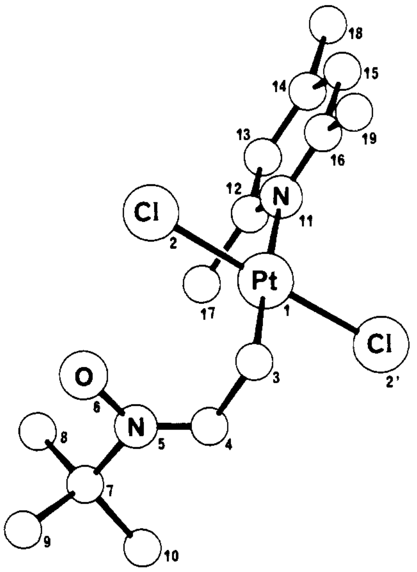

Figure 2. Molecular structure of complex **3**.[8] Typical distances not discussed in the text: C(3)-C(4), 1.53 (5); Pt-N(3), 2.15 (3) Å. Angles: C(3)-C(4)-N(5), 120 (3); C(4)-N(5)-O(6), 126 (3); N(5)-O(6)-Cl(2), 98 (3)°.

indicate the existence of a priviledged conformation of complex **3** similar to that observed in the crystalline state (Scheme I).

The ^1H NMR spectrum of complex **1** [$CDCl_3$, $Si(CH_3)_4$ ppm]—δ 1.63 and 1.72 (2 s, 2 × 9 H, $(CH_3)_3C$), 3.50 (d $J_{H\text{-}H}$[9] = Hz, +dd, $J_{^{195}Pt\text{-}H} = 84$, $J_{H\text{-}H} = 9$ Hz, 2 H, $Pt\text{-}CH_2$), 7.77 (d,[12] $J_{H\text{-}H} = 9$ Hz, +dd,[12] $J_{^{195}Pt\text{-}H} = 33$, $J_{H\text{-}H} = 9$ Hz, 1 H, CH=), 8.15 (s[12] + d,[12] $J_{^{195}Pt\text{-}H} = 25$ Hz, 1 H, exchanged with D_2O, OH)—is very similar to that of complex **3**, the signals of the collidine ligand being replaced by those of coordinated tBuNO (1.72, s, 9 H). Therefore complex **1** is very probably transformed into complex **3** upon ligand exchange between the coordinated tBuNO and the collidine added to the mixture of complexes **1** and **2** (vide supra) (Scheme I). The unstability of complex **1** compared with complex **3** should derive from the larger trans labilizing ability of the tBuNO ligands compared to collidine,[1] therefore favoring its cis position relative to a strongly labilizing alkyl ligand. The isomerization of complex **1** in the presence of excess tBuNO, leading to the corresponding *cis*-dichloro complex, should increase the lability of the chloride ligands and favor HCl elimination and the formation of complex **2**.

The formation of complexes **1** and **2** is the first example of a reaction between a nitrosoalkane and ethylene coordinated to a transition metal. The reactions of nitrosoalkanes and -arenes with olefins are not yet fully understood.[15] Since a simple addition of free tBuNO to coordinated ethylene is unlikely, because nitrosoalkanes are not known to exhibit a nucleophilic reactivity,[16] the reported reaction could occur between ethylene and tBuNO both activated by platinum. The mechanism and possible developments of this reaction, which leads to a double functionalization of ethylene, are under study.

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Supplementary Material Available: Atomic fractional coordinates and thermal parameters (Table 1), anisotropic thermal parameters of heavy atoms (Table 2), and interatomic distances and angles of complexes **2** and **3** (3 pages). Ordering information is given on any current masthead page.

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Dioxygen Ligand Transfer. Synthesis and Rearrangement of a Heterobimetallic Dioxygen Adduct

Sir:

Considerable research has recently been devoted to dioxygen complexes of transition metals and in particular to the equilibrium involving the absorption-desorption of molecular oxygen.[1-5] Very little has been done, however, on the process of transferring the dioxygen ligand to a third entity. We now report a case in which the transfer of molecular oxygen from one metal (Co) to another (Mo) can be followed.

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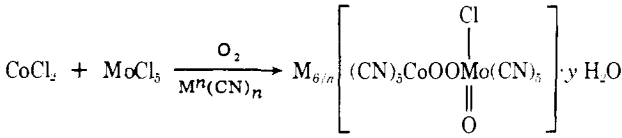
An earlier study of model compounds for olefin autoxidation catalysts led to the synthesis of bimetallic dioxygen adducts containing both cobalt and molybdenum[6,7] (eq 1).

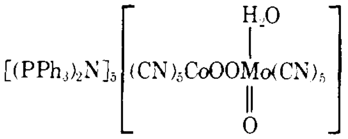


$$\mathrm{CoCl_2 + MoCl_5 \xrightarrow[M^n(CN)_n]{O_2} M_{6/n}\left[(CN)_5CoOO\overset{\displaystyle Cl}{\underset{\displaystyle O}{Mo}}(CN)_5\right]\cdot y\,H_2O} \qquad (1)$$

1a, M = K
b, M = Ba
c, M = $(CH_3)_4N$
d, M = $(C_2H_5)_4N$

The low solubility of these compounds in organic solvents brought us to prepare the bis(triphenylphosphine)iminium salt. Addition of a chilled (0 °C) aqueous solution (0.01 M) of bis(triphenylphosphine)iminium chloride (7.0 g, 0.0122 mol) to the green reaction mixture of **1a** (0.0128 mol) precipitated a pale blue solid which was filtered, washed several time with water, and dried over P_2O_5 to give a pale green solid (**2**): IR (KBr) 3640-3200 (OH, H_2O), 2128, 2118, 2108, 2038 (-CN), 1640 (H_2O), 915-912 (Mo=O), 892 (O—O), 770 (?), 410 (Co—CN?), 355 (Mo—CN). Anal. Calcd for $C_{190}H_{152}CoMoN_{15}O_4P_{10}$: C, 71.90; H, 4.83; Co, 1.86; Mo, 3.02; N, 6.62; O, 2.02; P, 9.76. Found:[8] C, 70.40; H, 4.83; Co, 1.88; Mo, 2.98; N, 6.32; O, 2.01.

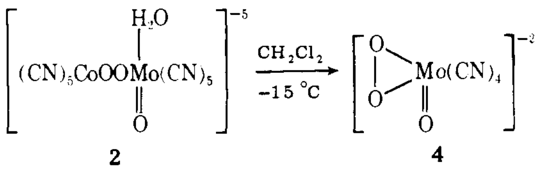
The absence of Cl and the absorption bands attributed to H_2O suggest a displacement of chloride ion during the cation exchange. The sulfuric acid treatment of **2** gave rise to 0.6 mol of O_2/mol of peroxo ligand and only traces of H_2O_2.[9] This behavior is analogous to the other salts having a Mo=O group.[7] The thermal treatment of **2**, on the other hand was reversible and thus different from compounds **1**. Upon heating in the solid state at 188 °C under reduced pressure (4.10^{-2} mm), **2** gave a beige-colored solid (**3**) which under N_2 failed to oxidize I^- and lacked the 890-cm^{-1} absorption band attributed to O-O vibration. When **3** was placed in an oxygen atmosphere, it regained the pale green color as well as the peroxydic character (chemical and spectroscopic) of **2**. This reversibility could be repeated several time, but was not observed in solution.



$$\mathrm{[(PPh_3)_2N]_5\left[(CN)_5CoOO\overset{\displaystyle H_2O}{\underset{\displaystyle O}{Mo}}(CN)_5\right]}$$

2

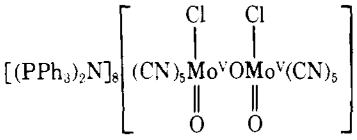
Another property of **2** different from that of **1** was its facile rearrangement in organic solvents.[10] Standing at −15 °C for a few hours in CH_2Cl_2, CH_3NO_2, or CH_3CN, and $(C_2H_5)O$, **2** yielded yellow-amber crystals, characterized as a peroxo molybdenum complex (**4**):[11] IR[12] (KBr) 2220, 2160, 2130, 2100, 2060 (-CN), 936 (?), 915 (Mo=O), 900 (O—O), 860-850 (Mo—O?), 360 (Mo—CN). Anal. Calcd for $C_{76}H_{60}MoN_6O_3P_4$: C, 68.88; H, 4.56; Mo, 7.24; N, 6.34; O, 3.62; P, 9.35. Found:[8] C, 68.22; H, 4.68; Mo, 6.98; N, 6.70; O, 4.77.



2 **4**

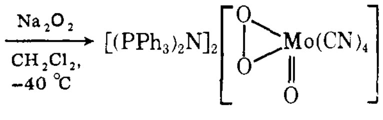
The presence of a peroxo ligand was confirmed by a standard iodometric titration, indicating the formation of 1 mol of H_2O_2/mol of **4**.[13] Treatment with sulfuric acid, on the other hand, gave no apparent O_2 evolution; this same behavior is also observed for other known molybdenum peroxo compounds.[14] Thermal treatment (188 °C, 4.10^{-2} h) yielded irreversibly a brownish solid lacking all peroxidic character.

Supporting evidence for the anion structure in **4** was obtained when **4** was prepared by a different synthetic route. Reacting the dimeric molybdenum(V) compound **5**[6] (0.5 g, 1.09×10^{-4} mol), known to be a precursor of **2**,[15] with sodium peroxide (0.053 g, 1.09×10^{-4} mol) suspended in 15 mL of CH_2Cl_2 at −40 °C yielded upon warming to room temperature and addition of diethyl ether and petroleum ether (2:3) a yellow solid (0.016 g, 1.17×10^{-4} mol, 53% yield) which was shown, after purification, to be identical (IR, melting point) with **4**.[16,17]



$$\mathrm{[(PPh_3)_2N]_8\left[(CN)_5\overset{\displaystyle Cl}{\underset{\displaystyle O}{Mo^V}}O\overset{\displaystyle Cl}{\underset{\displaystyle O}{Mo^V}}(CN)_5\right]}$$

5



4

All molybdenum peroxo compounds known have been obtained with the aid of either hydrogen peroxide or other peroxidic compounds.[4,18]

Formation of **4** in the presence of cobalt constitutes to our knowledge the first example of direct peroxidation of a molybdenum compound with oxygen. The necessity of the second metal to perform this could have implications in many multimetallic heterogeneous catalytic processes as well as certain biological oxygenation systems.

We are presently studying the mode of formation of the molybdenum peroxo compound **4** from the heterobimetallic complex **2**, as well as other bimetallic systems where similar transfers seem to be operative.

Acknowledgment. The authors are grateful to Dr. W. S. Sheldrick of G.B.F. in Braunschweig for performing the crystal structure determination.

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(9) Standard iodometric titration of **2** was identical with that of the corresponding potassium salt.[6]
(10) This facile rearrangement was the major cause of failure in obtaining a monocrystal of **2** for X-ray analysis.
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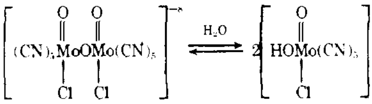

the monomer being the entity reacting to give **1a**.[14]
(16) It was suggested by a referee that reaction of **5** to give **4** could be due to NaO_2 impurities in commercial Na_2O_2. Treatment of **5** with KO_2 showed that this was not the case.

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Drastic Fluorescence Enhancement and Photochemical Stabilization of Cyanine Dyes through Micellar Systems

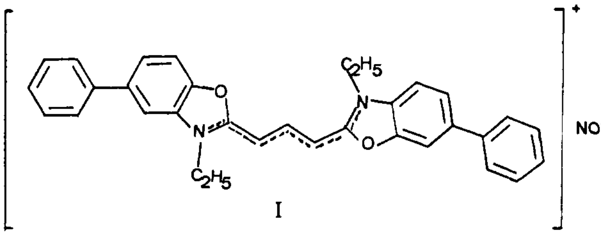
Sir:

Cyanine dyes play an important role as sensitizers in photographic processes.[1] Also, they have been widely employed as model chromophores in monolayer assemblies.[2] A common behavior found with this class of molecules is their photochemical instability. Conformational changes occurring after excitation along the polymethine chain was found to precede the degradation process.[3] These structural fluctuations account also for the relatively low fluorescence yield observed for a variety of cyanine dyes. In fact, by decreasing the flexibility of these molecules through chemical rigidization, high fluorescence yields and photostability may be obtained.[4]

In the present communication, micellar effects on the fluorescence behavior and photostability of the cyanine dye I will be examined. It will be shown that, by suitable choice of the micellar system, drastic enhancements of the emission intensity and stability of this dye can be achieved.

Fluorescence spectra were run on a Hitachi Perkin-Elmer MPF-44A spectrofluorimeter which is equipped with a corrected spectra unit. The instrument displays true fluorescence spectra, the measured quantity being photon flux per unit wavelength interval. The emission quantum yields were obtained by comparison with the standard quinine sulfate. Emission lifetimes were obtained using PRA single-photon counter.

The cyanine dye I was of high purity (elemental analysis, thin-layer chromatography). Sodium lauryl sulfate (NaLS), Merck, "for tenside investigation", was purified by repeated recrystallization from diethyl ether and water. The purified product was used to synthesize magnesium lauryl sulfate [$Mg(LS)_2$] and cadmium lauryl sulfate [$Cd(LS)_2$], whereby a previously described procedure[5] was followed. Deionized water was distilled from permanganate and subsequently twice from a quartz still.



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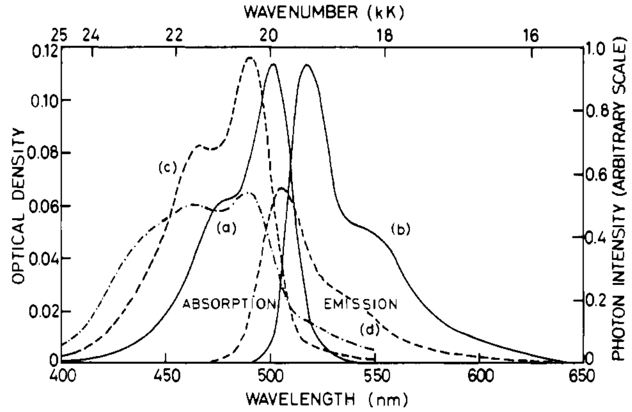

Figure 1. (a) Absorption spectrum of a solution of 10^{-6} M cyanine I in 10^{-2} M aqueous NaLS and (b) fluorescence spectrum of the same solution at an exciting wavelength of 480 nm. (c) Absorption spectrum of a 10^{-6} M cyanine I in water, and (d) fluorescence spectrum of the same at 480 nm excitation (scale is ten times the scale of b). (e) Absorption spectrum of a solution of 10^{-6} M cyanine I in water after 12 h.

Figure 1 displays the absorption and fluorescence spectrum of the cyanine dye I (10^{-6} M) in water and aqueous micellar solution. The optical phenomena in water were found to be time dependent. With freshly prepared solutions the spectra indicated by the dashed lines c and d were obtained. The absorption curve displays here a maximum at 484 and a shoulder at 465 nm, while the emission peak is located at 506 nm. The intensity of the principal absorption decreases with time, a broad shoulder appearing at ~440 nm. Concomitantly, the intensity of the fluorescence decreases. These observations are attributed to the effect of dye aggregation, the absorptions at 484, 465, and 440 nm being assigned to monomer, dimer, and H aggregates, respectively.

Addition of micellar NaLS to the aqueous solution induces drastic changes in the behavior of the cyanine dye. Time-dependent phenomena are no longer observed, the absorption and emission curves indicated by the solid lines in Figure 1 remaining unchanged over a period of days or weeks. The absorption band in the micellar solution shows essentially the same characteristic as the monomer dye, as observed in methanol. This is indicative of no chromophore aggregation in the former medium. The emission maximum is located at 517 nm which is red shifted by 11 nm with respect to water and 7 nm with respect to methanol. From these observations it may be inferred that the cyanine is predominantly associated with the surfactant aggregates. Attractive electrostatic and hydrophobic interactions occurring between the dye and the anionic micelle make such an association particularly favorable.

Apart from preventing dye association, the micellar aggregates also strongly enhance the fluorescence emission of the cyanine dye. Emission quantum yields obtained in several micellar and homogeneous phases are listed in Table I. Comparison of the ϕ_F values in NaLS solution with those in methanol and water indicates a fivefold enhancement in the former case and at least a fifteenfold one in the latter. Parallel with the augmentation of the quantum yield goes an increase in the excited-state lifetime. τ_F values in NaLS and methanol are 1.2 ± 0.2 and 0.5 ± 0.5 ns as determined by single-photon counting technique. This indicates that the decreased quantum yield in methanol is caused by an increase in the rate of radiationless relaxation processes and not to a change of the radiative rate constant.

This inhibition of the radiationless decay by the micellar aggregates may be rationalized in terms of a rigidization of the cyanine dye by the local environment encountered in the micelle. Compound I has hydrophobic and polar groups and hence is expected to be solubilized in the palisade layer of the aggregate. A common behavior found with such a type of molecules is that the polar groups tend to be directed toward the

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