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The higher stability of the picket-fence porphyrin derivatives relative to those obtained with other porphyrins (H₂TPP, H₂TPFPP, H₂TMP[2, 3, 5]) indicates that the oxo group of the Mn=O moiety of 2 probably lies in the hydrophobic cavity formed by the four pivalamide pickets of this porphyrin.
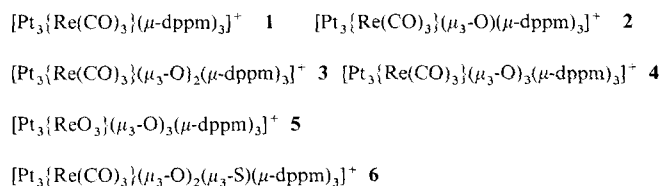
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Models for Bimetallic Catalysts: Multiple Oxidation States in Pt₃Re Cluster Cations**

Leijun Hao, Jianliang Xiao, Jagadese J. Vittal, and Richard J. Puddephatt*

Binding between oxo ligands and the small metal clusters present in the important oxide-supported bimetallic Pt–Re catalysts may occur at the metal-support interface and also during oxidation–reduction cycles.[11] However, knowledge of how oxygen interacts with the metal clusters is limited due to the difficulties in characterizing the heterogeneous materials. There are also few related metal oxo clusters to act as model com-

[*] Prof. R. J. Puddephatt, L. Hao, Dr. J. Xiao, Dr. J. J. Vittal
Department of Chemistry, The University of Western Ontario
London, Ontario N6A 5B7 (Canada)
Telefax: Int. code + (519)661-3022

pounds.[2, 3] The oxidation of 1 (dppm = Ph₂PCH₂PPh₂) with Me₃NO or oxygen to give the clusters 2 and 3, respectively, was reported earlier.[4] Here we show that further oxidation of 3 to give the novel clusters 4–6 is possible (Scheme 1). The oxidation of 1 to 4, 5, or 6 leads to an increase in cluster electron count by

$[Pt_3\{Re(CO)_3\}(\mu\text{-dppm})_3]^+$ **1** $[Pt_3\{Re(CO)_3\}(\mu_3\text{-O})(\mu\text{-dppm})_3]^+$ **2**

$[Pt_3\{Re(CO)_3\}(\mu_3\text{-O})_2(\mu\text{-dppm})_3]^+$ **3** $[Pt_3\{Re(CO)_3\}(\mu_3\text{-O})_3(\mu\text{-dppm})_3]^+$ **4**

$[Pt_3\{ReO_3\}(\mu_3\text{-O})_3(\mu\text{-dppm})_3]^+$ **5**

$[Pt_3\{Re(CO)_3\}(\mu_3\text{-O})_2(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$ **6**

12 electrons (from 54 to 66 electrons) and the formation of 5 from 1 involves a 12-electron oxidation (from Pt₃Re⁺ to Pt₃Re¹³⁺) without cluster fragmentation. Such multielectron processes appear to be unprecedented in cluster chemistry.

The trioxo cluster 4 could be prepared either by the thermal reaction of 1 with hydrogen peroxide or the photochemical reaction of 1 with oxygen. In both cases, NMR monitoring showed that the reaction proceeded via the intermediacy of the dioxo cluster 3 (Scheme 1) and, as predicted on this basis, reaction of
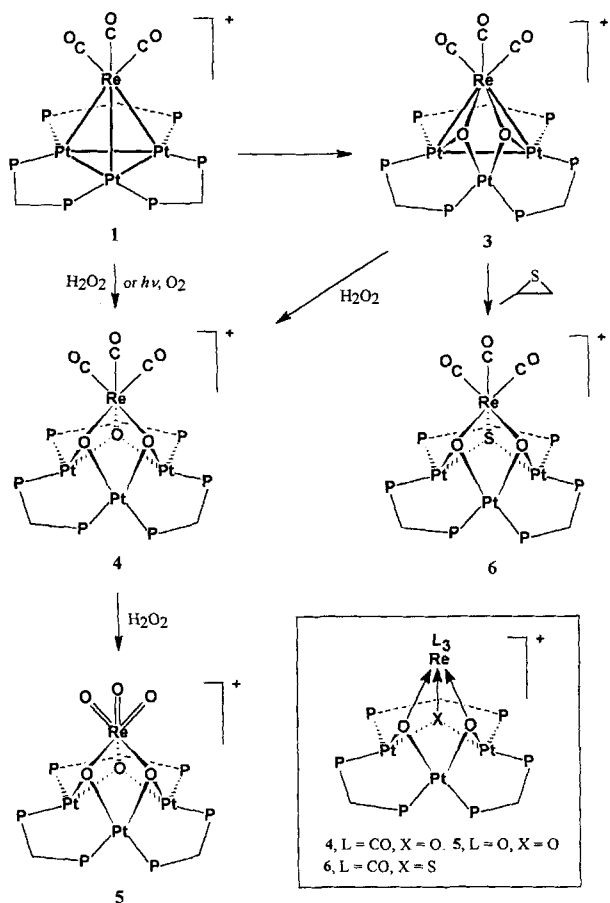
Scheme 1.

cluster 3 with H₂O₂ led to addition of a third oxo ligand giving 4 in high yield. The analogous dioxo(thio) cluster 6 was obtained by sulfur atom addition in the reaction of cluster 3 with propene sulfide. Finally, the hexaoxo cluster 5 was obtained by further oxidation of 4 with H₂O₂; cluster 5 has low solubility in acetone and so precipitates as it is formed. The Re(=O)₃ frag-

ment present in **5** is also present in $[Pt_3(ReO_3)(\mu\text{-dppm})_3]^+$, which was obtained by the high-temperature reaction of **1** or **3** with O_2.[5] The oxidation of Re–CO groups to Re=O groups finds precedent in the oxidation of $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$ to $[(\eta^5\text{-}C_5Me_5)ReO_3]$ in reaction with H_2O_2 or $O_2/h\nu$.[6] For the Pt_3Re clusters **1** and **3**, oxidation by oxygen atom addition evidently takes place first at the Pt–Re bonds; the $Re(CO)_3$ to $Re(=O)_3$ transformation has a higher activation energy.

Complexes **4** and **5** each give a single resonance in the ^{31}P NMR spectrum due to the phosphorus atoms and two resonances in the ^1H NMR spectrum due to the methylene protons of the dppm ligands, indicating a structure with C_{3v} symmetry. The magnitudes of the coupling constants $^1J(Pt,P)$ (3401 Hz for **4**, 3561 Hz for **5**) are greater than for the precursor **1** (2411 Hz), as expected since the phosphorus atoms are *trans* to the oxygen atoms rather than to the metal–metal bonds. The IR spectrum of **4** contains $\nu(CO)$ bands at 1987 and 1856 cm^{-1}, whose positions are close in energy to those in **1–3**;[4] the spectrum of **5** contains $\nu(Re=O)$ bands at 937 and 900 cm^{-1}, comparable to those observed in $[Pt_3(ReO_3)(\mu\text{-dppm})_3]^+$ (935 and 893 cm^{-1})[5] and $[(\eta^5\text{-}C_5Me_5)ReO_3]$ (909 and 878 cm^{-1}).[6]

The cluster **6** is C_2 symmetric and, as expected, the ^{31}P NMR spectrum exhibited three resonances due to the dppm ligands, with $^1J(Pt,P)$ values of 3388 and 3283 Hz (P atoms *trans* to oxygen atoms) and 3190 Hz (P atoms *trans* to the sulfur atom). The IR spectrum contains $\nu(CO)$ bands at 1989, 1865, and 1856 cm^{-1}. The structure of **6**, as the $[PF_6]^-$ salt, was confirmed crystallographically (Fig. 1).[7] Table 1 summarizes the changes
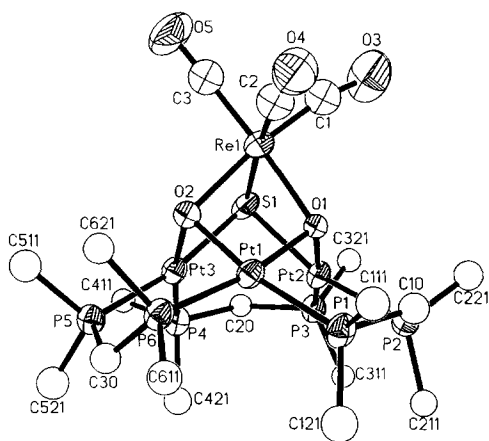

Fig. 1. A view of the structure of the cluster cation **6**. Only the *ipso* carbon atoms of the phenyl groups are shown for clarity.

in Pt–Pt and Pt–Re distances in **1**, **3**, and **6** as two oxo (**3**) and two oxo and one thio ligand (**6**), respectively, are added to cap the Pt_2Re faces of cluster **1**. It is immediately apparent that because of additional chalcogenido ligands all metal–metal separations increase in this series of clusters, and that complex **6** contains no metal–metal bonds.

Table 1. Comparison of the metal–metal distances in **1**, **3**, and **6**.

	1	**3**	**6**
Pt1-Pt2	2.611(1)	2.826(1)	3.254(2)
Pt1-Pt3	2.593(1)	3.094(1)	3.157(2)
Pt2-Pt3	2.608(1)	3.081(1)	3.143(2)
Pt1-Re	2.684(1)	2.843(1)	3.132(2)
Pt2-Re	2.649(1)	2.854(1)	3.378(2)
Pt3-Re	2.685(1)	3.228(1)	3.465(2)

Cluster **1** is intensely red-black and the color appears to be associated with the metal–metal bonds, while the clusters **4–6** are yellow or white, consistent with the absence of metal–metal bonds in all cases. The cluster electron count increases from 54 in **1** to 66 in each of **4–6** (each μ_3-O or μ_3-S ligand contributes four electrons, each terminal CO or O contributes two electrons). The additional 12 electrons in **4–6** cause the cleavage of all metal–metal bonds. Hence the $Pt_3Re(\mu_3\text{-X})_3$ framework established for **6** is a model for the series **4–6** (X = O, S). A valence-bond representation of the bonding in **4–6** is shown in the inset in Scheme 1. Thus the metal centers in **4** and **6** are considered as octahedrally surrounded Re^I ions and square-planar surrounded Pt^{II} ions (PtP_2O_2 or PtP_2OS coordination); the sum of the oxidation states of the metal atoms increases from +1 in **1** to +7 in **4** and **6**. The platinum coordination is the same in **5**, but the rhenium is oxidized to Re^{VII} with octahedral ReO_6 coordination and the sum of oxidation states of the metal centers is now +13. We know of no cluster complexes containing this type of rhenium coordination but related mononuclear complexes are known.[8] For example, the complexes $[LReO_3]^+$ (L = 1,4,7-triazacyclononane, 1,4,7-trithiacyclononane) are related to **5** if the Pt_3O_3 ring is considered as a tridentate pseudo-crown ether ligand.[8] The high oxidation state of rhenium in **5** is shown by the Re ($4f_{7/2}$) binding energy of 45.6 eV in the X-ray photoelectron spectroscopy (XPS), only slightly lower than in Re_2O_7 (46.7 eV).[9]
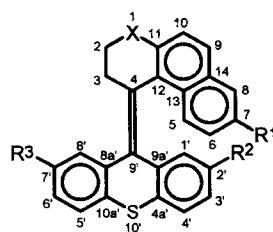
The use of polyhedral skeletal electron theory to predict the extent of metal–metal bonding is central to the systematic study of cluster complexes. Previously, the effect of a 12-electron increase in cluster electron count could only be studied by using structurally similar clusters of different metals. A well-known example is found in the clusters $[Cp_4Fe_4(CO)_4]$ (60 electrons, six M–M bonds) and $[Cp_4Co_4S_4]$ (72 electrons, no M–M bonds).[10] The clusters **1** (54 electrons) and **4–6** (66 electrons) provide a particularly good example because all are based on the Pt_3Re core and because the intermediate 58- and 62-electron clusters are also known.[4] Similarly, the ability to increase the sum of the oxidation states of the metal atoms in the cluster **1** by six (**1** → **4**, **1** → **6**) or by 12 (**1** → **5**), while maintaining the cluster integrity is unprecedented.[11] There is a close analogy between the structure of the $Re(CO)_3(\mu\text{-O})_3$ unit in **4** and that proposed for rhenium carbonyl complexes bound to oxide supports. The chemistry of **4** gives credence to the theory that oxophilic rhenium centers are present at the oxide support/bimetallic alloy interface in supported Pt–Re catalysts.[1, 12]
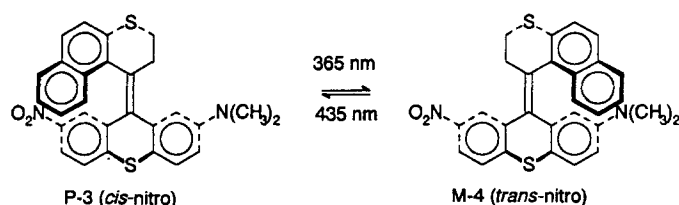
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A Highly Stereoselective Optical Switching Process Based on Donor–Acceptor Substituted Dissymmetric Alkenes**

Wolter F. Jager, Johannes C. de Jong, Ben de Lange, Nina P. M. Huck, Auke Meetsma, and Ben L. Feringa*

The development of organic materials for optical data storage and molecular optical devices requires components whose physical properties can be modulated by light.[1] For a few bistable molecular systems based on photocyclization reactions impressive results have been obtained.[2] So far the bistable molecules are detected primarily by UV/Vis spectroscopy (photochromism),[1, 2] although detection based on changes in other properties such as refractive index[3] and conductivity[4] is also successfully employed.

The first chiroptical molecular switch, based on the bistability of the helical *cis* and *trans* thioxanthenes 1 and 2, was reported by our group.[5] These pseudoenantiomers[6] interconvert stereospecifically M-*cis* ⇌ P-*trans*; in other words the *cis–trans* isomerization of 1 and 2 is accompanied by a reversal of helicity. For these compounds a difference in the relative proportion of the two photostationary states of only 4% was reached (irradiation with *λ* = 300 nm: 64% M-*cis*, 36% P-*trans*; irradiation with *λ* = 250 nm: 68% M-*cis*, 32% P-*trans*), whereas 10% racemization (M-*cis* → P-*cis*; P-*trans* → M-*trans*) was observed after 20 switching cycles.[5]

We describe here a remarkably selective switching process based on the intrinsic chirality of donor–acceptor substituted

[*] Prof. Dr. B. L. Feringa, Dr. W. F. Jager, Dr. J. C. de Jong, Dr. B. de Lange, Drs. N. P. M. Huck, Drs. A. Meetsma
Department of Organic and Molecular Inorganic Chemistry
Groningen Centre for Catalysis and Synthesis
University of Groningen
Nyenborgh 4, NL-9747 AG Groningen (The Netherlands)
Telefax: Int. code + (50)634296

1 : X = CH₂, R¹ = CH₃, R² = OCH₃, R³ = H
2 : X = CH₂, R¹ = CH₃, R² = H, R³ = OCH₃
3 : X = S, R¹ = H, R² = NO₂, R³ = N(CH₃)₂
4 : X = S, R¹ = H, R² = N(CH₃)₂, R³ = NO₂

dissymmetric *cis* and *trans* 3 and 4, respectively (Scheme 1). The absorption maxima of these compounds are red-shifted relative to those of 1 and 2, allowing the switching process to take place in the visible. Moreover, increased thermal and photochemical stability towards racemization was obtained by the introduction of a sulfur atom at the 1-position.

Scheme 1. Chiroptical molecular switch based on the photoisomerization of P-3 and M-4.

The photochemical isomerization P-3 (*cis*-nitro) ⇌ M-4 (*trans*-nitro) (Scheme 1) is detected by chiroptical techniques. Major advantages over other photochromic systems are: a) a more discriminative detection technique, since unlike UV spectra, circular dichroism (CD) and optical rotatory dispersion (ORD) spectra of both molecular forms P-3 (*cis*-nitro) and M-4 (*trans*-nitro) can reverse sign and are roughly mirror images; b) photochemical isomerization during readout[11] (fatigue) can be excluded by using ORD techniques employing a wavelength outside the absorption region.

The formation of the central double bond is the key step in the synthesis of 3 and 4 outlined in Scheme 2. Hydrazone 5 was
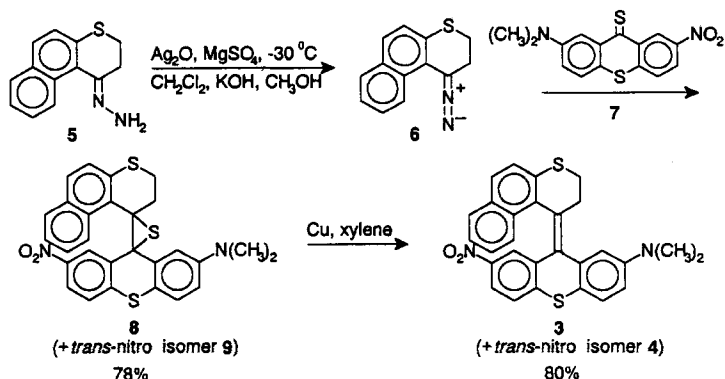
Scheme 2.

oxidized to the corresponding diazo compound 6 (Ag₂O, CH₂Cl₂, −30 °C), and subsequent 1,3-dipolar cycloaddition[7] with thioketone 7 was followed by extrusion of N₂ to provide the episulfides 8 (*cis*-nitro) and 9 (*trans*-nitro). The episulfides were desulfurized by reduction with copper powder to afford