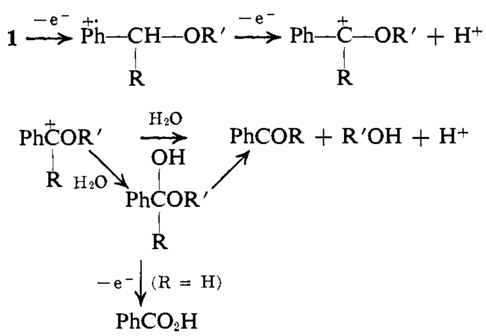
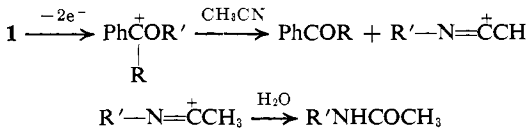
Mechanistically, we envisage a process similar to the following



Since oxygen nonbonded electrons are more difficult to ionize than toluene π electrons, the initial step of this reaction undoubtedly involves the phenyl group. This is rapidly followed by loss of a proton and a second electron transfer forming a carbonium ion. The work of Eberson and coworkers[6,7] provides strong analogy for the formation of benzylic cations and the attached oxygen function should make the present examples especially favorable. Several alternate reaction pathways exist for the benzylic cation, but due to the sodium carbonate these will all produce carbonyl products. The oxidation of dibenzyl ether in acetonitrile without added carbonate gives benzaldehyde and benzylacetamide. Since the starting ether is stable to the electrogenerated acid this implies that the carbonate is responsible for carbonyl products and the following reactions take place in its absence.



$$1 \xrightarrow{-2e^-} \text{Ph}\underset{\text{R}}{\overset{+}{\text{C}}}\text{OR}' \xrightarrow{\text{CH}_3\text{CN}} \text{PhCOR} + \text{R}'\text{—N}{=}\overset{+}{\text{C}}\text{CH}_3$$

$$\text{R}'\text{—N}{=}\overset{+}{\text{C}}\text{CH}_3 \xrightarrow{\text{H}_2\text{O}} \text{R}'\text{NHCOCH}_3$$

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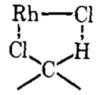
Molecular Oxygen as a Bridging Ligand in a Transition Metal Complex

Sir:

The catalytic hydrogenation activity[1] of chlorotris(triphenylphosphine)rhodium(I) is considered to be due to either (a) a vacant site in the five-coordinate species $\text{RhH}_2\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$, or (b) a six-coordinate species $\text{RhH}_2\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{S}$, where S is a weakly bound, and readily replaced, solvent molecule. Our attempts to produce suitable crystals of the methylene chloride adduct of this active hydrogenating species for an X-ray diffraction study have been unsuccessful. However, we decided to extend our investigation to other formally coordinatively unsaturated rhodium complexes where either chloroform or methylene chloride appears to be firmly retained in the solid state. The type of weak complex that was considered possible could be represented by



where a bond to a weakly coordinated chlorine atom could be reinforced by a hydrogen bond of a type that is well documented.[2,3] Our first choice was the apparently simple molecular oxygen complex[1,4] $\text{RhClO}_2\text{-}[\text{P}(\text{C}_6\text{H}_5)_3]_2\cdot\text{CH}_2\text{Cl}_2$. It is the surprising result of this investigation that we wish to report.

The complex was prepared by bubbling oxygen through a solution of the red form of chlorotris(triphenylphosphine)rhodium (0.25 g) in methylene chloride (15 ml) for 5 min. The first crop of brown diamagnetic crystals (~30% yield) was collected after a slow crystallization at 7° for 48 hr. All measurements were made on this material, which appears to be homogeneous.[5] Carbon and hydrogen analyses[6] (*Anal.* Calcd: C, 57.0; H, 4.1. Found: C, 57.7; H, 4.22) are in good agreement with the formulation, but chlorine analysis has proved difficult (calcd, 13.6; found, ~15) owing to the interference of rhodium and/or phosphorus. However, any serious objections to the formulation involve the identification of oxygen, and in addition to the evidence from the refinement (*vide infra*) some supporting data are available. The infrared spectrum (Nujol mull) shows a complex absorption at *ca.* 845 cm^{-1}, but this can be interpreted as being consistent with both a coordinated oxygen molecule and a perturbed methylene chloride molecule. The best supporting evidence for the assignment of oxygen comes from studies of the thermal decomposition products where molecular oxygen has been positively identified by gas chromatography.[7] Infrared spectra of solids remaining after heating to 200° *in vacuo* show the appearance of a band at ~1120 cm^{-1} which could be assigned to a triphenylphosphine oxide complex.[8]

The complex crystallizes in the triclinic crystal system with space group $P\bar{1}$; lattice parameters a = 13.889 (7), b = 13.678 (6), c = 11.433 (5) Å, α = 105.73 (4)°, β = 115.74 (3)°, γ = 100.97 (4)°; and two formula units per unit cell ($\rho_{\text{obsd}} = 1.469$ (by flotation), $\rho_{\text{calcd}} = 1.470$ g cm^{-3}). The structure has been solved from conventional Patterson and electron density maps, and has been refined using 1658 statistically reliable reflections measured on a manual Picker diffractometer with Cu Kα X-radiation with $2\theta \leq 80°$. The current model using a rigid-body description of phenyl groups has refined to a conventional reliability factor of 0.050

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(5) A second product has been identified in this system. These yellow orthorhombic crystals are the major product if the quantity of $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ is significantly increased. We tentatively formulate this compound as $\text{RhClO}_2(\text{P}(\text{C}_6\text{H}_5)_3)_3\cdot x\text{CH}_2\text{Cl}_2$, where x is in the range 2–3.

(6) Carried out in the microanalytical laboratory, Department of Chemistry, University of Alberta.

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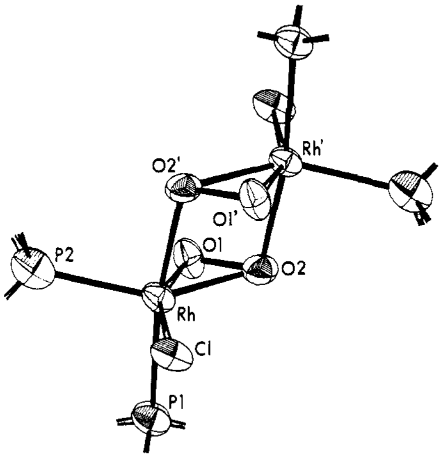

Figure 1. A perspective view of the central fragment $Rh_2O_4P_4C_2$. Selected distances (Å) and angles (deg) with standard deviations in parentheses are: Rh–P(1), 2.316 (5); Rh–P(2), 2.280 (5); Rh–Cl, 2.390 (5); Rh–O(1), 1.98 (1); Rh–O(2), 2.19 (1); Rh′–O(1), 2.78 (1); Rh′–O(2), 2.07 (1); O(1)–O(2), 1.44 (2); P–C, 1.83 (2) (av); Rh–Rh; 3.340 (2); P(1)–Rh–P(2), 100.3 (2); P(1)–Rh–C, 90.5 (2); P(1)–Rh–O(1), 87.5 (3); P(1)–Rh–O(2), 92.6 (3); P(2)–Rh–O(2), 95.7 (2); P(2)–Rh–O(1), 106.3(3); P(2)–Rh–O(2), 143.4 (3); Cl–Rh–O(1), 157.9 (3); Cl–Rh–O(2), 118.5 (3); O(1)–O(2)–Rh′, 102.5 (3).

for the observed data, which have been corrected for the small absorption and decomposition effects. Changing the bridging atoms [labeled O(1) and O(2)] to nitrogen atoms leads to a reliability factor 0.051, with physically unreal thermal parameters for these atoms. These refinements of the X-ray data strongly support[9] the suggestion that the atoms labeled O(1) and O(2) are indeed oxygen atoms.

The structure contains dimeric units, situated at inversion centers in the crystal, and corresponding to a molecular formula $\{RhClO_2[P(C_6H_5)_3]_2\}_2$. The disordered methylene chloride molecules are in no way coordinated to the rhodium atoms. The overall geometry of each rhodium atom can be described in terms of a distorted trigonal bipyramid, and the essential features of the structure are shown in Figure 1. While each rhodium atom is five-coordinate, this state is achieved in an entirely unexpected way. The equatorial positions are occupied by one phosphine, one chlorine, and an oxygen molecule. The axial positions are occupied by the second phosphine and one oxygen atom from the oxygen molecule that is bonded in the equatorial plane of the other rhodium atom of the dimer.

The rhodium–oxygen bonding can be rationalized using the conventional molecular orbital scheme for molecular oxygen. Within this framework[10] the oxygen molecule has an electron configuration $\pi^{*2}\pi^{*0}$ rather than the ground-state electron configuration $\pi^{*1}\pi^{*1}$. The bonding within the fragment RhO(1)-O(2) is then described by ligand-to-metal donation from a fully occupied π orbital and back-donation (metal to ligand) to the empty π^* orbital. This model has proved valuable in the interpretation of the wide range of oxygen–oxygen distances (1.30–1.66 Å) that has been observed by Ibers and his coworkers.[2,11,12] The retention of this model seemed desirable to us, and this particular structure may be explained by observing that the full π^* orbital of this μ-bonded oxygen molecule, which would be perpendicular to the RhO(1)-O(2) triangle, is available for the formation of a σ bond to Rh′. The angle of 102.5 (3)° for O(1)-O(2)-Rh′ certainly seems reasonable when the electron density plots[13] for the molecular orbitals of molecular oxygen are considered. This model can accommodate a wide range of O(1)-O(2)-Rh′ angles if it is noticed that the full π orbital is also available for donation to the second rhodium atom, and the observed angle could be considered to be a compromise between these two possible bonding extremes.

It is interesting to note that the bischloro-bridged species does not form even though it appears to be just as feasible from a geometric point of view. The preference for the oxygen bridge over the relatively common chlorine bridge suggests, perhaps, a particularly favorable energy relationship between the occupied π^* orbital of the coordinated oxygen molecule and the d_{z^2} orbital of the rhodium atom (the z axis is here defined as the pseudothreefold axis of the distorted trigonal bipyramid). The use of the π^* orbitals for σ-bond formation is not without precedent;[14] see, for example, the treatment of O_2F_2.

This particular view of the bonding of the central Rh_2O_4 unit in this structure does not allow an immediate discussion of the oxygen–oxygen distance, since the participation of both orbitals of each O_2, as proposed here, produces opposite effects; *i.e.*, π^* as an acceptor orbital leads to a decrease in oxygen–oxygen bond order while π^* as a donor orbital leads to an increase in oxygen–oxygen bond order. This comparison might be possible when the structural parameters for molecules $RhClO_2[P(C_6H_5)_3]_2L$ are known, and current research is directed at the preparation and characterization of such complexes. The particular distances that are observed in this compound allow a simple alternative description of the bonding. The structure can be treated as a distorted octahedral complex of rhodium(III) with a chelating peroxide ion. Within this description, the bridges are formed from one of the lone pairs on one oxygen atom of each peroxide ion.

This structure raises an interesting question as to whether oxygen complexes containing just the π^* donor bond can be made. This could be considered analogous to the bent transition metal nitrosyl complexes which have been treated as NO^- complexes.[15–17]

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