absorption maximum of the Ag^{II}TPPC4 (system I) complex (542 nm) is far removed from excitation. We can thus conclude that, in the SERS spectrum of free-base porphyrin in the colloid/Triton X-100/TPPC4 system, the relative decrease in the surface enhancement of Raman scattering is compensated for by a contribution of the resonance enhancement.

If all of the above facts are combined together, they prove that the surfactant coverage of Ag colloid particles prevents the direct chemical interaction of the porphyrin with the metal surface while the scattering enhancement remains sufficient for obtaining a good quality SERS spectrum. Moreover, our recent experiments show that the selection of the specific molecular structure of surfactant is not the only possibility and that, e.g., synthetic polypeptides can play a similar role.[12]

The results can be summarized as follows. The formation of the Ag^{II}TPPC4 complex upon chemisorption of TPPC4 on the Ag colloid surface represents an extreme example of the metal surface influence upon molecular structure of a species studied by SERS. The disadvantage of alteration of the structural information provided by SERS (as induced by metalation of the porphyrin) is compensated for by the possibility to use this alteration to probe the porphyrin–surface geometry. For example, we took advantage of these effects to monitor porphyrin–peptide interactions.[12] On the other hand, the surfactant application can be one way to minimize the metal surface perturbational effect on the molecule studied. Our results demonstrate the advantages as well as the drawbacks of SERS spectroscopy of porphyrins and give several hints for extraction of information about the porphyrin-containing systems of biological importance from the SERS data.

Registry No. Ag, 7440-22-4; Triton X-100, 9002-93-1; TPPC4, 14609-54-2.

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High Oxidation State Compounds Containing Hydrazine and Hydrazido Ligands Bound to a $W(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[2,6\text{-}NC_5H_3(CH_2NTosyl)_2]$ Core

Recently, we have found that complexes that contain the MCp^*Me_3 core ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Mo or W,[1] Re[2]) and a variety of N_2H_x or NH_y ligands can be prepared and that the N–N bond can be cleaved in η^2-hydrazine to give ammonia, catalytically in the case of M = Mo or W in the presence of protons and a reducing agent.[1] In the belief that long-term stability of such catalysts will be limited by loss of alkane in the presence of acid, we have begun to search for related systems that do not contain metal–carbon bonds. We report examples of such complexes here.

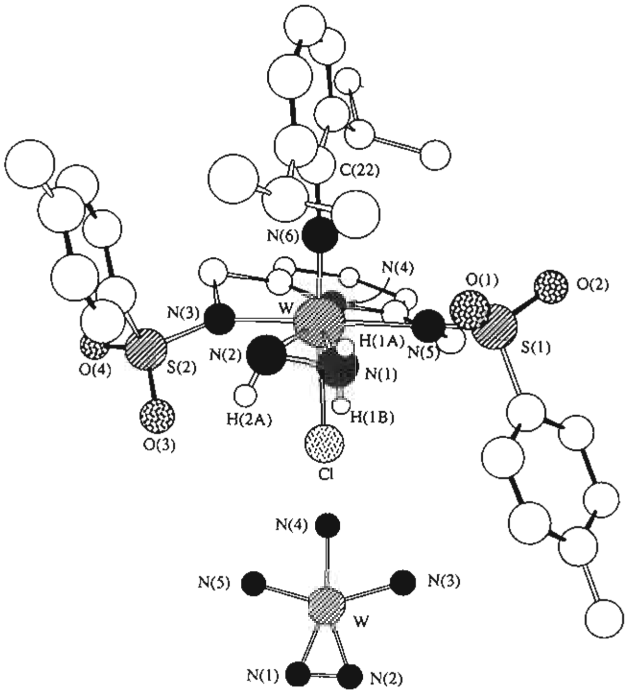
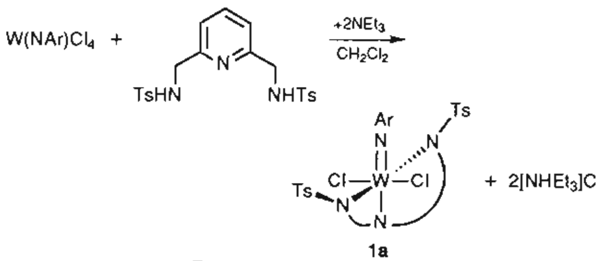


Figure 1. A view of **2** (with hydrogen atoms on the hydrazido(1−) ligand shown) and a view showing the equatorial ligands in the pentagonal arrangement.

A core of the type $M(NAr)[2,6\text{-}NC_5H_3(CH_2NR)_2]$ (Ar = $2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) would be isolobal with the MCp^*Me_3 core, *if* the imido ligand behaves as a $2\pi,1\sigma$ ligand and if square-pyramidal derivatives (pyridine donor *not* trans to the imido ligand) are favored. $W(NAr)Cl_4$[3] reacts with 1 equiv of 2,6-pyridinebis(tosylmethylamine)[4] in the presence of 2 equiv of NEt_3 to give *trans*-$W(NAr)[N(NTs)_2]Cl_2$ ($N(NTs)_2 = 2,6\text{-}NC_5H_3\text{-}(CH_2NTosyl)_2$) (**1a**) in 80% yield (eq 1). The singlet at 5.48 ppm in the proton NMR spectrum for the methylene protons in the $N(NTs)_2$ ligand is consistent with a C_{2v} symmetry for **1a**. Subsequent reaction of **1a** with AgOTf (OTf = triflate) gives a related molecule, $W(NAr)[N(NTs)_2](OTf)Cl$ (**1b**) (eq 2), in 89% isolated yield. The proton NMR spectrum for **1b** reveals an AB



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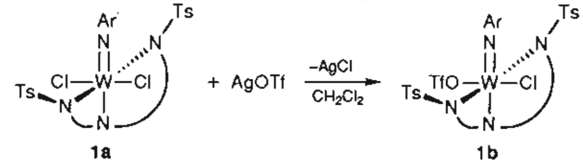

(2)

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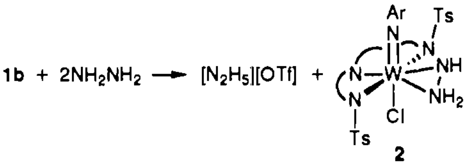
quartet for the methylene protons, which suggests that no mirror plane passes through the methylene carbon atoms. However, the aryl ring must not be able to rotate rapidly, since two types of isopropyl methyl groups are observed by NMR.

The reaction between **1b** and 2 equiv of hydrazine yields W(NAr)[N(NTs)$_2$](η^2-NHNH$_2$)Cl (**2**) (eq 3) in 49% yield. We



2

(3)

propose that the reaction proceeds via a hydrazine adduct (see **3** below), which is subsequently deprotonated rapidly by hydrazine. The structure of **2**, as determined in an X-ray crystallography study, is shown in Figure 1.[5] The core of the molecule can be loosely described as a pentagonal bipyramid with the tridentate and hydrazido ligands defining the equatorial plane and the imido and chloride ligands occupying axial positions. The five ligands in the equatorial positions bend away slightly from the ideal plane containing them and the W atom; the W atom sits ~0.23 Å above the least-squares plane defined by the five nitrogen atoms. Both WC$_2$N$_2$ rings are puckered. The fact that the N(3)-W-N(5) angle (146.0 (3)°) is considerably less than 180° allows the hydrazido ligand to bind to W in η^2-fashion in the pseudoequatorial plane. The W-N(1) and W-N(2) distances (2.07 (1) and 2.061 (8) Å) and N(1)-W-N(2) angle (39.8 (4)°) are within experimental error the same as those found in isoelectronic Cp*WMe$_4$(η^2-NHNH$_2$),[6] whose structure is roughly analogous (three methyl groups and the hydrazido ligand in a pentagonal arrangement). The N(1)-N(2) distance (1.41 (1) Å) should be compared with the N-N distances in the two independent molecules of WCp*Me$_4$(η^2-NHNH$_2$) (1.39 (3) and 1.35 (3) Å),[6] [WCp*Me$_3$(η^2-NHNH$_2$)]$^+$ (1.39 (1) Å),[6] and [Co{MeC(CH$_2$PPh$_2$)$_3$}(η^2-NHNH$_2$)]$^+$ (1.384 (14) Å).[7] It is interesting to note that H(2A), which was located, points away from the imido ligand and that the O(3)···H(2A) distance is only 2.2 (1) Å, which could be construed as a hydrogen bond. (The NH proton in Cp*WMe$_4$(η^2-NHNH$_2$) also points away from the Cp* ligand.) In this circumstance no orbital is available to receive the lone electron pair on N(2), and if the imido ligand in **2** behaves as a 2π, 1σ ligand, the metal electron count in any case is 18.

One would expect that the hydrazido ligand in **2** could be protonated easily. Addition of 1 equiv of triflic acid to **2** yields yellow [W(NAr)[N(NTs)$_2$](η^2-NH$_2$NH$_2$)Cl][OTf] (**3**). Compound **3** is virtually insoluble in hydrocarbon solvents and diethyl ether, and only sparingly soluble in dichloromethane and THF. The structure of **3** is proposed to be analogous to that of **2**. Note added in proof: The structure of **3** has now been solved and shown to be essentially the same as that of **2** with W-N bond lengths of 2.11 and 2.12 Å and an N-N bond length of 1.42 Å. The proton NMR spectrum of **3** in CD$_2$Cl$_2$ shows only one broad resonance at 8.60 ppm for the protons in the NH$_2$NH$_2$ ligand, consistent with rapid proton exchange or hydrazine exchange in η^2-N$_2$H$_4$ under these conditions. Low solubility of **3** has prevented elucidation of the exchange process at low temperature. Monometallic complexes that contain unsubstituted η^2-hydrazine are extremely rare.[7] There is a remote possibility that the proton has added somewhere other than the electron pair on N(2).

Reduction of **2** and **3** by zinc amalgam and subsequent addition of concentrated HCl to the reaction mixture generates 1.19 and 1.67 equiv of ammonia, respectively.[8] Analogous reactions in the presence of 2,6-lutidine hydrochloride yield only 0.46 and 0.61 equiv of ammonia, respectively. We believe that protonation of the hydrazido(1−) and hydrazine ligands in **2** and **3** competes with reduction, although experimental problems so far have prevented confirmation that hydrazine is formed in such circumstances.

We conclude that the W(NAr)[N(NTs)$_2$] core shows some characteristics of the WCp*Me$_3$ core[1,2] in forming complexes that contain N$_2$H$_y$ ligands which can be reduced in the presence of protons to give ammonia. Future studies will focus on variations of this ligand set and expansion of the chemistry of complexes that contain it and related ligand systems that are relevant to the reduction of dinitrogen to ammonia. Note added in proof: An example of a NHNH$_2$(1−) complex of molybdenum in a sulfur coordination sphere has just been published (Sellmann, D.; Kern, W.; Pöhlmann, G.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1991**, *185*, 155). A NHNMe$_2$ derivative was structurally characterized.

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Supplementary Material Available: Text giving experimental details, NMR spectral data, analytical data, and a description of the X-ray structure determination, a labeled ORTEP drawing, and tables listing crystal data, final positional parameters, final thermal parameters, bond distances and angles, and least-squares planes (19 pages); a listing of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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(5) Crystal data for WClS$_2$O$_4$N$_7$C$_{35}$H$_{44}$ at −72 (1) °C: monoclinic, space group $P2_1/n$, a = 13.892 (2) Å, b = 16.111 (3) Å, c = 16.537 (3) Å, β = 95.60 (2)°, Z = 4, ρ = 1.641 g cm^{-3}, μ = 34.31 cm^{-1}. A total of 5236 reflections were collected in the range of 2.8° < 2θ < 45° ($h,k,\pm l$). Of these, 5082 were unique and 3534 with $I > 3.00\sigma(I)$ were used in the structure solution. $R(F)$ = 0.043 and $R_w(F)$ = 0.045. One acetonitrile molecule was found in each asymmetric unit of the cell. There is no contact between the tungsten molecule and acetonitrile in the asymmetric unit.

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(8) (a) Complexes **2** and **3** ((3–4) × 10^{-2} mmol) and 6 equiv of zinc amalgam (and 12 equiv of lutidine hydrochloride) were placed in a 50-mL Schlenk flask, and then cold THF (10 mL) was added. The reaction flask was sealed with a rubber septum, and the mixture was stirred at room temperature for two days. Concentrated HCl (0.1 mL) was added to the reaction mixture by syringe. The solvent was then removed in vacuo, and the residue was extracted with distilled water. The colorless extract was tested quantitatively for ammonia by using the indophenol method.[8b] (b) Chaney, A. L.; Marbach, E. P. *Clin. Chem.* **1962**, *8*, 130.

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Low-Temperature Spectroelectrochemical Study of (Bu$_4$N)Re$_2$Cl$_9$ and (Bu$_4$N)$_2$Re$_2$Cl$_8$: Discovery of Re$_2$Cl$_9{}^{3-}$

In the 27 years since the recognition[1] of the first quadruple metal-metal bond in Re$_2$Cl$_8{}^{2-}$, dirhenium halide complexes have continued to challenge both experimentalists and theoreticians. We now report that the spectroelectrochemical study of (Bu$_4$N)$_2$Re$_2$Cl$_8$ and (Bu$_4$N)Re$_2$Cl$_9$ at low temperature has resulted in the identification of the new species Re$_2$Cl$_8{}^0$, Re$_2$Cl$_9{}^0$, Re$_2$Cl$_9{}^{3-}$, and transient Re$_2$Cl$_9{}^{4-}$. Furthermore, the octa- and nonahalide forms are shown to interconvert in a systematic fashion, controlled by oxidation level.

Redox processes alter the occupancy of the metal-based orbital manifold responsible for Re-Re multiple bonding in the octahalide. Elegant electrochemical investigations[2] of variously substituted

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