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Modeling Surface Reactivity of Metal Oxides: Synthesis and Structure of an Ionic Organorhenyl Perrhenate Formed by Ligand-Induced Dissociation of Covalent Re_2O_7

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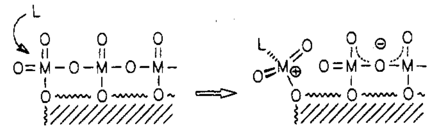
Summary: Treatment of $[Re_2O_7]_x$ with the carbodiphosphorane $Ph_3P{=}C{=}PPh_3$ leads to quantitative dissociation of the binary covalent metal oxide into the organorhenyl perrhenate $[(Ph_3P)_2C{=}ReO_3]^+[ReO_4]^-$, the first cationic organorhenium(VII) oxide structurally characterized so far. The molecular structure of the latter reveals a trigonal-planar bis(phosphonio)methylidene ligand with a considerable degree of Re—C π-bonding character, the tetrahedral trioxorhenium(VII) cation being stabilized by charge delocalization of four strong π-donor ligands. The pattern of reactivity is discussed in light of modeling domains of localized reactivity at extended metal oxide lattices.

Reactions of low-valent transition-metal cluster compounds with unsaturated organic substrates have been discussed by modeling chemisorption phenomena and the surface reactivity of *metallic domains* of heterogeneous catalysts.[1] Despite the knowledge accumulated on reactivity patterns of organometallic oxides[2] and organometallic oxometalates[3] over the last decade, there are only a few well-documented reactions of simple binary metal oxides with unsaturated or polar organic molecules that may resemble surface reactivity of *oxidic domains* of heterogeneous transition-metal catalysts.[4] To the best of our knowledge, we add to the typical reactivity patterns of metal oxides the first example of ligand-induced dissociation of covalent $[M_{m+x}O_{n+y}]$ into an organometallic salt, the Lewis acidic oxo cation $[L{-}M_mO_n]^+$ being stabilized by the neutral and monodentate organic ligand L and by the corresponding and noncoordinating oxometalate $[M_xO_y]^-$. We propose that this type of ligand-induced dissociation of a polarizable oxidic lattice into corresponding ion pairs may serve as a model in understanding the process of activation of neutral organic molecules trapped by highly Lewis acidic oxo cations generated at active-surface sites of oxidic transition-metal catalysts.

Scheme 1. Source of Localized Reactivity: Ligand-Induced Dissociation of a Covalent Metal Oxide Lattice into Separate Ion Pairs and Its Homogeneous Model Reaction



$$[M_{n+x}O_{m+y}] + L \longrightarrow [L{-}M_nO_m]^+ [M_xO_y]^-$$

Phosphorus ylide chemistry of high-valent oxo and imido complexes has not been systematically explored so far.[5,6] This prompted us to investigate reactions of $[Re_2O_7]_x$ with various ylidic reagents. Here we report on the reaction with the carbodiphosphorane $Ph_3P{=}C{=}PPh_3$ (**1**). The knowledge concerning the coordination chemistry of **1** is limited. Kaska *et al.* studied remarkable reactions of **1** with low-valent phosphane and carbonyl compounds,[7] whereas Schmidbaur and Zybill demonstrated the use of **1** in stabilizing complexes of Cu, Ag, and Au with low coordination numbers.[8,9] The latter group also concludes that even copper(II) chloride behaves as an oxidizing agent leading to the nonorganometallic copper(I) salt $[Ph_3P{-}C(Cl){-}PPh_3]^+[CuCl_2]^-$ as a result of a redox reaction.[8] Despite this discouraging aspect of redox behavior, we anticipated that **1**, being a sterically demanding ligand

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with strong σ- and π-donor capacity, might stabilize the electronically and coordinatively unsaturated rhenyl cation $[\text{-ReO}_3]^+$ [10] by charge delocalization in a tetracoordinate fashion.

Reaction of 1 with $[Re_2O_7]_x$ (1/*x* equiv) suspended in absolute THF at −78 °C leads to precipitation of a yellow microcrystalline solid which is recovered from suspension in 89% yield. The ^{13}C NMR spectrum of this material reveals a triplet (δ_C 69.1, $^1J_{PC}$ = 122.3 Hz) for the α-C atom of the ylidic ligand. It was anticipated that a certain low-field shift compared to the corresponding α-protonated cation $[Ph_3P{-}C(H){-}PPh_3]^+$ (δ_C 1.7, $^1J_{PC}$ = 123.7 Hz)[11] would be a feature characteristic for complexation of the masked carbodianion in 1 at a highly π-acidic complex fragment such as $[\text{-ReO}_3]^+$.[10] Evidence for complete dissociation of $[Re_2O_7]_x$ into the organorhenyl perrhenate $[(Ph_3P)_2C{=}ReO_3]^+[ReO_4]^-$ (2) was provided by electrical conductivity measurements, elemental analysis, and vibrational spectra.[12]

In order to confirm the proposed structure, yellow crystals suitable for X-ray analysis[13] were grown from acetonitrile. The molecular structure of 2 is shown in Figure 1. The latter reveals the presence of a tetracoordinate trioxorhenium cation of local C_{3v} symmetry stabilized by a bis(triphenylphosphonio)methylidene ligand and a noncoordinating perrhenate ion.[14] By looking at the α-C atom as an sp^2-hybridized carbanion (sum of angles 159.9°) stabilized by the rhenyl cation $[\text{-ReO}_3]^+$ and by the negative hyperconjugative effect[15] of both $[\text{-PPh}_3]^+$ substituents,[16] we can expect a maximum of one σ- and one π-bond to the metal center (Scheme 2, resonance contribution **II**). Stabilization of the carbanion by a strong negative hyperconjugative effect at the expense of the metal–carbon π-interaction is reflected by resonance formula **I** (Scheme 2).

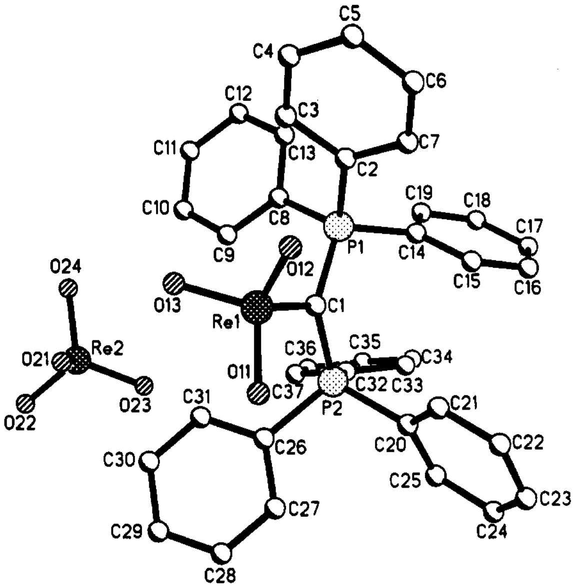
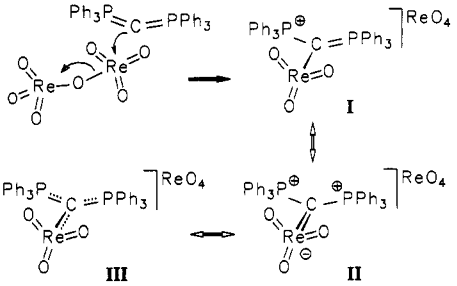


Figure 1. Perspective view of the molecular structure of **2**. Selected bond distances (Å): Re1–C1, 1.991(7); Re1–O11, 1.684(9); Re1–O12, 1.679(8); Re1–O13, 1.692(9); C1–P1, 1.777(8); C1–P2, 1.764(8). Selected bond angles (deg): Re1–C1–P1, 118.4(4); Re1–C1–P2, 118.4(4); P1–C1–P2, 123.1(4); angles at Re1, ranging from O11–Re1–C1 (108.0(4)) to O11–Re1–O12 (110.6(4)), average of all 109.5; angles at Re2, ranging from O21–Re2–O22 (105.2(6)) to O21–Re2–O23 (113.8(6)), average of all 109.4.

Scheme 2. Reaction of $[Re_2O_7]_x$ with $Ph_3P{=}C{=}PPh_3$ and Resonance Contributions within the Cation of 2



According to a recent review by Herrmann *et al.*,[10] all structurally characterized neutral complexes of the type $[R{-}ReO_3]$ exhibit rhenium–carbon bonds longer than that in 2, the first cationic organorhenium(VII) oxide in this series.[17] On the other hand, the bond distance Re1–C1 = 1.991(7) Å found in 2 is longer than in classical rhenium alkylidene complexes (~1.87–1.97 Å)[18] but 0.05 Å shorter than in the low-valent rhenium vinylidene complex $Re({=}C{=}CHPh)Cl(dppe)_2$.[19] Taking the high-valent rhenium complex with three competing π-donor ligands $ReO_2({=}CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ as a comparison (Re=C = 1.869(9) Å and Re—C = 2.114(9) Å),[20] we have to consider at least a significant Re=C double-bond character for this α-phosphonio-substituted methylidene ligand. Both C1—P distances (average 1.771 Å) are only slightly shorter (Δ = 0.035 Å) than the distances $P{-}C_{ar}$ (average 1.806 Å) of the phenyl groups, indicating that there is a rather weak contribution of resonance formula **I** to the electronic ground state of **2**.[21] The long Re—C bond distance compared to those in other alkylidene complexes may be partly due to the limited number of empty metal d orbitals competing for electron density of four π-donor ligands

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(12) Anal. Calcd for $C_{37}H_{30}O_7P_2Re_2$ (mol wt 1021.01): C, 43.53; H, 2.96. Found: C, 43.18; H, 3.11. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 69.13 (t, $^1J_{PC}$ = 61.2 Hz, P—*C*Re—P), 123.19 (dd, $^1J_{PC}$ = 91.7 Hz, $^3J_{PC}$ = 1.3 Hz, *i*-C_{ar}), 130.08 (vt, N_{PC} = 12.9 Hz, *m*-C_{ar}), 133.88 (vt, N_{PC} = 10.2 Hz, *o*-C_{ar}), 134.77 (s, *p*-C_{ar}). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ 29.5. Electrical conductivity (in MeCN, 20 °C): $\Lambda = 79$ cm^2 Ω^{-1} mol^{-1} at 2.12×10^{-3} M. Raman (CH_2Cl_2): 982 (vs), 956 (s) cm^{-1}. IR (KBr): 964 (s), 904 (vs) cm^{-1} (ν(Re—O)). Force field calculations on the vibrational spectra: Kiefer, W.; Pikl, R.; Sundermeyer, J.; Weber, K. To be submitted for publication.

(13) Crystallographic data for **2**: a = 15.155(3) Å, b = 24.368(5) Å, c = 19.016(4) Å, V = 7022.6(8) Å^3, d(calcd) = 1.931 g cm^{-3}, and Z = 8 in orthorhombic space group *Pbca*. Of 6799 reflections collected (20 °C, Mo Kα, absorption correction ψ scan), 6167 were unique and 4219 ($F > 3\sigma(F)$) were refined to R = 0.036 and R_w = 0.030. Other details: direct phase determination; full-matrix least squares; hydrogen positions of riding model with fixed isotropic U.

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and partly due to the electron-withdrawing effect of both $[\text{-PPh}_3]^+$ substituents competing with $[\text{-ReO}_3]^+$.

Unexpectedly, the Re—O bond orders in the cation $[(\text{Ph}_3\text{P})_2\text{C}{=}\text{ReO}_3]^+$ (average Re—O distance 1.685 Å) and in the anion $[\text{O}{=}\text{ReO}_3]^-$ (average 1.687 Å) are essentially the same. Therefore, the electron-donating capacity of the masked carbodianion 1 may be compared with that of an oxo ligand. Consequently, we observe a similar pattern of reactivity with many other high-valent oxo and imido complexes of groups 5–8.

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Supplementary Material Available: Tables containing complete crystal and data collection parameters, positional parameters and estimated standard deviations, intramolecular distances and angles, and thermal parameters and an ORTEP plot for **2** (7 pages). Ordering information is given on any current masthead page.

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(21) A measure of strong negative hyperconjugative interaction between α-C and P is documented by the molecular structure of the free ligand 1: average α-C-P 1.610 Å; P–C_{ar} 1.853 Å; Δ, 0.243 Å; P–C–P, 134.4°: (a) Hardy, G. E.; Zink, J. I.; Kaska, W. C.; Baldwin, J. C. *J. Am. Chem. Soc.* **1978,** *100,* 8001. (b) Vincent, A. D.; Wheatley, P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 617.

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