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# New Synthetic Approach to Cyclic Oxycarbene Complexes from Platinum(II)−Alkynyl and −Alkyne Complexes and Oxirane. X-ray Crystal Structure of *trans*-$[Pt(Me)\{=\overline{CCH(p\text{-tolyl})CH_2CH_2O}\}(PPh_3)_2][BF_4]\cdot 0.25CH_2Cl_2$

Rino A. Michelin,* Mirto Mozzon, Barbara Vialetto, and Roberta Bertani

*Istituto di Chimica Industriale and Centro di Studio per la Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Facoltà di Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padova, Italy*

Franco Benetollo

*Istituto di Chimica e Tecnologie Inorganiche dei Materiali Avanzati del CNR, Corso Stati Uniti 4, 35100 Padova, Italy*

Gabriella Bombieri

*Istituto di Chimica Farmaceutica, Università di Milano, Viale Duca degli Abbruzzi, 20131 Milano, Italy*

Robert J. Angelici*

*Department of Chemistry, Iowa State University, Ames, Iowa 50011*

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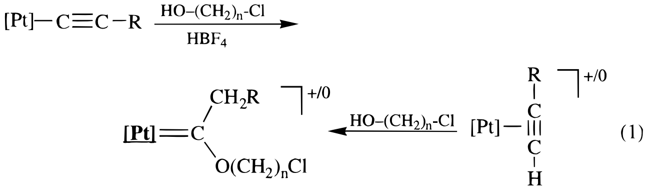
*Summary: The cyclic five-membered platinum(II) oxycarbene complex trans-*$[Pt(Me)\{=\overline{CCH(p\text{-tolyl})CH_2CH_2O}\}(PPh_3)_2][BF_4]$ (**1**) *can be prepared in good yield under very mild conditions either by reaction of trans-*$[Pt(Me)(C{\equiv}C\text{-}p\text{-tolyl})(PPh_3)_2]$ *with oxirane in the presence of 1 equiv of* $HBF_4$ *or by reaction of the cationic solvato complex trans-*$[Pt(Me)(PPh_3)_2(solv)][BF_4]$ *with oxirane and 1.5 equiv of p-tolylacetylene. The X-ray crystal structure of* **1** *is reported.*

## Introduction

Cyclic carbenes of transition-metal complexes are of relevant chemical interest, owing to their increasing importance in organic synthesis.[1] Their syntheses have been accomplished by various strategies,[2] which, in our case, involve cycloaddition reactions of the halo alcohols $HO(CH_2)_nX$ ($n = 2, 3$; X = Cl, Br) or the three-membered heterocycles $\overline{YCH_2}CH_2$ (Y = O, NH, S) to unsaturated ligands such as CO,[3] CS,[4] and RNC.[5] This synthetic strategy also proved effective with RCN ligands in Pt(II) complexes to form N-heterocycles such as 2-oxazolines and 1,3-oxazines.[6]

Recently we reported[7] that, in contrast with the above-mentioned CO and RNC reactions, no cyclic oxycarbenes were formed from Pt(II)−alkyne or −alkynyl complexes and the halo alcohols $HO(CH_2)_nCl$ ($n = 2, 3$); instead, alkyl((chloroalkyl)oxy)carbene complexes were isolated as the only reaction products (eq 1), likely occurring via vinylidene intermediates.[8]



[**Pt**] = *trans*-$[Pt(Me)(PPh_3)_2]^+$, *trans*-$[Pt(C{\equiv}CPh)(PMe_2Ph)_2]^+$, *cis*-$[Pt(PMe_2Ph)(Cl)_2]$; R = Ph, p-tolyl; n = 2, 3

In this paper we detail the first study on the reactivity of alkynyl and alkyne complexes of platinum(II) with oxirane, leading to the formation in good yield of cyclic oxycarbenes and thus representing a new and straightforward procedure to this type of ligand.

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⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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## Experimental Section

**General Procedures and Materials.** All reactions were carried out under an $N_2$ atmosphere. All the solvents were of reagent grade and were used without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer (abbreviations: s = strong, m = medium). Proton and carbon-13 NMR spectra were obtained on a Bruker AC-200 spectrometer. $^1$H NMR shifts were recorded relative to the residual $^1$H resonance in the deuterated solvent: $CDCl_3$, $\delta$ 7.23. The $^{13}C\{^1H\}$ NMR shifts are given relative to the solvent resonance: $CD_2Cl_2$, $\delta$ 53.8. The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) was run on a Varian FT 80-A spectrometer; the chemical shift is referenced to external 85% $H_3PO_4$ with the downfield value taken as positive. In all the NMR spectra $J$ values are in Hz (abbreviations used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected.

The complexes *trans*-$[Pt(Me)Cl(PPh_3)_2]$[9] and *trans*-$[Pt(Me)(C\equiv C\text{-}p\text{-tolyl})(PPh_3)_2]$[7] were prepared according to literature procedures. Oxirane (*Caution!* Oxirane, ethylene oxide, is highly flammable and toxic.) and *p*-tolylacetylene were commercially available products and used as received.

**Synthesis of *trans*-[Pt(Me){=CCH(*p*-tolyl)CH₂CH₂O}(PPh₃)₂][BF₄] (1). Method A.** To a suspension of *trans*-$[Pt(Me)(C\equiv C\text{-}p\text{-tolyl})(PPh_3)_2]$ (200 mg, 0.235 mmol) in oxirane (20 mL) at 0 °C was added a 0.126 M ethereal solution of $HBF_4$ (1.86 mL, 0.235 mmol) to give a clear solution, which was stirred for an additional 2 h at 0 °C. The solution was then taken to dryness under reduced pressure and the oily residue was treated with benzene (20 mL) to form a white solid, which was washed with warm benzene (2 × 10 mL) and then dried under vacuum. Yield: 181 mg (78%). Mp: 169−170 °C dec. Anal. Calcd for $C_{48}H_{45}OBF_4P_2Pt$: C, 58.73; H, 4.62. Found: C, 59.00; H, 4.75. IR (Nujol, cm$^{-1}$): $\nu$(C−O) 1248 (s). $^1$H NMR ($\delta$, $CDCl_3$): −0.207 [t, $^3J$(HP) 8.20, $^2J$(HPt) 46.4, 3H, $CH_3$], 1.12 (m, 1H, CH−), 1.88 (m, 1H, CH), 2.50 [s, 3H, $CH_3$ (*p*-tolyl)], 3.63 (s, 1H, CH), 4.18 (m, 1H, OCH), 4.82 (m, 1H, OCH). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$): 22.48 [s, $^1J$(PPt) 2945.3]. $^{13}C[^1H$-coupled] NMR ($\delta$, $CD_2Cl_2$): 306.95 [t, $^2J$(CP) 6.2, $^1J$(CPt) 849.4, $C_{carbene}$], 88.66 [t, $^1J$(CH) 156.9, $^3J$(CPt) 53.3, $OCH_2$], 72.05 [d, $^1J$(CH) 123.11, $^2J$(CPt) 67.88, $CH(C_6H_4\text{-}p\text{-Me})$], 26.47 [t, $^1J$(CH) 135.17, $CH_2$], 21.38 [q, $^1J$(CH) 126.2, $CH_3$], −3.32 [t, $^2J$(CP) 2.45, $^1J$(CPt) 368.5, $CH_3$−Pt].

**Method B.** To a solution of *trans*-$[Pt(Me)Cl(PPh_3)_2]$ (204 mg, 0.265 mmol) in $CH_2Cl_2$ (20 mL) at room temperature was added a 0.46 M solution of $AgBF_4$ in acetone (0.63 mL, 0.291 mmol). After it was stirred for 1 h, the suspension was filtered off to remove AgCl, and the solution was taken to dryness under reduced pressure to give a white solid of the solvato complex *trans*-$[Pt(Me)(PPh_3)_2(solv)][BF_4]$ (solv = $CH_2Cl_2$). To this solution, at 0°C, was added oxirane (20 mL), and this mixture was then treated with *p*-tolylacetylene (0.05 mL, 0.39 mmol). The reaction mixture was stirred for 3 h at 0 °C. Then the clear, pale yellow solution was taken to dryness under reduced pressure and the oily residue treated with benzene (10 mL) to give a white solid of the product. It was filtered off, washed with *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 163 mg (63%).

**Crystal Structure Determination.** Crystal data for **1** are collected in Table 1. X-ray diffraction data were collected on a four-circle Philips PW1100 (Febo System)[10] diffractometer in the $\theta/2\theta$ scan mode with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). A total of 8353 reflections were measured ($2\theta_{max} = 52°$). There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz−polarization effects and for absorption, as described by North et al.[11] The structure was solved by heavy-atom methods.[12] Refinement was carried out by full-matrix least squares; the function minimized was $\sum w(F_o^2 - F_c^2)^2$, with the weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0182P)^2 + 32.78P]$, where $P = \max(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the $BF_4$ anion and for the clathrate solvent, which were refined isotropically. The H atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U_{equiv}$ of the parent carbon atom). For a total of 504 parameters, $R_w' = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2} = 0.118$ (on $F^2$), $S = 1.33$, and conventional $R = 0.042$, based on $F$ values of 6691 reflections having $F_o^2 \geq 2.5\sigma(F_o^2)$. Scattering factors were taken from ref 13. Structure refinement and final geometric calculations were carried out with the SHELXL93[14] and PAST[15] programs, while drawings were obtained using ORTEPII.[16]

**Table 1. Crystal Data for Compound 1**

| | |
|---|---|
| formula | *trans*-[Pt(Me){=CCH(*p*-tolyl)CH₂CH₂O}(PPh₃)₂][BF₄]·0.25CH₂Cl₂ |
| fw | 994.35 |
| cryst dimens, mm | 0.28 × 0.32 × 0.42 |
| cryst syst | monoclinic |
| *a*, Å | 13.451(2) |
| *b*, Å | 12.920(3) |
| *c*, Å | 25.710(5) |
| $\beta$, deg | 91.42(4) |
| *V*, Å$^3$ | 4467(2) |
| space group | $P2_1/n$ |
| $\rho$(calcd), g cm$^{-3}$ | 1.48 |
| Z | 4 |
| *F*(000) | 1986 |
| $\lambda$(Mo K$\alpha$), Å | 0.710 69 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 3.279 |
| no. of rflns measd | 8353 |
| scan method | $\theta/2\theta$ |
| $2\theta_{max}$, deg | 52 |
| no. of obsd rflns ($I \geq 2.5\sigma(I)$) | 6690 |
| final *R*(*F*) | 0.041 |
| $R_w(F^2)$ | 0.113 |
| w | $1/[\sigma^2(F_o^2) + 0.0000P)^2 + 32.78P]$[a] |
| no. of params refined | 503 |
| GOF | 1.27 |

[a] $P = (\max F_o^2 + 2F_c^2)/3$.

## Results and Discussion

**Synthesis.** The reactions leading to the synthesis of the cyclic oxycarbene **1** are shown in Scheme 1. Route *a* involves the reaction of the acetylide precursor with oxirane in the presence of 1 equiv of $HBF_4$ at 0 °C for 3 h, while route *b* involves the reaction in oxirane at 0 °C for 3 h of the cationic solvato species *trans*-$[Pt(Me)(PPh_3)_2(solv)][BF_4]$, derived by treatment of *trans*-$[Pt(Me)(Cl)(PPh_3)_2]$ in $CH_2Cl_2$ with 1 equiv of an acetone solution of $AgBF_4$, with a slight excess of *p*-tolylacetylene. The yields of **1** by the two methods were 78 and 63%, respectively. Complex **1** is a white solid, stable

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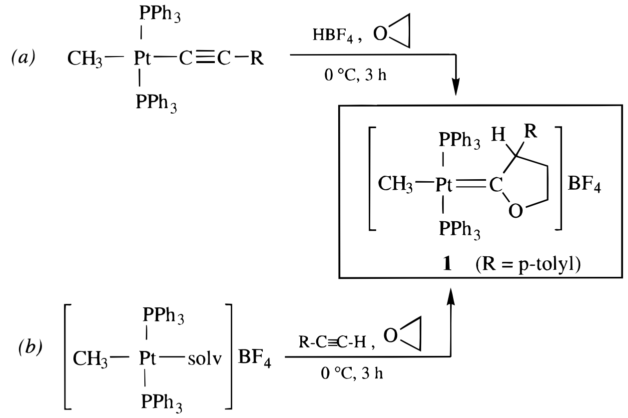
**Scheme 1**



in the solid state and in solution, and it was characterized by microanalysis, IR, and multinuclear NMR and also by an X-ray analysis. In the IR spectrum a strong absorption at ca. 1250 cm$^{-1}$ is assigned to $\nu_{str}$(C−O) of the carbene ligand, also in analogy with this type of assignment for other alkylalkoxycarbene complexes of Pt(II),[17] while the strong band at ca. 1050 cm$^{-1}$ is due to the tetrafluoroborate anion. The $^{31}$P{$^{1}$H} NMR spectrum confirms the trans geometry (a singlet with $^{195}$Pt satellites for the phosphines). This geometry is also supported by the $^{1}$H NMR spectrum, which shows the $CH_3$ ligand as a triplet resonance, flanked by $^{195}$Pt satellites, due to coupling with the two magnetically equivalent $PPh_3$ ligands (see Experimental Section). In the $^{1}$H NMR each proton of the $-CH_2-$ groups of the ring appears as a distinct multiplet, due to geminal coupling and the adjacent protons. A similar behavior was previously observed for other cyclic carbene complexes of Pt(II).[5c] The $^{13}$C NMR spectrum gives additional information about the ring structure of the carbene ligand, which can be deduced from the analysis of the $^{13}$C-coupled spectrum. In fact, the $^{1}J$(CH) values in saturated heterocyclic compounds are related to the electronegativity of the heteroatom and to the influence of ring strain on hybridation, and they provide information about the ring size of the heterocycle.[18] In the case of **1**, the $^{1}J$(CH) values (ca. 123−156 Hz) of the carbene ligand are in agreement with those found for five-membered O-heterocycles.[18] The carbene carbon resonates at 306.95 ppm with a $^{1}J_{CPt}$ value (849 Hz) typical of carbene complexes.[19]

**X-ray Crystal Structure.** Crystals of **1** suitable for single-crystal X-ray analysis were grown by slow diffusion of diethyl ether into a dichloromethane solution. Selected bond lengths and angles are collected in Table 2, and an ORTEP plot of the molecular structure of the cation is illustrated in Figure 1.

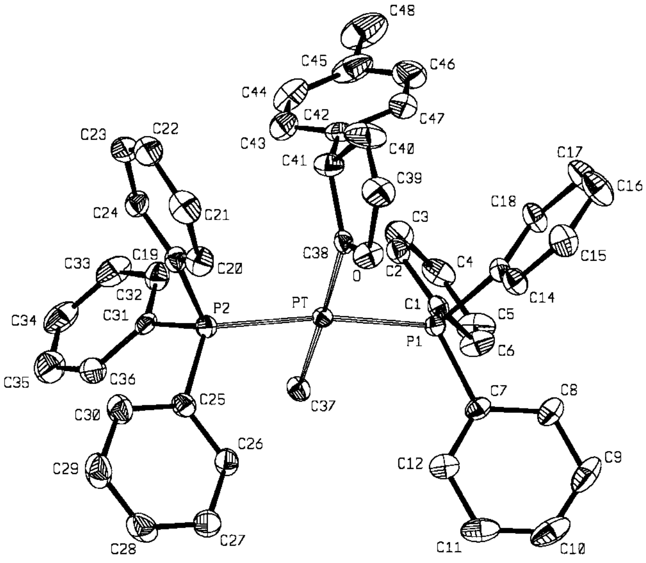


**Figure 1.** ORTEP drawing of *trans*-[Pt(Me){═CCH(*p*-tolyl)$CH_2CH_2O$}$(PPh_3)_2$] (cation of **1**).

**Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1**

| | | | |
|---|---|---|---|
| Pt−P(1) | 2.306(2) | Pt−P(2) | 2.314(2) |
| Pt−C(37) | 2.122(9) | Pt−C(38) | 2.013(8) |
| P(1)−C(1) | 1.819(8) | P(1)−C(7) | 1.829(9) |
| P(1)−C(13) | 1.820(8) | P(2)−C(19) | 1.831(9) |
| P(2)−C(25) | 1.824(9) | P(2)−C(31) | 1.833(9) |
| O−C(38) | 1.27(1) | O−C(39) | 1.50(1) |
| C(38)−C(41) | 1.53(1) | C(39)−C(40) | 1.45(2) |
| C(40)−C(41) | 1.50(2) | C(41)−C(42) | 1.51(1) |
| C(42)−C(43) | 1.36(2) | C(42)−C(47) | 1.39(2) |
| C(43)−C(44) | 1.37(2) | C(44)−C(45) | 1.36(2) |
| C(45)−C(46) | 1.40(3) | C(45)−C(48) | 1.53(2) |
| C(46)−C(47) | 1.38(2) | | |
| P(2)−Pt−C(37) | 86.5(2) | P(1)−Pt−C(38) | 95.0(2) |
| C(37)−Pt−C(38) | 174.9(3) | P(2)−Pt−C(38) | 94.0(2) |
| P(1)−Pt−C(37) | 84.9(2) | P(1)−Pt−P(2) | 170.43(7) |
| Pt−P(1)−C(13) | 116.5(3) | Pt−P(1)−C(7) | 116.4(3) |
| Pt−P(1)−C(1) | 110.5(3) | C(7)−P(1)−C(13) | 100.0(4) |
| C(1)−P(1)−C(13) | 106.3(4) | C(1)−P(1)−C(7) | 106.2(4) |
| Pt−P(2)−C(31) | 112.2(3) | Pt−P(2)−C(25) | 115.0(3) |
| Pt−P(2)−C(19) | 114.3(3) | C(25)−P(2)−C(31) | 105.2(4) |
| C(19)−P(2)−C(31) | 105.7(4) | C(19)−P(2)−C(25) | 103.5(4) |
| C(38)−O−C(39) | 114.2(7) | Pt−C(38)−O | 121.7(6) |
| O−C(38)−C(41) | 109.1(7) | Pt−C(38)−C(41) | 128.8(6) |
| O−C(39)−C(40) | 103.1(9) | C(39)−C(40)−C(41) | 108(1) |
| C(38)−C(41)−C(40) | 103.0(8) | C(40)−C(41)−C(42) | 121(1) |
| C(38)−C(41)−C(42) | 117.0(8) | C(41)−C(42)−C(47) | 124(1) |
| C(41)−C(42)−C(43) | 120(1) | C(43)−C(42)−C(47) | 117(1) |
| C(42)−C(43)−C(44) | 121(1) | C(43)−C(44)−C(45) | 124(1) |
| C(44)−C(45)−C(48) | 124(1) | C(44)−C(45)−C(46) | 116(2) |
| C(46)−C(45)−C(48) | 120(1) | C(45)−C(46)−C(47) | 120(1) |
| C(42)−C(47)−C(46) | 122(1) | | |

The complex geometry is defined by a distorted square arrangement of the donor atoms with the two phosphines mutually trans. The best mean plane of the coordinated atoms exhibits deviations of 0.008(2), 0.009(2), −0.171(9), and −0.137(8) Å for P(1), P(2), C(37), and C(38), respectively, with a Pt deviation of −0.0618(4) Å. The values of the P(1)−Pt−P(2) and C(37)−Pt−C(38) angles are 170.43(7) and 174.9(3)°, respectively, which further support the irregularities in the coordination sphere. The contraction of the P(1)−Pt−P(2) angle is likely related to the need to leave more space in order to accommodate the carbene ligand. This latter ligand has a half-chair conformation, and its mean plane forms a dihedral angle of 107(4)° with that of the tolyl ligand and of 96.3(3)° with the coordination plane (the torsion angle C(38)−C(41)−C(42)−C(43) is 94(1)°). Two of the three bond angles at C(38) deviate significantly from 120°, the O−C(38)−C(41) angle being 109.3(7)°, which is comparable to the values of the corresponding angle

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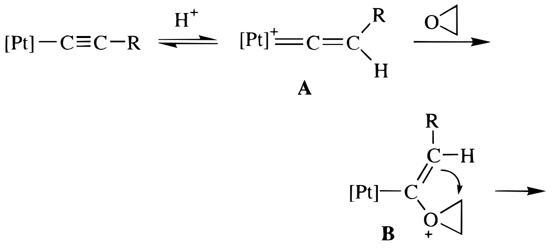
for similar Pt(II) alkylalkoxycarbenes,[7,20] while Pt−C(38)−C(41) is 128.8(6)°. On the other hand, the Pt−C(38)−O bond angle is 121.7(6)° and this contraction (compared to that observed for the symmetric Pt−C(38)−C(41) angle) appears to be related to a Pt···O contact of 2.89(1) Å.

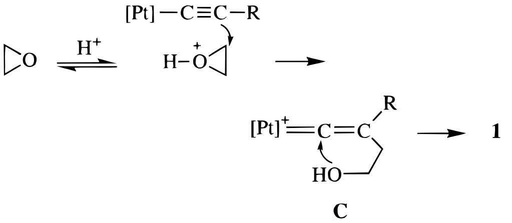
The Pt−C(38) and C(38)−O bond distances of 2.014(8) and 1.27(1) Å are relatively short and may be compared with those found for cationic alkylalkoxycarbenes of Pt(II) having a methyl group as the trans ligand, such as *trans*-$[\mathrm{Pt(Me)\{C(OMe)Me\}(PMe_2Ph)_2}][\mathrm{PF_6}]$ ($\mathrm{Pt{-}C_{carbene}} = 2.13(1)$ Å, $\mathrm{C_{carbene}{-}O} = 1.33$ Å)[20a] and *trans*-$[\mathrm{Pt(Me)\{\overline{COCH_2CH_2CH_2}\}(PMe_2Ph)_2}][\mathrm{PF_6}]$ ($\mathrm{Pt{-}C_{carbene}} = 2.00(2)$ Å, $\mathrm{C_{carbene}{-}O} = 1.26(2)$ Å).[20b]

**Possible Mechanisms.** Route *a* to **1** by reaction of the acetylide complex with oxirane in the presence of acid (Scheme 1) could proceed (eq 2) by initial protonation of the acetylide ligand to give the reactive vinylidene complex **A**; the latter undergoes attack by the oxirane to give **B**, which cyclizes to the product **1**. Since no vinylidene complexes of Pt(II) have been detected[8] upon protonation of Pt(II)−acetylide complexes, the formation of **A** would presumably occur to only a small extent. However, such protonated acetylides (**A**) have been proposed as intermediates in reactions of Pt(II) acetylides with alcohols in the presence of acid to form Pt(II)−alkoxycarbene complexes.[8a] These latter species were first synthesized by Chisholm and Clark upon reaction of terminal alkynes in MeOH or EtOH in the presence of *trans*-$[\mathrm{Pt(CH_3)Cl(PR_3)_2}]$ and $\mathrm{AgPF_6}$.[21] If **A** were highly electrophilic, it could presumably react even with the weakly nucleophilic oxirane[22] to generate **B**. The $\mathrm{CH_2}$ groups of the oxirane in this intermediate would then be more electrophilic and susceptible to attack by the β-carbon of the vinyl unit, resulting in the formation of **1**.



(2)

Another possible mechanism (eq 3) involves initial protonation of the oxirane, which would then be activated to attack the weakly nucleophilic β-carbon of the acetylide to give the reactive (hydroxyethyl)vinylidene complex **C**, which would cyclize by attack of oxygen at the vinylidene α-carbon and transfer of the OH proton to the vinylidene β-carbon. Protonated oxirane is known[22] to undergo attack by a variety of weak nucleophiles. While both mechanisms (eqs 2 and 3) are possible, it is not now possible to assign a specific mechanism to the reaction that leads to **1** by route *a*.



(3)

The formation of **1** from [Pt−solv]$^+$, HC≡CR, and oxirane by route *b* (Scheme 1) could occur by either of the mechanisms in eqs 2 and 3. The acid (H$^+$) required in both of these mechanisms could be generated by the reaction of [Pt−solv]$^+$ with HC≡CR to give [PtC≡CR] and H$^+$.

While the synthesis of cyclic oxycarbene complexes from acetylenes as shown in Scheme 1 provides a simple route to such complexes, further studies of the mechanism are required. Work is in progress to explore the range of alkynyl and/or alkyne complexes of various transition metals which would undergo reactions with oxirane to form cyclic oxycarbenes as well as those using other three-membered heterocycles such as aziridine and thiirane.

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**Supporting Information Available:** Tables giving anisotropic thermal parameters, all bond lengths and angles, fractional atomic coordinates and equivalent isotropic displacement parameters, and fractional coordinates of hydrogen atoms (7 pages). Ordering information is given on any current masthead page.

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(21) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202 and references therein.

(22) Barton, D.; Ollis, W. D. *Comprehensive Organic Chemistry*; Stoddardt, J. F., Ed.; Pergamon Press: Oxford, U.K., 1979; Vol. 1.