Organometallics **1994,** *13,* 1510–1513

Air Oxidation of *trans*-[$PtBr\{C(H){=}C{=}CMe_2\}(PPh_3)_2$] to the Hydroperoxyalkynylplatinum(II) Compound *trans*-[$PtBr\{C{\equiv}CCMe_2(OOH)\}(PPh_3)_2$]

Jacqueline M. A. Wouters, Kees Vrieze, and Cornelis J. Elsevier*

Anorganisch Chemisch Laboratorium, J. H. van 't Hoff Instituut, Universiteit van Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Martin C. Zoutberg and Kees Goubitz

Laboratorium voor Kristallogfrafie, J. H. van 't Hoff Instituut, Universiteit van Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received October 19, 1993⊛

Summary: The σ-allenylplatinum(II) compound [PtBr{C(H)=C=CMe$_2$}(PPh$_3$)$_2$ (1) reacts in daylight with molecular oxygen to form the new (3-hydroperoxy-3-methylbut-1-ynyl)platinum(II) complex [PtBr{C≡C-CMe$_2$(OOH)}(PPh$_3$)$_2$] (2). An X-ray crystal structure determination of this organometallic hydroperoxide confirmed the proposed structure. Space group $P\bar{1}$, a = 11.763(2) Å, b = 16.856(7) Å, c = 11.417(2) Å, and α = 105.39(5)°, β = 91.93(3)°, γ = 95.55(2)°, V = 2168(2) Å^3, Z = 2, R = 0.035, and R$_w$ = 0.057. Alkynylplatinum(II) compound 2 shows a trans square planar geometry with a Pt—C bond of 1.909(9) Å. The formation of 2 is proposed to take place via photosensitization of oxygen to singlet oxygen, followed by an Alder ene reaction with the C=C=C—H moiety of 1. The reactivity of 2 has been compared with the reactivity of t-BuOOH and appeared to be unable to oxidize cyclohexene.

Introduction

The organometallic chemistry of transition elements involving σ- and π-bonded 1,2-dienyl (allenyl) and 1,2,3-butatrienyl moieties currently receives considerable attention.[1] We have been interested in the synthesis of σ-allenylpalladium(II) and -platinum(II) complexes,[2] and the reactivity of these complexes toward carbon monoxide and isocyanides, giving rise to double insertion with the formation of 4-alkenyl-2(3*H*)-furanoyl–Pt(II) and –Pd(II) compounds,[3a,b] or palladium– and platinum(II)–vinylketenimine compounds,[3c] respectively. So far, no report about the reactions of oxygen with such (σ-allenyl)-palladium or -platinum compounds has been made. As, unlike the configurationally unstable compounds *trans*-[$PdBr\{C(H){=}C{=}CRR'\}(PPh_3)_2$], the corresponding platinum complexes *trans*-[$PtBr\{C(H){=}C{=}CRR'\}(PPh_3)_2$] appeared to be configurationally integer,[2c,d] the reactivity of the latter toward oxygen in air was investigated, and in this paper we describe the slow air oxidation of *trans*-[$PtBr\{C(H){=}C{=}CMe_2\}(PPh_3)_2$] to a novel type of organometallic hydroperoxide.

Experimental Section

General Considerations. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker AC 100 and AC 200 spectrometers, and infrared spectra were measured on a Perkin-Elmer 283 spectrophotometer. Mass spectra were measured on a Varian Mat 711 double focusing mass spectrometer and were performed by the Institute for Mass Spectroscopy of the University of Amsterdam. Elemental analyses were carried out at the Analytical Department of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands. The σ-allenyl starting compound 1 was synthesized according to literature procedures.[1]

Synthesis of *trans*-[$PtBr\{C{\equiv}CCMe_2(OOH)\}(PPh_3)_2$] (2). A solution of *trans*-[$PtBr\{C(H){=}C{=}CMe_2\}(PPh_3)_2$] (1) (239 mg, 0.28 mmol) in benzene (40 mL) was saturated with dry oxygen in daylight. After standing for ca. 40 h the solvent was evaporated and the residue was washed with pentane and dried *in vacuo*, which led to the isolation of pale yellow 2 in 78% yield (196 mg). Crystals suitable for X-ray diffraction were grown by slowly distilling hexane into a saturated solution of 2 in benzene at ambient temperature. ^{1}H NMR (CD_2Cl_2 (C_6D_6), 100 MHz): δ 0.58 (0.95) (s, 6H, 2 CH_3), 6.04 (6.58) (s, 1H, OOH), 7.4 (7.0) (m, 18H, meta and para Ph), 7.7 (7.9) (m, 12H, ortho Ph). ^{31}P NMR (CD_2Cl_2, 40.5 MHz): δ 21.7 (s, ^1J(Pt,P) = 2632 Hz). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ 26.15 (s, CH_3), 79.43 (t, ^2J(P,C) = 13.6 Hz, Pt—CC), 105.01 (s, Pt—CC), 128.21 (t, ^3J(P,C) = 5.0 Hz, Ph, meta C), 130.93 (t, ^1J(P,C) = 29.4 Hz, Ph, ipso C), 130.94 (s, Ph, para C), 135.38 (t, ^2J(P,C) = 5.0 Hz, Ph, ortho C). IR (KBr, cm^{-1}): 3500 (s) ν(OO—H), 2120 (w) ν(C≡C), 842 (m), ν(O—O). Anal. Calcd for $C_{41}H_{37}BrO_2P_2Pt{\cdot}0.75C_6H_6$: C, 57.09; H, 4.37; O, 3.34; P, 6.42. Found: C, 57.48; H, 4.50; O, 2.95; P, 6.86. FD-mass: found *m/z* = 899; calcd $M^{\bullet+}$ = 899.

Attempted Reaction of 2 with Cyclohexene. Cyclohexene (4 μL, 0.06 mmol) was added to a solution of *trans*-[$PtBr\{C{\equiv}CCMe_2(OOH)\}(PPh_3)_2$] (2) (50 mg, 0.06 mmol) in C_6H_6 (2 mL). The reaction was monitored by taking ^{1}H NMR spectra every hour. Neither heating the solution for 5 h at 80 °C nor stirring the solution for 2 days at room temperature in daylight initiated any reaction at all. Compound 2 remained unaltered in the reaction mixture.

X-ray Structure Determination and Refinement of *trans*-[$PtBr\{C{\equiv}CCMe_2(OOH)\}(PPh_3)_2$] (2). Crystals of 2 are triclinic, space group $P\bar{1}$, with two formula units $C_{41}H_{37}BrO_2P_2Pt{\cdot}0.75C_6H_6$ in a unit cell of dimensions *a* = 11.763(2) Å, *b* =

---

* To whom correspondence should be addressed.

⊛ Abstract published in *Advance ACS Abstracts,* February 15, 1994.

(1) (a) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993,** *12,* 1993 and references cited therein. (b) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993,** *115,* 1170. (c) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990,** *9,* 289. (d) Hoffmann, R. W.; Lanz, R. M.; Metternich, R.; Tarara, G.; Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 1145. (e) Larock, R. C.; Chow, M.-S. *Organometallics* **1986,** *5,* 603. (f) Stang, P. J.; Datta, A. K. *Organometallics* **1989,** *8,* 1024.

(2) (a) Collman, J. P.; Cawse, J. N.; Kang, J. W. *Inorg. Chem.* **1969,** *8,* 2574. (b) Elsevier, C. J.; Klein, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986,** *5,* 716. (c) Wouters, J. M. A. Ph.D. Thesis, Universiteit van Amsterdam, 1992. (d) Wouters, J. M. A.; Elsevier, C. J.; Häming, L.; Stam, C. H. Submitted to *Organometallics.*

(3) (a) Wouters, J. M. A.; Avis, M. W.; Elsevier, C. J.; Kyriakidis, C. E.; Stam, C. H. *Organometallics* **1990,** *9,* 2203. (b) Wouters, J. M. A.; Avis, M. W.; Elsevier, C. J.; Vrieze, K.; Kyriakidis, C. E.; Stam, C. H. Submitted to *Organometallics.* (c) Wouters, J. M. A.; Klein, R. A.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Organometallics* **1993,** *12,* 3864.

0276-7333/94/2313-1510$04.50/0

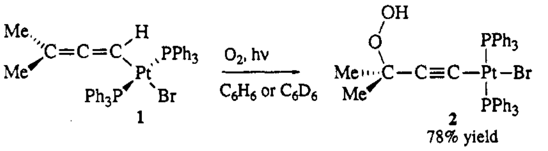
Table 1. Crystal Data and Details of the Structure Determination of [PtBr{C≡CCMe$_2$(OOH)}(PPh$_3$)$_2$] (2)

A. Crystal Data	
formula	$C_{41}H_{37}BrP_2O_2Pt{\cdot}0.75C_6H_6$
cryst syst	triclinic
space Group	$P\bar{1}$
a, Å	11.763(2)
b, Å	16.856(7)
c, Å	11.417(2)
α, deg	105.39(5)
β, deg	91.93(3)
γ, deg	95.55(2)
V, Å^3	2168(2)
Z	2
D_{calc}, g cm^{-3}	1.47
F_{000} electrons	929
μ(Mo Kα), cm^{-1}	42.8
abs corr max	1.38
abs corr min	0.84
appr cryst size, mm	0.15 × 0.45 × 0.45
B. Data Collection	
radiation (λ, Å)	Mo Kα (0.710 69)
temp, K	293
θ_{max}, deg	23
data set	$-12 \le h \le 12, -18 \le k \le 18, 0 \le l \le 12$
$\omega/2\theta$	θ–2θ
ref refln	010 and 001
no. of reflns	6041
no. of unique reflns	5973
no. obs reflns ($I > 2.5\ \sigma(I)$)	5109
C. Refinement	
no. of params	606
weighting scheme	$w = (5.48 + F_o + 0.0214F_o^2)^{-1}$
final R_f, R_w	0.035, 0.057
max shift/error	0.8
residual dens max, e Å^{-3}	1.0
residual dens min, e Å^{-3}	−0.8
extinction factor	0.17×10^{-6}

16.856(7) Å, c = 11.417(2) Å, α = 105.39(5)°, β = 91.93(3)°, and γ = 95.55(2)°. V = 2168(2) Å^3, D_x = 1.47 g cm^{-3}, and μ(Mo Kα) = 42.8 cm^{-1}. A crystal with approximate dimensions 0.15 × 0.45 × 0.45 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation and θ–2θ scan. A total of 5973 unique reflections was measured within the range $-12 \le h \le 12, -18 \le k \le 18, 0 \le l \le 12$. Of these, 5109 were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0.55 Å^{-1}. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $36° < 2\theta < 37°$. Corrections for Lorentz and polarization effects were applied. Also a number of peaks were found in this Fourier analysis which were attributed to a benzene molecule. This was subsequently isotropically refined to a population parameter of 0.75. The position of the Pt and Br atoms was determined by the Patterson method. The rest of the non-hydrogen atoms were derived from a ΔF synthesis. After isotropic refinement the H-atoms were derived from a subsequent ΔF synthesis. Block-diagonal least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, converged to R = 0.035, R_w = 0.057, $(\Delta/\sigma)_{max}$ = 0.79. A weighting scheme $w = (5.48 + F_o + 0.021F_o^2)^{-1}$ was used. An extinction correction was used and an empirical absorption correction[4] was applied, with coefficients in the range 0.84–1.38. A final difference Fourier map revealed a residual electron density between −0.8 and +1.0 e Å^{-3}. Scattering factors were taken from literature,[5] the anomalous dispersion for Pt, Br, and P was taken into account. All calculations were performed with XRAY76.[6]

Results

When a solution of [PtBr{C(H)=C=CMe$_2$}(PPh$_3$)$_2$] (**1**) in C_6H_6 was exposed to air in daylight the compound reacted in 40 h with 1 equiv of molecular oxygen to form the new hydroperoxo-organometallic compound [PtBr{C≡CCMe$_2$(OOH)}(PPh$_3$)$_2$] (**2**) (eq 1). The reaction was monitored by taking samples at 5-h intervals by ^{1}H NMR spectroscopy. When pure oxygen was bubbled through the solution of **1** in benzene, the reaction rate was not significantly increased. When the reaction was carried out in the dark, no formation of [PtBr{C≡CCMe$_2$(OOH)}(PPh$_3$)$_2$] (**2**) took place, not even when the solution was heated to 80 °C. This demonstrates that light is a prerequisite for the reaction to occur. When **1** was dissolved in C_6D_6 in daylight and dry oxygen was bubbled through the solution, the formation of **2** took place without any uptake of a deuterium atom, indicating that there is no H/D exchange with the solvent and that the proton bonded at oxygen probably originates from the allenic CH group.



(1)

The (3-hydroperoxy-3-methylbut-1-ynyl)platinum complex **2** is a surprisingly stable compound in the solid state, which can be stored for long periods in air at room temperature. Compound **2** was identified by ^{1}H, ^{31}P, and ^{13}C NMR, IR, FD-mass spectroscopy, and elemental analysis (see Experimental Section).

The ^{31}P NMR spectrum shows a singlet at 21.69 ppm, which indicates that the two triphenylphosphine ligands are situated in mutual *trans* positions. The platinum–phosphorus coupling of 2632 Hz is slightly smaller than the comparable coupling of 3079 Hz in **1**.[1] The ^{1}H NMR spectrum of **2** reveals a singlet for the two methyl groups and two multiplets for the meta/para and ortho phenyl protons of the phosphine ligands. Furthermore a singlet at 6.04 ppm is observed for the hydroperoxy proton, which is at a much lower frequency than the hydroperoxide proton of *t*-BuOOH and (α-cumyl)OOH (δ = 7.97 and 7.87 ppm, respectively, all in chlorinated solvents).[7] The ^{13}C NMR spectrum of the peroxide compound is in agreement with the proposed structure, only the quaternary carbon atom C(3) is not observed. In the IR spectrum the ν(C≡C) frequency occurs at 2120 cm^{-1}, which is a normal value as compared with the ν(C≡C) in [Pt(C≡CR)$_2$(PR'$_3$)$_2$] complexes.[8] The ν(OO—H) and the ν(O—O) moieties absorb at 3500 and 842 cm^{-1}, respectively, which data are comparable to those in *t*-BuOOH (ν(OOH) at 3550 and ν(O—O) at 838 cm^{-1}).[9]

Solid State Structure of [PtBr{C≡CCMe$_2$OOH}(PPh$_3$)$_2$] (2). The molecular structure of **2** along with the adopted numbering scheme is given in Figure 1. Selected bond lengths and bond angles are listed in Table 2. The crystal structure consists of two formula units $C_{41}H_{37}BrP_2O_2Pt{\cdot}0.75C_6H_6$ in a unit cell. The coordination around

---

(4) Walker, N.; Stuart, D. *Acta Crystallogr. A* **1983**, *39*, 158.

(5) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. A* **1968**, *24*, 321; *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 55.

(6) Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Amon, H. L.; Heck, H.; Flack, H. *The XRAY76 system*; Tech. Rep. Tr-446; Computer Science Center, University of Maryland: Baltimore, Maryland, 1976.

(7) O'Driscoll, K. F.; Richezza, E. N. *J. Polym. Sci.* **1960**, *46*, 211.

(8) (a) Burgess, J.; Howden, M. E.; Kemmit, R. C. W.; Sridhara, N. S. *J. Chem. Soc., Dalton Trans.* **1987**, 1577. (b) Massai, H.; Sonogaski, K.; Hagihara, N. *J. Organomet. Chem.* **1971**, *26*, 271.

(9) Hiatt, R. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. II, p 41.

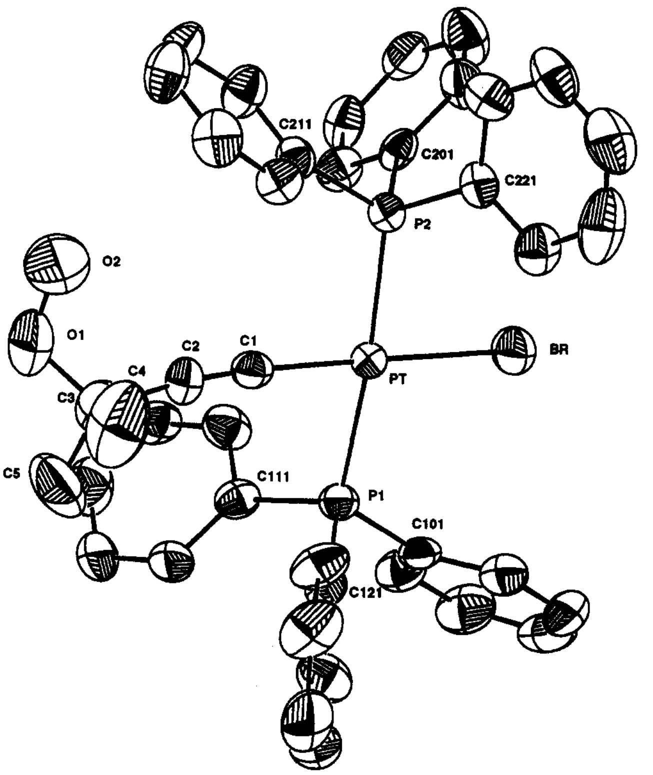


Figure 1. ORTEP drawing of $[PtBr\{C{\equiv}CCMe_2(OOH)\}(PPh_3)_2]$ (2).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[PtBr\{C{\equiv}CCMe_2(OOH)\}(PPh_3)_2]$ (2)

	Around Pt		
Pt–Br	2.478(1)	Br–Pt–P1	94.71(6)
Pt–P1	2.317(2)	Br–Pt–P2	86.51(6)
Pt–P2	2.309(2)	Br–Pt–C1	179.0(3)
Pt–C1	1.990(9)	P1–Pt–P2	172.77(7)
		P1–Pt–C1	84.3(3)
		P2–Pt–C1	94.4(2)
	Within Ligand		
C1–C2	1.15(1)	Pt–C1–C2	175.7(8)
C2–C3	1.49(1)	C1–C2–C3	173(1)
C3–C4	1.55(2)	C2–C3–C4	109(1)
C3–C5	1.54(2)	C2–C3–C5	110.8(9)
C3–O1	1.46(1)	C2–C3–O1	111.8(8)
O1–O2	1.38(2)	C4–C3–C5	113(1)
		C4–C3–O1	114(1)
		C5–C3–O1	98(1)
		C3–O1–O2	108(1)

platinum can be described as approximately square planar, with the coordination positions around Pt taken by the two phosphorus atoms P(1) and P(2) in mutual *trans* positions, by C(1) of the acetylide ligand, and by Br. When a least-squares plane is defined with these four atoms, P(1) and P(2) lie above and C(1) and Br below this plane. Accordingly, the geometry can be ascribed as square planar with a distortion toward a tetrahedron. A standard for such distortions is the parameter Δ,[10] which is 0.95 for 2. This value is comparable with that for other *trans*-$[PtBr(R)(PPh_3)_2]$ complexes[11-14] (Δ = 0.89–0.96) and with the Δ values calculated for our complexes *trans*-$[PtBr(R)(PPh_3)_2]$ (0.93–0.98).[1-3]

The Pt–P and the Pt–Br distances are all of the same magnitude and can be regarded as normal. The Pt–C(1) bond distance of 1.990(9) Å in 2 is of the same order as those in other platinum(II)–acetylide complexes.[15] The Pt–C(1)–C(2) angle of 175.7(8)° deviates from the ideal Pt–C–C angle in acetylide complexes of 180°, which is due to steric demands of the neighboring ligands and crystal packing forces.[16]

The C(1)—C(2) bond distance of 1.15(1) Å is slightly shorter than a formal C≡C triple bond but is normal compared to other C≡C bonds in platinum(II)–acetylide complexes.[15,16] The C—C and C—O bond distances are normal single bond distances. However, the O—O bond distance of 1.38(2) Å is shorter than the O—O bond distances in sodium hydroperoxide (1.49 Å)[17] and in several complexes containing a C—O—O—C fragment (1.46–1.48 Å).[18] This is probably due to the thermal movements of O(2). For the same reason the proton bonded at O(2) has not been observed by X-ray crystallography.

Discussion

There are two reactions known in which an organic molecule reacts with oxygen to give hydroperoxides, *viz.* autoxidation and photosensitized oxidation.[19] The slow air oxidation of a C–H bond to a COOH group is called autoxidation. The reaction occurs when compounds are allowed to stand in air and is catalyzed by light. The autoxidation of cumene to cumene hydroperoxide is the first step in the well-known commercial process for the coproduction of phenol and acetone.[20] Autoxidations are generally believed to proceed via a free radical chain mechanism.[21] Oxygen itself, which is a diradical, is too unreactive to be the species that abstracts the hydrogen, but a trace of free radical (e.g. R•) might be produced by some initiating process and react with oxygen to give R–O–O•, a radical which does abstract hydrogen followed by a chain reaction.

The photosensitized oxidations of alkenes with singlet oxygen also lead to the formation of hydroperoxides.[19] The reagent here, however, is not oxygen in the ground state but in an excited singlet state. One way to produce singlet oxygen is by energy transfer from a triplet sensitizer (sens) to oxygen.

$$\text{sens} \xrightarrow{h\nu} {}^1\text{sens} \rightarrow {}^3\text{sens} \qquad (2)$$

$$^3O_2 \xrightarrow{^3\text{sens}} {}^1O_2(^1\Delta_g) \qquad (3)$$

Additions of singlet oxygen to alkenes, to give allylic hydroperoxides, are believed to proceed analogously to

---

[10] De Ridder, D. J. A. To be published. The parameter Δ = 0 for a perfect tetrahedron, and Δ = 1 for a perfect square planar geometry.

[11] Huffman, J. C.; Laurent, M. P.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*, 2639.

[12] Rayaraman, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103.

[13] Gassman, P. G.; Gennick Cesa, I. *Organometallics* **1984**, *3*, 119.

[14] Cardin, C. J.; Cardin, D. J.; Parge, H. E.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1986**, 2315.

[15] Sünkel, K. *J. Organomet. Chem.* **1988**, *348*, C12.

[16] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Stone, F. G. A., Abel, E., Wilkinson, G., Eds.; Pergamon Press: New York, 1980.

[17] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, *9*, 1464.

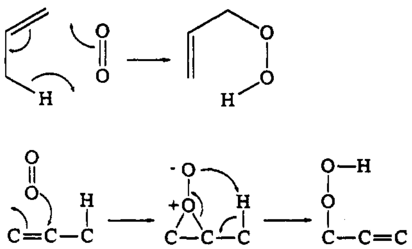
[18] *International Tables of Distances and Configuration in Molecules and Ions*; Sutton, L. E., Phil, D., Eds.; The Chemical Society: Burlington House, London, 1965.

[19] March, J. In *Advanced Organic Chemistry*; John Wiley and Sons: New York, 1985; pp 633.

[20] Reichle, W. T.; Konrad, F. M.; Brooks, J. R. In *Benzene and its Industrial Derivatives*; Hancock, E. G., Ed.; Benn: London, 1975.

[21] Sheldon, R. A.; Kochi, J. K. In *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981 (see also references therein).

Scheme 1. Possible Mechanisms for the Addition of Singlet Oxygen to Alkenes

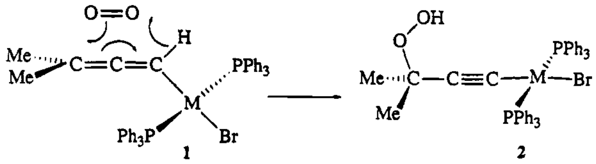


the Alder "ene" reaction.[22] Another possible mechanism involves addition of singlet oxygen to the double bond to give a peroxirane, followed by internal proton transfer[22] (Scheme 1).

The autoxidation of allenes is not known, probably because these compounds dimerize at room temperature, before the formation of a hydroperoxide is observed. Reactions of allenes with singlet oxygen are known.[23] For example, two molecules of singlet oxygen react with the double bonds of an allene in two [2 + 2] cycloaddition reactions, thus forming a tetraoxaspirobutane. This compound is not stable and decomposes into carbon dioxide and two ketone molecules, without formation of hydroperoxides.

In view of the very clean reaction (no side products and no H/D exchange with the solvent) and the high yield of the reaction of 1 with oxygen to give 2, we suggest that this reaction proceeds via a photosensitized reaction, rather than via a free radical chain mechanism (see Scheme 2). The role of platinum in the oxidation reaction may be, apart from stabilizing the allene fragment,[1] that it acts as a sensitizer of triplet oxygen to singlet oxygen. In a subsequent step, this activated oxygen may react with the terminal double bond of the allene, after which the hydroperoxide is most likely formed in a concerted mechanism or, alternatively but less likely, via a peroxirane and a H shift. Although the proposed mechanism is in our opinion the most likely one, we cannot exclude other possibilities, such as reactions involving Pt(III) as an intermediate.[24]

Scheme 2. Proposed Mechanism for the Reaction of 1 with $^1O_2$



The reactivity of $[\mathrm{PtBr\{C{\equiv}CCMe_2OOH\}(PPh_3)_2}]$ (2) may be compared to that of *t*-BuOOH, which is a common initiator in autoxidations of alkenes and is a good reactant for epoxidation reactions of alkenes.[21] Therefore we tested the reactivity of 2 in a benzene solution toward cyclohexene.[25] However, compound 2 proved to be very stable since, even after prolonged heating, no formation of cyclohexene oxide was observed, indicating that the platinum substituent has an influence on the hydroperoxide reactivity. The extent of this influence must as yet be assessed.

Conclusion

The unexpected air oxidation of 1 results in the isolation of a new organometallic hydroperoxide species 2, which has surprising stability.

Acknowledgment. The authors thank Profs. D. J. Stufkens and G. van Koten for helpful discussions and suggestions.

Supplementary Material Available: Tables of calculated fractional coordinates and isotropic thermal parameters of all atoms, anisotropic thermal parameters, and all bond distances and angles and an ORTEP diagram (11 pages). Ordering information is given on any current masthead page.

OM930720X

---

(22) (a) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419. (b) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (c) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. (d) Foote, C. S. *Pure Appl. Chem.* **1971**, *27*, 635.

(23) (a) Greibrokk, T. *Tetrahedron Lett.* **1973**, 1663. (b) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1985**, *26*, 5029. (c) Akasaka, T.; Fukuoka, K.; Ando, W. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1367.

(24) (a) Usón, R.; Forniér, J.; Tomás, M.; Menjón, B.; Bau, R.; Sünkel, K.; Kuwabara, E. *Organometallics* **1986**, *5*, 1576. (b) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 763.

(25) Cyclohexene has a low oxidizability, see: Howard, J. A. *Adv. Free Radical Chem.* **1972**, *4*, 49.