86 (108), 85 (41), 71 (105), 55 (101) (see ref 10).
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and cyclic voltammetric data for this species are consistent with the formation of a π-vinyl ether complex,[18] analogous to **2a**. Though the ^{1}H NMR of **2b** is similar to that of **2a**, these data clearly establish the formation of a different complex than that obtained from **1** in methanol. Taking into account the method of preparation, we conclude that the complex **2b** is $[Os(NH_3)_5(\eta^2\text{-}trans\text{-}CH_3CH{=}C(OCH_3)(CH_3))]^{2+}$ and assign **2a** to be the cis stereoisomer. A comparison of chemical shifts for these complexes with those reported for the free ligands further supports this assignment. Solutions of either **2a** or **2b** fail to show interconversion in acetone after several days.

When a DME solution of the enol **3a** is treated with 1 equiv of CH_3OTf (Aldrich), the major product formed is the *cis*-vinyl ether complex, **2a**. An NMR of the isolated product mixture in acetone-d_6 shows only trace amounts of the trans material. If it is assumed that nucleophilic attack by the enol occurs with retention of stereochemistry, the complex **3a** must also show a cis configuration.

When a DMF solution of **3a** is treated with 1 equiv of the oxidant $Fe(Cp)_2^+$, the organic ligand is surrendered over a period of several hours in the form of its tautomer 2-butanone. If pentaammineosmium(II) is generated in the presence of this species[19] a material is formed, **4**, which is readily characterized as the η^2-coordinated ketone complex $[Os(NH_3)_5(\eta^2\text{-}CH_3CH_2COCH_3)]^{2+}$. Microanalytical, electrochemical, and NMR data are in good agreement with that reported for the acetone analogue[20] in which a crystal structure confirms this bonding mode for ketones on pentaammineosmium(II).

With the hope of determining the thermodynamically favored tautomer of C_4H_8O on pentaammineosmium(II), several attempts were made to interconvert the enol (**3a,b**) and the ketone (**4**) complexes by acid or base catalysis without success. Noteworthy, however, is the resistance of these species toward deprotonation. A wet acetone-d_6 solution of **3a,b** was treated with an equivalent of Proton Sponge (pK_a 12.4) and allowed to stand 24 h after which time no reaction or deuterium exchange at the enol position was detected. This behavior is in contrast to that reported for the complex $PtCH_2(CHOH)(acac)Cl$ which acts as a moderate acid (pK_a = 3.5).[21] A methanol-d_4 solution of the ketone **4** with 1 equiv of NaOMe (ca. 1 mM) shows isotopic exchange only at the ammines over this time period. A summary of the chemistry described appears in Figure 1.

Pentaammineosmium(II) differs from the metal ions, such as Hg^{2+} and Pd^{2+}, which have commonly been used to activate alkynes for addition reactions,[1] in being less electrophilic, but much more given to back-bonding interactions. Why the kind of chemistry we have described is not more commonly observed for other metal centers answering to the same general description is a matter of some interest.

Acknowledgment. We gratefully acknowledge Dr. M. G. Finn for his helpful suggestions and insight. Support of this work by National Science Foundation Grants CHE85-11658 and CHE84-14329 (400 MHz NMR) and National Institutes of Health Grant GM13638-23 is gratefully acknowledged.

(18) Characterization of **2b**: ^{1}H NMR (acetone-d_6, BPh_4^- salt) 1.46 (d, 3 H, CCH_3), 1.61 (s, 3 H, CCH_3), 3.42 (q, 1 H, CH), 3.53 (s, 3 H, OCH_3), 3.72 (b, 12 H), 4.82 (b, 3 H), (BPh_4^-: 6.77 (8 H), 6.92 (16 H), 7.33 (16 H)); CV (acetone; TBAH) $E_{1/2}$ = 0.54 V, NHE. Anal. Calcd for $C_{53}H_{65}OsON_5B_2$: C, 63.66; H, 6.55; N, 7.00. Found: C, 63.58; H, 6.73; N, 6.86.

(19) Synthesis of $[Os(NH_3)_5(\eta^2\text{-}CH_3CH_2COCH_3)](OTf)_2$ (**4**): A solution of $Os(NH_3)_5(OTf)_3$ (250 mg) and 2-butanone (15 mL) (Aldrich) was stirred with Mg (1.0 g, activated with I_2) for 1.5 h. The brilliant orange solution was filtered, reduced in volume to 1 mL, and then treated with Et_2O (10 mL). The resulting ppt was collected, washed with ether, and dried under vacuum. NMR (acetone-d_6) 5.43 (b, 3 H), 4.00 (b, 12 H), 2.16 (m, 1 H), 1.60 (s, 3 H), 1.25 (m, 1 H), 1.20 (m, 1 H); CV (DMF, 100 mV/s) TBAH) $E_{p,a}$ = 0.37 V; $E_{p,c}$ = -0.61 V, NHE. Anal. Calcd for $C_6H_{23}OsS_2F_6O_7N_5{\cdot}^1/_4Et_2O$ (as observed in NMR): C, 12.68; H, 3.69; N, 10.57; S, 9.67. Found: C, 12.35; H, 3.58; N, 10.34; S, 9.78.

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(21) Deprotonation of this Pt(II)-enol complex is accompanied by an isomerization in which the Pt coordinates to the enolate carbon. See ref 3 and 4.

Artificial Photosynthesis of β-Ketocarboxylic Acids from Carbon Dioxide and Ketones via Enolate Complexes of Aluminum Porphyrin

Yasuhiro Hirai, Takuzo Aida, and Shohei Inoue*

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo Bunkyo-ku, Tokyo 113, Japan

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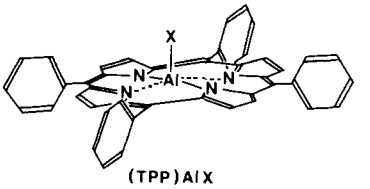
Photochemical fixation of carbon dioxide is of much interest in connection with biological photosynthesis by green plants as well as from the viewpoint of carbon resource utilization.[1] One of the important steps in the assimilation of carbon dioxide is the carboxylation of a carbonyl compound into ketocarboxylic acid, where the reaction proceeds via an enolate species as reactive intermediate. For example, in "four carbon (C_4)" pathway and "Crassulacean acid metabolism (CAM)" processes, pyruvate is converted with the aid of ATP into phosphoenolpyruvate, which is subsequently carboxylated to give oxaloacetate by the action of pyruvate carboxylase.[2] In relation to this interesting biological process, some artificial systems have been exploited for the synthesis of β-ketocarboxylic acid derivatives from carbon dioxide and ketones using nucleophiles such as metal carbonates, thiazolates, phenolates, alkoxides, and strong organic as well as inorganic bases,[3] which promote the enolization of ketones in the intermediate step.

We wish to report here a novel, visible light-induced fixation of carbon dioxide with the enolate complex of aluminum porphyrin, giving β-ketocarboxylic acid under mild conditions.

Typically, into a 50-mL round-bottomed flask fitted with a three-way stopcock containing a benzene-d_6 solution (7.5 mL) of $(TPP)AlOC(C_6H_5){=}CHCH_3$ (**2a**,[4] $R^1 = C_6H_5$, $R^2 = CH_3$; TPP:



(TPP)AlX

1 $-X{=}-N(CH_2CH_3)_2$

2a-2f $=-O-\overset{R^1}{\overset{|}{C}}{=}CH-R^2$

3a-3f $=-O-\overset{R^2}{\overset{|}{C}}-CH-\overset{O}{\overset{\|}{C}}-R^1$

5,10,15,20-tetraphenylporphinato) generated in 87% yield by the reaction of 1-phenyl-1-propanone (0.13 mmol) with (TPP)AlN-$(C_2H_5)_2$ (**1**,[5] 0.12 mmol) under dry nitrogen and freed of the

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(4) **2a**: ^{1}H NMR (C_6D_6, C_6H_6 (δ 7.40) as internal standard) 6.92 (t, p-H), 6.71 (t, m-H), 4.85 (d, o-H), 3.29 (q, C*H*), -0.73 (d, CH_3) (The stereochemistry of the enolate complex has been discussed in the following: Arai, T.; Murayama, H.; Inoue, S. *J. Org. Chem.* **1989**, *54*, 414). **2a**/MeIm: ^{1}H NMR (C_6D_6) δ 6.92 (t, p-H), 6.73 (t, m-H), 4.75 (d, o-H), 2.94 (q, C*H*), -0.79 (d, CH_3), 1.63 (s (br), N-CH_3 (MeIm)).

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