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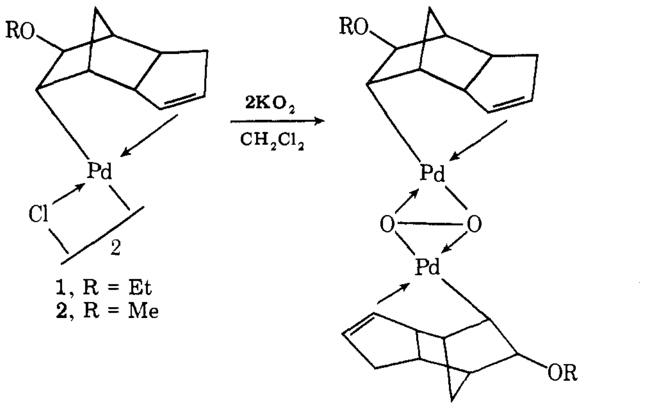
Received July 3, 1978

Preparation of New Palladium Dioxygen Complexes Using Superoxide Ion

Sir:

Since the discovery of dioxygen complex of iridium by Vaska,[1] transition metal-dioxygen complexes have attracted the attention of many investigators.[2] The majority of these complexes have been prepared by reaction of gaseous molecular oxygen with low valent transition metal complexes. Dioxygen complexes formed by this method have inevitably phosphine or isonitrile ligand which is required for stabilization of the low valent state of the starting transition metal complexes.

We report here that reaction of superoxide ion, O_2^-, with binuclear palladium complexes involving chloride bridges and both a metal-carbon σ bond and π-coordinate bond to cause anion exchange of Cl^- with O_2^- leads to formation of new dioxygen complexes having olefinic ligands. Experimentally, 640 mg (1 mmol) of palladium complex **1**[3] in 15 mL of CH_2Cl_2 was added dropwise to excess amount of finely powdered potassium superoxide (8 mmol, 4 equiv) suspended in 15 mL of CH_2Cl_2[4] at −40 °C and then the reaction mixture was slowly warmed to room temperature. Gradual evolution of oxygen was observed and the mixture was stirred for 4 h under 1 atm of nitrogen pressure. After removal of excess KO_2 and KCl by filtration, the filtrate was condensed at reduced pressure. Addition of mixed solvent of ether and petroleum ether (2:3) and cooling at 0 °C afforded a crude product as a pale yellow solid quantitatively. After repeated recrystallizations 528 mg (88%) of crystals, **3**, was obtained: mp >125 °C dec; IR (KBr) ν(C—O) 1090 cm^{-1}; NMR ($CDCl_3$) δ 5.62 (2 H, m, olefinic), 6.21 (2 H, m, olefinic); mol wt (cryoscopy in benzene) calcd 598.8, found 606. Anal. Calcd for $C_{24}H_{34}O_4Pd_2$: C, 48.10; H, 5.72; Cl, 0.00. Found: C, 47.85; H, 6.10; Cl, 0.00.[5] Methoxy-substituted **3**, [(MeO-DiCp)PdO]$_2$, was also prepared by the reaction of **2** with an excess amount of KO_2 in CH_2Cl_2: mp >137 °C dec; IR (KBr) ν(C—O) 1085 cm^{-1}; NMR ($CDCl_3$) δ 5.47 (2 H, m, olefinic), 6.12 (2 H, m, olefinic). Anal. Calcd for $C_{22}H_{30}O_4Pd_2$: C, 46.25; H, 5.29; Cl, 0.00. Found: C, 46.17; H, 5.29; Cl, 0.00.[5] The ^{1}H NMR spectra of **3** and **4** are quite similar to those of **1** and **2**, except the peaks for olefinic protons show upfield shifts.



1, R = Et
2, R = Me

3, R = Et
4, R = Me

$$+\ O_2 + 2\mathrm{KCl} \quad (1)$$

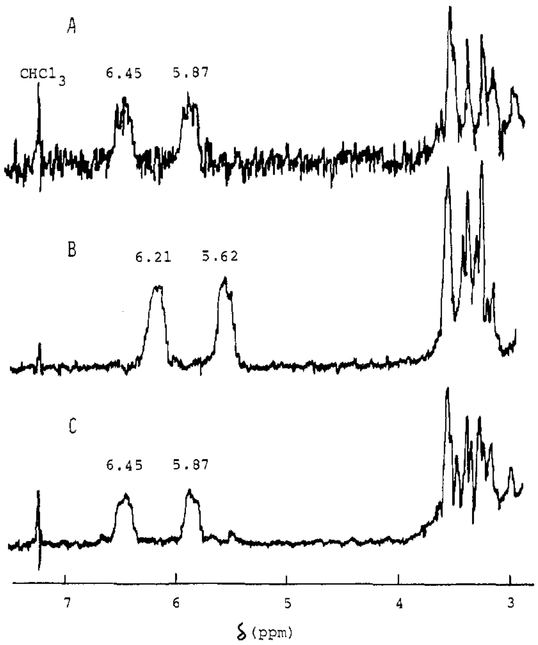
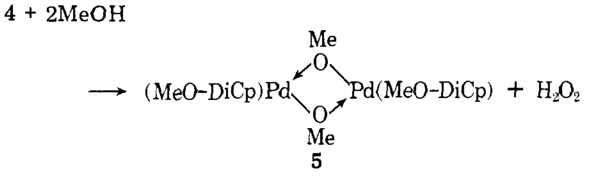


Figure 1. ^{1}H NMR spectra of palladium complexes in $CDCl_3$: (A) [(EtO-DiCp)PdCl]$_2$ freshly prepared; (B) [(EtO-DiCp)PdO]$_2$; (C) recovered complex after warming of [(EtO-DiCp)PdO]$_2$ at 50 °C for 10 h in $CHCl_3$.

The dioxygen bridged structure[6] was further confirmed by the reactions of **3** and **4**. It was found that the dioxygen bridge in the complexes is fairly labile. Warming of **3** and **4** in CH_2Cl_2 or $CHCl_3$ caused exchange of the dioxygen bridge to chloride ones and gave the starting complexes **1** and **2** quantitatively.[7]



$$\mathbf{4} + 2\mathrm{MeOH} \longrightarrow (\mathrm{MeO\text{-}DiCp})\mathrm{Pd}\begin{matrix}\mathrm{Me}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{Me}\end{matrix}\mathrm{Pd}(\mathrm{MeO\text{-}DiCp}) + \mathrm{H_2O_2} \quad (2)$$

5

Treatment of **4** by MeOH at room temperature afforded hydrogen peroxide[8] and methoxy-bridged complex **5**: mp >155 °C dec; IR (KBr) ν(C—O) 1082, 1053 (bridging) cm^{-1}; NMR ($CDCl_3$) δ 3.18 (6 H, s, OMe), 3.40 (6 H, s, OMe), 5.16 (2 H, m, olefinic), 5.63 (2 H, m, olefinic); mol wt (cryoscopy in benzene) calcd 600.8, found 645. Anal. Calcd for $C_{24}H_{36}O_4Pd_2$: C, 47.94; H, 5.99. Found: C, 47.81; H, 6.02. The reaction is also quantitative and suggests that dioxygen is coordinated as O_2^{2-} in the complex. Coordination bonds of oxygen to palladium are easily cleaved by treatment of the stronger ligand. When **4** is dissolved in CH_3CN at room temperature, a new complex (**6**) is formed. Ivory needles are re-

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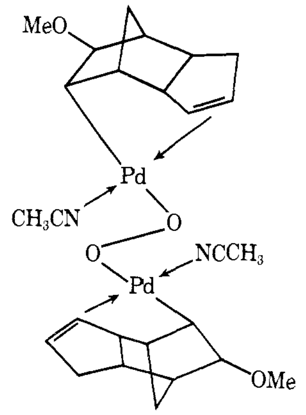
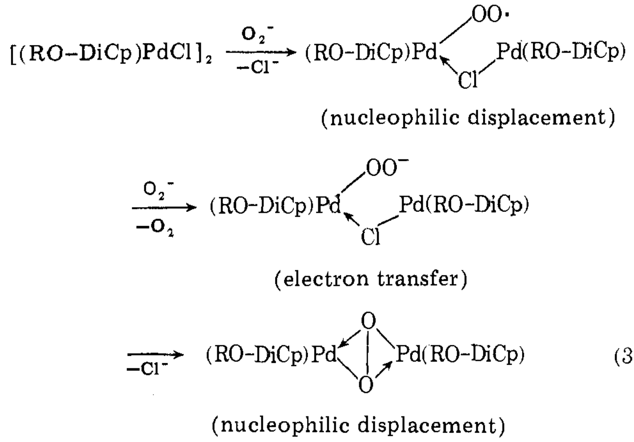


6

covered by addition of ether; mp >150 °C dec; IR (KBr) ν(C—O) 1093, ν(C≡N) 2220 cm^{-1}; Anal. Calcd for $C_{26}H_{36}O_4N_2Pd_2$: C, 47.79; H, 5.51; N, 4.29. Found: C, 48.51; H, 5.48; N, 4.56. These results and the nature of superoxide



$$[(\mathrm{RO{-}DiCp})\mathrm{PdCl}]_2 \xrightarrow[-\mathrm{Cl}^-]{\mathrm{O}_2^-} (\mathrm{RO{-}DiCp})\mathrm{Pd}\underset{\mathrm{Cl}}{\overset{\mathrm{OO}\cdot}{\diagup\!\diagdown}}\mathrm{Pd}(\mathrm{RO{-}DiCp})$$

(nucleophilic displacement)

$$\xrightarrow[-\mathrm{O}_2]{\mathrm{O}_2^-} (\mathrm{RO{-}DiCp})\mathrm{Pd}\underset{\mathrm{Cl}}{\overset{\mathrm{OO}^-}{\diagup\!\diagdown}}\mathrm{Pd}(\mathrm{RO{-}DiCp})$$

(electron transfer)

$$\xrightarrow[-\mathrm{Cl}^-]{} (\mathrm{RO{-}DiCp})\mathrm{Pd}\underset{\mathrm{O}}{\overset{\mathrm{O}}{|}}\mathrm{Pd}(\mathrm{RO{-}DiCp}) \qquad (3)$$

(nucleophilic displacement)

ion reported[9] suggest the scheme shown (eq 3) for the reaction to form dioxygen complexes. Both nucleophilic displacement[10] and electron transfer[11] involving O_2^- have been reported by several authors. The preparation method for dioxygen complexes reported here is quite simple and seems to be applicable for other transition metal systems. In addition, the dioxygen complexes having olefinic ligands may serve as good models for catalytic oxidation of hydrocarbons. Work along this line is now in progress.

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(4) CH_2Cl_2 is the best solvent for both starting complexes, **1** and **2**, and dioxygen complexes, **3** and **4**. In spite of the poor solubility of KO_2, the best yields of dioxygen complexes were obtained using CH_2Cl_2 as solvent. Addition of 18-crown-6 accelerated the reaction, but difficulty arose in clean recovery of dioxygen complexes. Me_2SO, the best solvent for KO_2, was strongly coordinated to palladium and gave no reaction products.

(5) Beilstein test was also negative.

(6) The M-O_2-M system, where dioxygen serves as bidentate to each of the two metal atoms, was formerly estimated for the synthetic oxygen carrying chelates such as the Co-O_2-Co system.[12] However, this is the first case for the noble metal-dioxygen complexes. X-ray analysis is now proceeding for the precise structure.

(7) Melting point and ^{1}H NMR and IR spectra for the recovered materials were completely identical with those for **1** and **2**, respectively. The results of elemental analysis were also satisfactory.

(8) Hydrogen peroxide (~60% of stoichiometric amount) was detected in the decomposition of **4** (0.25 mmol) in benzene-MeOH solution by iodometry. Incorporation of oxygen in the complexes **3** and **4** was further confirmed by the decomposition of **3** and **4** under oxygen-free conditions which gave various oxygenated products depending on the conditions.

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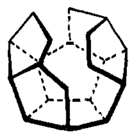
Received September 7, 1978

(C_2)-Dioxa-C_{20}-octaquinane, a Heterocyclic Trisecododecahedrane

Sir:

Any tactical elaboration of the pentagonal dodecahedrane molecule must involve the successful incorporation of 20 methine units by means of 30 carbon-carbon bonds into an all-cis network of 12 polyfused cyclopentane rings. If the synthetic approach proceeds stepwise with the proper deployment of spherical topology, then it becomes likely that certain penultimate intermediates will be attained which are more highly strained than the target compound due to enhanced levels of nonbonded interaction. A case in point is the as yet unknown triseco hydrocarbon **1**, where three sets of endo hydrogen atom pairs are seen to be directed into the highly crowded molecular interior. We describe here an efficient



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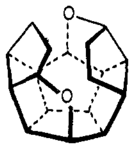

2

synthesis of **2** where two oxygen atoms have replaced pivotal methylene groups within such a framework. Although the impact of this structural change upon reduction of steric strain and/or molecular distortion must await the preparation of **1** and tandem physical measurements, the title compound (**2**), as constituted, represents the most advanced polyquinane structure known to this time.[1] Consequently, the present work provides evidence sufficient to justify the belief that **1** and related molecules where the spherical contour is highly developed should be amenable to conventional synthesis.

Previously, we reported the one-step preparation of diester **3a**[2] and diacid **3b**[3] by domino Diels-Alder addition of dimethyl acetylenedicarboxylate to 9,10-dihydrofulvalene[4] and their conversion to the C_2 symmetric bislactone **4**.[5] In gaining access to **2**, methodology has been developed for selective fission of the central bond in **4** and subsequent contraction of the heterocyclic rings, while strictly avoiding the serious complication of transannular bond formation so often witnessed with these molecules. To this end, **4** was reduced with lithium aluminum hydride in the tetrahydrofuran at 0 °C. Although the product of kinetic control was the endo,endo bislactol, rapid equilibration to **5a**, mp 252–255 °C (90%),[6] was seen upon dissolution in $CDCl_3$ or recrystallization from acetone. When admixed with freshly distilled thionyl chloride, **5a** was converted quantitatively to the highly reactive chloro ether **5b**, whose axial symmetry was substantiated by its 10-line ^{13}C NMR spectrum.[7] As expected, **5b** proved to be moisture sensitive, treatment with water or prolonged exposure to the atmosphere returning **5a**. Analogously, methanolysis of **5b** afforded the methyl acetal **5c**.[8]

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