pentaamine polyacrylonitrile complex, Figure 3, has an average peak potential that is shifted by almost 500 mV from that of the aquopentaamine complex to which the coated electrode was exposed. It falls very close to the reported formal potential of the corresponding acetonitrile complex measured in homogeneous solution.[14]

The nature of the surface chemistry which is responsible for the strong, long-lived attachment of the polymeric ligands to graphite surfaces has thus far been examined only cursorily. It was determined that pyrolytic graphite with edge planes exposed to the coating solutions could also be coated with PVP, but the resulting voltammograms for attached Ru(III)EDTA were more distorted and contained a larger number of smaller waves. This suggests that the presence of extensive oxygen functionality on the graphite may lead to less uniform environment within the polymer coatings. Platinum electrodes are also susceptible to dip coating by PVP, but the resulting films accept much smaller quantities of Ru-EDTA. Additional exploratory experiments are underway in these laboratories to extend the range of polymers, attachable metal complexes, and electrode materials that can be combined to yield electrode surfaces with catalytic and analytical utility.

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Rhenium Formyl and Carboxy Complexes Derived from the $(C_5H_5)Re(CO)_2(NO)^+$ Cation: Models for the Fischer–Tropsch and Water Gas Shift Reactions

Sir:

The conversion of coal into liquid fuels and petrochemicals is currently dependent upon the heterogeneous catalysis of the oxidation of CO in the water gas shift reaction 1[1] and of the reduction of CO as in the Fischer–Tropsch reaction 2.[2] The development of homogeneous analogues for both the catalysts and proposed intermediates involved in reactions 1 and 2 is the primary goal of much current research.[3,4]

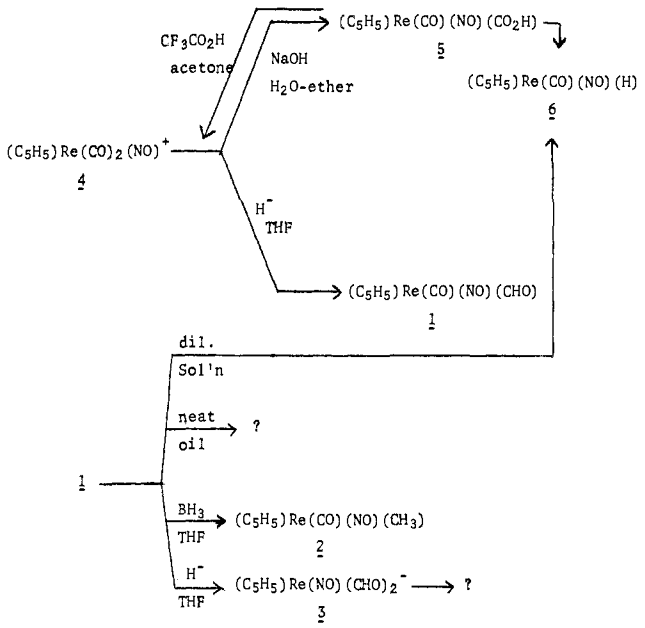
$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (1)$$

$$CO + H_2 \longrightarrow C_nH_{2n+2},\ C_nH_{2n+2}O_n,\ \text{etc.} \qquad (2)$$

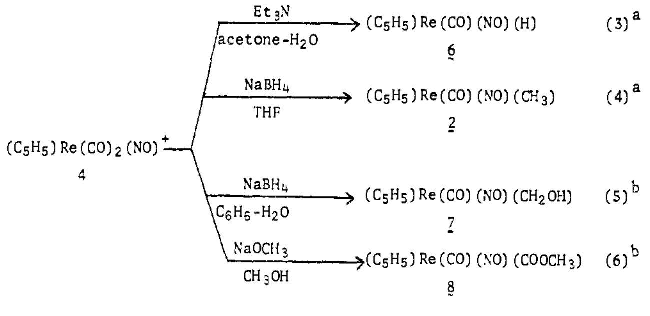
We,[4k] and others,[4e,5a,b] have recently reported the reduction of metal carbonyl compounds by borohydride reducing agents to give anionic metal formyl complexes which are models for initial intermediates in CO reduction.[2] The moderate kinetic stability observed for these anionic metal formyl compounds may be related to the delocalization of negative charge onto the formyl oxygen atom. We have now initiated studies of neutral metal formyl complexes to see if these compounds might also be stable. Previously, only two partially characterized neutral metal formyl complexes have been reported. $Os(Cl)(CO)_2(PPh_3)_2(CHO)$[5c] and $Ru(H)(Et_2O)(PPh_3)_3(CHO)$.[5d] Neutral formyl compounds were also desired for studies of the further reduction of metal formyl complexes since they should be more susceptible to reduction than anionic complexes.

We report here the synthesis and characterization of a neutral metal formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ (**1**), together with its subsequent reduction with borane to give $(C_5H_5)Re(CO)(NO)(CH_3)$ (**2**) and with lithium triethylborohydride to give the first diformyl metal complex $(C_5H_5)Re(NO)(CHO)_2^-$ (**3**) (Scheme I). In addition, we have reinvestigated the chemistry of $(C_5H_5)Re(CO)_2(NO)^+$ (**4**) (Scheme II)[6,7] and have prepared the new carboxy metal complex $(C_5H_5)Re(CO)(NO)(CO_2H)$ (**5**) which is an intermediate in the reaction of cation **4** with water to give

Scheme I. New Chemistry of the $(C_5H_5)Re(CO)_2(NO)^+$ Cation



Scheme II. Previously Reported Chemistry of the $(C_5H_5)Re(CO)_2(NO)^+$ Cation



[a] Reference 6. [b] Reference 7.

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$(C_5H_5)Re(CO)(NO)(H)$ (**6**).

The addition of a solution of potassium triisopropoxyborohydride in tetrahydrofuran (THF) to a stirred suspension of solid $(C_5H_5)Re(CO)_2(NO)^+PF_6^-$ (**4**) in THF at −78 °C results in a clear orange solution. The ^1H NMR spectrum (δ 16.29 (1 H), 5.87 (5 H); 60% vs internal *p*-xylene) and infrared spectrum (ν_{CO} 1991 (s), ν_{NO} 1723 (s), ν_{CHO} 1619 cm^{-1} (m)) of this solution indicate the formation of the neutral metal formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ (**1**). Ether extraction of the hydrolyzed reaction mixture, drying ($MgSO_4$), and *rapid* evaporation of solvent (all at 0 °C) yield slightly impure **1** as an orange oil (~25%). Similar results are obtained with lithium triethylborohydride as reducing agent except that little reaction occurs below −10 °C. While dilute solutions of **1** are only moderately air sensitive ($t_{1/2}$ for air oxidation was 5 min) and are relatively thermally stable ($t_{1/2}$ for conversion to $(C_5H_5)Re(CO)(NO)(H)$ in 25% yield was 10 h), the neat oil **1** undergoes more rapid decomposition to a mixture of products currently under investigation.

Treatment of a THF solution of formyl complex **1** with $BH_3{\cdot}THF$ (0 to 25 °C) yields the known methyl complex $(C_5H_5)Re(CO)(NO)(CH_3)$ (**2**) (~50%). This reaction constitutes the first transformation of a formyl ligand to a more reduced, coordinated ligand. The reaction closely parallels Masters' observation of the reduction of metal acyls to metal alkyls by borane.[8] The sequential conversion of **4** to **1** to **2** by H^- and BH_3, demonstrated here, clearly supports the postulated intermediacy of a metal formyl complex in the direct sodium borohydride reduction of **4** to **2** (reaction 4, Scheme II),[6] and of $(C_5H_5)W(CO)_3(PPh_3)^+$ to $(C_5H_5)W(CO)_2(PPh_3)(CH_3)$.[9]

Another potential intermediate in the reduction of cation **4** to methyl complex **2** has been reported by Nesmeyanov et al. (reaction 5), who claimed that the reduction of **4** with $NaBH_4$ in benzene-water gives $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**7**). Since the structure of **7** was assigned on the basis of its infrared spectrum and elemental analysis only,[10] we have reinvestigated this reaction using ^1H NMR. We have found that the primary product of reaction 5 is the formyl complex **1** identified by IR and NMR spectra. No evidence for significant amounts of **7** was obtained. The formation of **1** under the benzene-water conditions is not unexpected since the reaction of **4** with $NaBH_4$ should give **1** and BH_3. Since **1** is extracted into the benzene layer and BH_3 undergoes rapid hydrolysis in the water layer, there is little chance for **1** to be further reduced. A control experiment showed that **1** does not react with hydrogen gas, a byproduct of the BH_3 hydrolysis.

Since the properties of neither **1** nor its decomposition products agree with those reported for **7**,[10] the question remained as to what complex had been isolated by Nesmeyanov et al. from reaction 5.[7] The inevitable presence of NaOH in aqueous $NaBH_4$ suggested that, in analogy to reaction 6, $(C_5H_5)Re(CO)(NO)(CO_2H)$ might have been formed and not $(C_5H_5)Re(CO)(NO)(CH_2OH)$, compounds not easily distinguished by the data reported for **7**.[10] While we find that a 70% yield of $(C_5H_5)Re(CO)(NO)(CO_2H)$ (**5**) is in fact obtained from the addition of 1 mol of NaOH solution to cation **4** in ether-water, its properties do not match those reported for **7**. In particular, the metal carboxy complex **5** is a yellow, air-stable solid (gradual decomposition without melting under nitrogen starting at ~100 °C) which is insoluble in benzene, slightly soluble in ether, and soluble in acetone and THF: IR (Flurolube and Nujol mulls) ν_{OH} 2960 (m), 2860 (m), 2705 (m), and 2690 cm^{-1} (m), ν_{CO} 1985 (s), ν_{NO} 1715 (s), ν_{COO} 1585 (s), 1145 (s), and 1135 cm^{-1} (s); ^1H NMR (CD_3CN) δ 8.6 (1 H, v br), 5.84 (5 H). Treatment of **5** with CF_3CO_2H in acetone regenerates $(C_5H_5)Re(CO)_2(NO)^+$, while treatment with Et_3N in acetone converts **5** to hydride **6**. The acid-base properties of **4** and **5** provide strong evidence for Graham's postulated mechanism for reaction 3 of Scheme II.[6] While metal carboxy complexes have often been suggested as intermediates in metal carbonyl-$H_2{}^{18}O$ exchange reactions[11] and in homogeneous water gas shift systems,[3] only a few $M(CO_2H)$ and $M(CO_2^-)$ complexes have been described.[3a,12]

In another attempt to understand reaction 5, we have reacted cation **4** with excess hydride. Thus, treatment of **4** with 2 equiv of lithium triethylborohydride in THF (−78 to 25 °C) (or formyl complex **1** prepared in situ with 1 equiv of hydride) yields a solution of the first diformyl metal complex, $(C_5H_5)Re(NO)(CHO)_2^-$ (**3**): ^1H NMR δ 14.66 (2 H), 5.57 (5 H); IR ν_{NO} 1665 (s), ν_{CHO} 1540 (m) and 1530 cm^{-1} (m). The NMR and IR spectra of this solution gradually change, indicating the conversion of the diformyl complex to another species (already present to a slight extent in the initial spectra of **3**) which has not yet been adequately characterized.

Clearly, we have only begun to understand the chemistry of cation **4**. The wealth of its unusual derivatives hinted at by Scheme I and II can be attributed to the unique combination of several factors: (a) the generally high kinetic stability of complexes of the third row metals, (b) the substitutional inertness of most cyclopentadienyl carbonyl complexes, and (c) the enhanced reactivity of coordinated CO in cationic complexes. The result is, we believe, a system capable of providing a strikingly detailed and integrated model for key components of both the water gas shift and Fischer–Tropsch reactions.

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Supplementary Material Available: Experimental details for syntheses and reactions (5 pages). Ordering information is given on any current masthead page.

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(10) Characteristics reported[7] for $(C_5H_5)Re(CO)(NO)(CH_2OH)$: air-sensitive, pale brick solid (mp 69–71 °C dec); soluble in ethanol and methylene chloride and insoluble in hydrocarbons; IR (Nujol and hexachlorobutadiene mulls) 3300–3200 (s), 3120 (s), 2935 (s), 1980 (s), 1660 (s), 1420 (m), 1350–1260 (w), 1070 (m), 1010 (m), and 825 cm^{-1} (m); elemental analysis consistent with $C_7H_8NO_3Re$.

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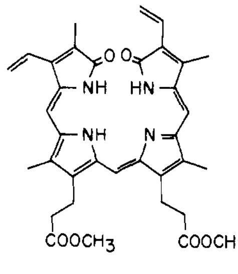
Spectroscopic Studies on Model Compounds of the Phytochrome Chromophore. Protonation and Deprotonation of Biliverdin Dimethyl Ester

Sir:

Phytochrome (P) is the pigment responsible for many photomorphogenic responses in plants.[1] It is a chromoprotein which is known to exist in two different forms, interconvertible by light: a red absorbing form (P_r, λ_{max} 667 nm) which is thermodynamically stable and physiologically inactive, and far-red absorbing form (P_{fr}, λ_{max} 730 nm) which is the physiologically active form of the pigment.[2,3] The chromophore of P has been found to have a bilitriene structure, but the structural differences between P_r and P_{fr} is still unclear. Various models have been suggested for explaining the phototransformation[4-13] and the importance of charged chromophoric structures has been recognized.[7,12]

We have started a systematic study of the spectral and conformational properties of model compounds for the chromophore of P aiming at a deeper insight into the mechanisms of action of the natural pigment. We report herein a spectroscopic study of the protonation and deprotonation of biliverdin dimethyl ester (**1**), a bile pigment which apparently has structure and absorption properties similar to those of the chromophore of P.[8,9,11] For the first time we present evidence, particularly obtained from resonance Raman experiments, on the presence of different protonated species of **1** in media of different acidities.



1

Compound **1** was synthetized from bilirubin and purified by recrystallization and column chromatography. The same results were obtained with a pure sample which was prepared in a different way by another group.[13] Chloroform was chromatographied on basic alumina before use. All solutions were oxygen free and were handled under N_2 and diffuse light. Proton concentration was controlled by shaking the chloroform solution of **1** with aqueous HCl of known concentration.

The pH dependence of the absorption spectrum is shown in Figure 1.

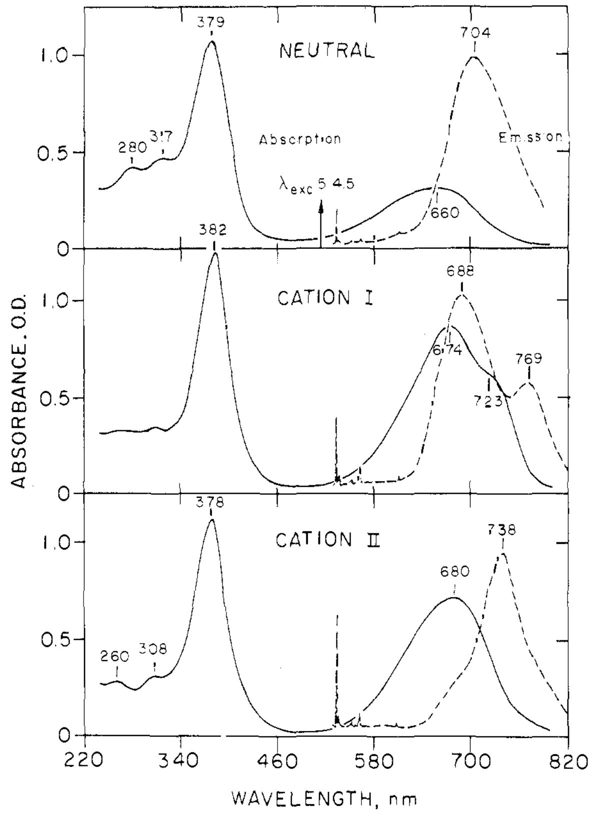


Figure 1. Absorption and emission spectra of **1** in chloroform. Notation on the ordinate refers to absorption spectra only; emission spectra (uncorrected) are given in relative units.

The absorption spectrum of **1** in neutral chloroform shows a broad band centered at 660 nm ("red" band), a strong band at 379 nm ("blue" band), and two small peaks at 317 and 280 nm (Figure 1, top). In mildly acidic solutions (shaking with 1 N HCl) major changes are observed in the red band (Figure 1, middle): the maximum is shifted to 674 nm, a shoulder is observed at 723 nm, and the overall intensity is increased by a factor of 2.5. The blue band shifts to 382 nm and the transitions at shorter wavelengths are smoothed out. In strong acidic solutions (shaking with concentrated HCl) a different absorption spectrum is observed (Figure 1, bottom). The red band slightly decreases in intensity, loses its structure, and shifts to 680 nm. The blue band shifts to the blue (378 nm) and two bands are observed at 308 and 260 nm. We shall refer to the species responsible for the absorption spectra observed in weak and strong acidic solutions as cation I and cation II, respectively.

Resonance Raman (RR) spectroscopy is a method which has already been successfully used to study chromophoric groups in photobiological systems.[14,15] The different identity of cations I and II is more evident from the RR spectra shown in Figure 2. The spectra presented here were measured using the 514.5-nm Ar^+ laser line for excitation, and represent the first report on the applicability of the RR technique to the study of bile pigments.[16]

The RR spectrum is drastically changed when passing from a neutral solution of **1** to cation I. Among other changes, the disappearance of vibrational lines at 1244, 1300, and 1435 cm^{-1}, the appearance of a strong band at 1317 cm^{-1}, and the shifts and intensity changes observed around 1600 and 1700 cm^{-1} are remarkable.

The RR spectrum of cation II is completely different from that of the neutral compound as well as from cation I. New vibrational lines appear at 1153, 1267, and 1325 cm^{-1}, two strong lines of comparable intensity can be observed at 1619 and 1631 cm^{-1}, and the vibration around 1700 cm^{-1} disappears.

Further evidence for the different character of cations I and II is extracted from the fluorescence spectra shown in Figure 1. These spectra were recorded on the Raman spectrometer. The high sensitivity of the detection system of the instrument allows the measurement of the emission spectra of **1** at room

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