Studies of the Structures and Bonding of Unsaturated Dirhenium Carbonyl Cluster Complexes

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Crystallographic Analyses: Red crystals of **1** suitable for x-ray diffraction analyses were obtained from a methylene chloride/hexane solution by slow evaporation of a solvent at 25 °C. Yellow crystals of **3** suitable for x-ray diffraction analyses were obtained from a benzene/octane solution by slow evaporation of a solvent at 15 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[1] Correction for Lorentz and polarization effects were also applied using SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and were refined by full-matrix least-squares on F^2 by using the SHELXTL software package.[2] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Compounds **1** and **3** crystallized in the monoclinic crystal system. For **1** the space group $P2_1/n$ was uniquely identified on the basis of the systematic

absences observed in the data. For **3** the space group $P2_1/n$ was uniquely identified on the basis of the systematic absences observed in the data. ax,ax-$Re_2(CO)_8(PPh_3)_2$ crystallized in the monoclinc space group. The space group C2/c was identified on the basis of the systematic absences in the data and by the successful solution and refinement of the structure. Compound **1** and ax,ax-$Re_2(CO)_8(PPh_3)_2$ both crystallized on a center of symmetry.
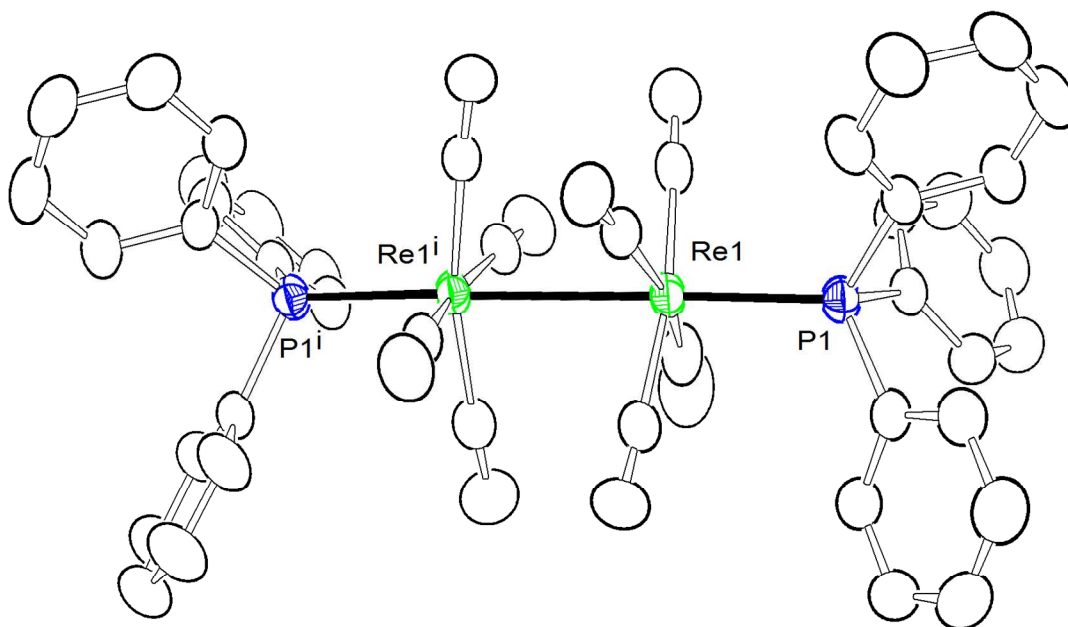

Figure S1. An ORTEP diagram of the molecular structure of ax,ax-$Re_2(CO)_8(PPh_3)_2$ showing 40% thermal ellipsoid probability. The hydrogen atoms are omitted for clarity. Selected interatomic bond distances (Å) and angles ($^\circ$) are as follow: Re1 - Re1^i = 3.0643(3), Re1 - C1 = 1.969(4), Re1 - C4 = 1.973(4), Re1 - C2 = 1.977(4), Re1 - C3 = 1.979(4), Re1 - P1 = 2.3910(9); P1 - Re1 - Re1 = 177.75(2)

Table 1. Crystallographic Data for Compounds 1, 3 and $Re_2(CO)_8(PPh_3)_2$.

Compound	1	3	ax,ax-$Re_2(CO)_8(PPh_3)_2$
Empirical formula	$AuRePO_4C_{22}H_{15}$	$AuReIPO_8C_{26}H_{15}$	$Re_2P_2O_8C_{44}H_{30}$
Formula weight	1514.95	1182.62	1121.04
Crystal system	Monoclinic	Monoclinic	Monoclinic
Lattice parameters			
a (Å)	9.2034(2)	12.1444(17)	13.8222(7)
b (Å)	14.6713(2)	18.231(3)	26.6145(13)
c (Å)	16.4820(3)	14.795(2)	11.1011(5)
α (deg)	90.00	90.00	90.00
β (deg)	101.35	112.643(2)	103.976(1)
γ (deg)	90.00	90.00	90.00
V ($Å^3$)	2181.98(7)	3023.3(7)	3962.9(3)
Space group	$P2_1/n$	$P2_1/c$	$C2/c$
Z value	2	4	4
ρ_{calc} (g / cm^3)	2.306	2.598	1.879
μ (Mo Kα) (mm^{-1})	12.36	13.95	6.24
Temperature (K)	294(2)	294(2)	294(2)
$2\Theta_{max}$ (°)	50.06	50.06	50.06
No. Obs. ($I > 2\sigma(I)$)	3559	4027	3159
No. Parameters	262	352	253
Goodness of fit (GOF)	1.078	1.112	1.027
Max. shift in cycle	0.004	0.09	0.006
Residuals[a]: R1; wR2	0.0192; 0.0434	0.0671; 0.1741	0.0197; 0.0472
Absorption Correction, Max/min	Multi-scan 1.000 / 0.533	Multi-scan 1.000 / 0.484	Multi-scan 1.000 / 0.622
Largest peak in Final Diff. Map (e^- / $Å^3$)	0.79	2.34	1.03

[a] $R1 = \Sigma_{hkl}(||F_{obs}|-|F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $wR2 = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2}$; $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data}-n_{vari})]^{1/2}$.

Computational Details. Density functional theory (DFT) calculations were performed with the Amsterdam Density Functional (ADF) suite of programs[3] by using the PBEsol functional[4] with valence quadruple-ζ + 4 polarization function, relativistically optimized (QZ4P) basis sets for rhenium and gold, valence triple-ζ + 2 polarization function (TZ2P) basis set for iodide and double-ζ function (DZ) basis sets for the phosphorus, carbon, oxygen, and hydrogen atoms with none frozen cores. The molecular orbitals for **1 − 4** and $Re_2(CO)_{10}$ and their energies were determined by geometry-optimized calculations, with scalar relativistic corrections, that were initiated by using the atom positional parameters as determined from the crystal structure analyses.[5,6] Electron densities at the bond critical points and Mayer bond orders were calculated by using the Bader Quantum Theory of Atoms In a Molecule (QTAIM) model.[7,8] Natural bond orbital (NBO) analyses were performed using GENNBO 6.0 package embedded in ADF 2013.[9] Time-dependent DFT (TDDFT) calculations were performed for models in the gas phase by using the PBEsol functional with the same basis sets.
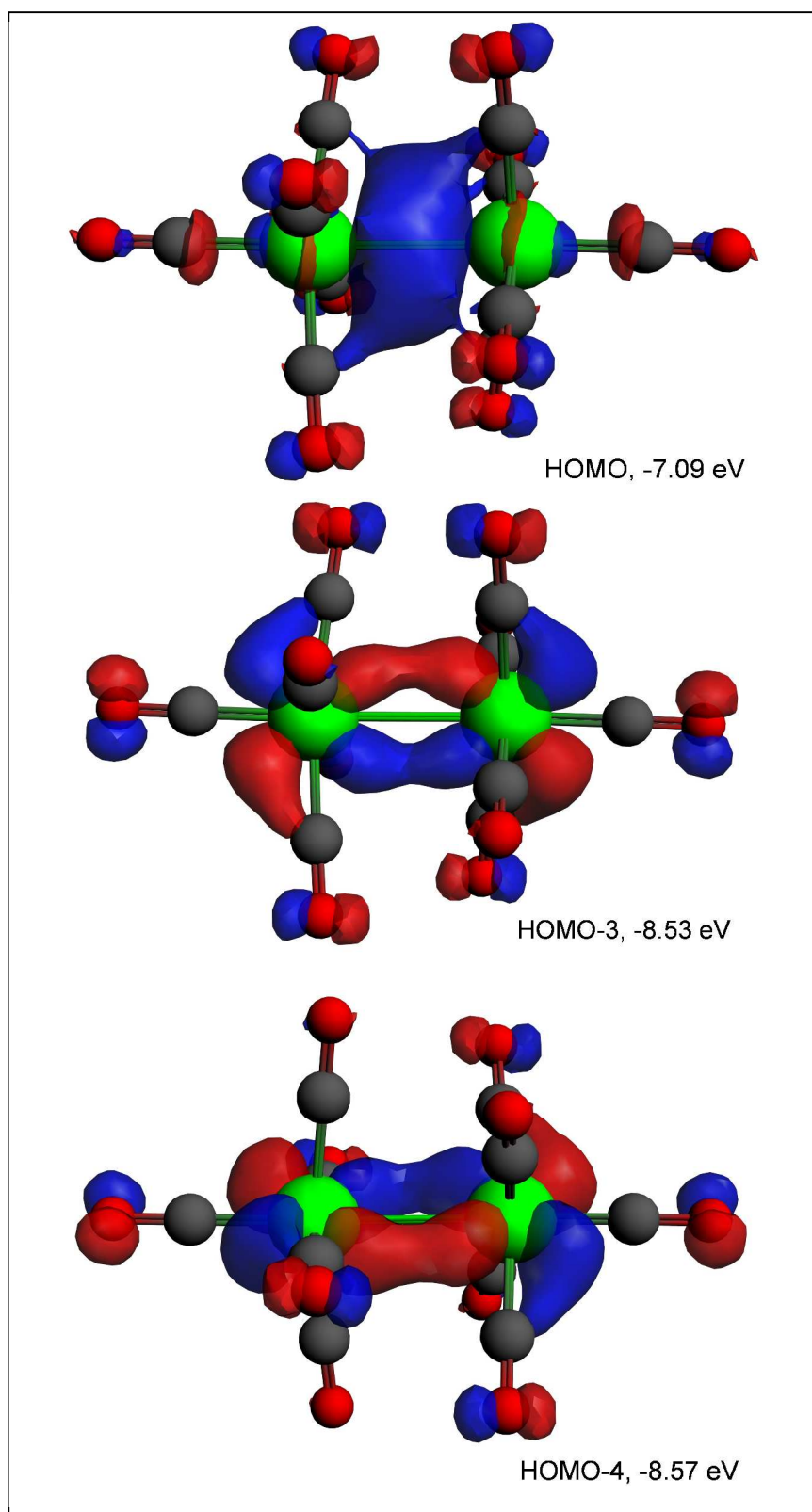
Figure S2. Selected PBEsol molecular orbital diagrams with calculated energies for $Re_2(CO)_{10}$ showing the Re – Re bonding: HOMO, HOMO-3 and HOMO-4. Isovalue = 0.04.

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