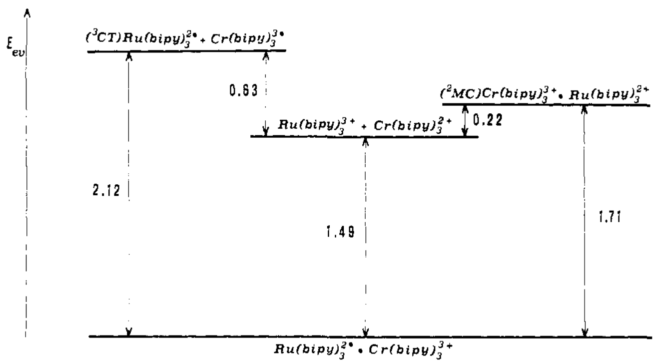

Figure 1. Energetics of the $\mathrm{Cr(bpy)_3}^{3+}/\mathrm{Ru(pby)_3}^{2+}$ system. The difference in SRP of the two couples gives the free energy of the redox products, while zero-zero transition energies are used for the two excited states. These excitation energies can be considered as free energies of excitation on the reasonable assumption that entropy changes associated with excitation are small.

$$\mathrm{Cr(bpy)_3}^{3+} \overset{h\nu}{\rightarrow}\rightarrow ({}^2\mathrm{MC})\mathrm{Cr(bpy)_3}^{3+} \quad (3)$$

$$\mathrm{Ru(bpy)_3}^{2+} \overset{h\nu}{\rightarrow}\rightarrow ({}^3\mathrm{CT})\mathrm{Ru(bpy)_3}^{2+} \quad (4)$$

$$({}^2\mathrm{MC})\mathrm{Cr(bpy)_3}^{3+} + \mathrm{Ru(bpy)_3}^{2+} \rightarrow \mathrm{Cr(bpy)_3}^{2+} + \mathrm{Ru(bpy)_3}^{3+} \quad (5)$$

$$({}^3\mathrm{CT})\mathrm{Ru(bpy)_3}^{2+} + \mathrm{Cr(bpy)_3}^{3+} \rightarrow \mathrm{Ru(bpy)_3}^{3+} + \mathrm{Cr(bpy)_3}^{2+} \quad (6)$$

$$({}^3\mathrm{CT})\mathrm{Ru(bpy)_3}^{2+} + \mathrm{Cr(bpy)_3}^{3+} \rightarrow \mathrm{Ru(bpy)_3}^{2+} + ({}^2\mathrm{MC})\mathrm{Cr(bpy)_3}^{3+} \quad (7)$$

In order to discriminate between these possible pathways, flash experiments have been carried out using I^- as a selective scavenger of $({}^2\mathrm{MC})\mathrm{Cr(bpy)_3}^{3+}$. A concentration of 5×10^{-3} M I^- is sufficient to completely quench the emission of $\mathrm{Cr(bpy)_3}^{3+}$. Flash experiments have shown that in these conditions the quenching of $({}^2\mathrm{MC})\mathrm{Cr(bpy)_3}^{3+}$ by I^- is not accompanied by the formation of any observable amounts of $\mathrm{Cr(bpy)_3}^{2+}$.[17] When solutions containing 1×10^{-4} M $\mathrm{Cr(bpy)_3}^{3+}$, 3.3×10^{-5} M $\mathrm{Ru(bpy)_3}^{2+}$, and 5×10^{-3} M I^- are flashed, $\mathrm{Cr(bpy)_3}^{2+}$ is still observed as a transient product, but in smaller amounts (about one half) than observed in the absence of I^-. Since complete scavenging of $({}^2\mathrm{MC})\mathrm{Cr(bpy)_3}^{3+}$ gives partial disappearance of the $\mathrm{Cr(bpy)_3}^{2+}$ product, the conclusion is that both electron-transfer pathways, i.e., reactions 3 and 5, and reactions 4 and 6, take place in the $\mathrm{Cr(bpy)_3}^{3+}/\mathrm{Ru(bpy)_3}^{2+}$ system. The energetics of this system is shown in Figure 1. The thermal back-electron-transfer reaction (reaction 8),

$$\mathrm{Cr(bpy)_3}^{2+} + \mathrm{Ru(bpy)_3}^{3+} \rightarrow \mathrm{Cr(bpy)_3}^{3+} + \mathrm{Ru(bpy)_3}^{2+} \quad (8)$$

which involves a free energy change of −34.6 kcal/mol, has a bimolecular rate constant $k_8 = 2.6 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ as determined from the second-order decay of the $\mathrm{Cr(bpy)_3}^{2+}$ transient.

The results obtained on the $\mathrm{Cr(bpy)_3}^{3+}/\mathrm{Ru(bpy)_3}^{2+}$ system demonstrate experimentally the electron-transfer mechanism proposed by Bolletta et al.[13] for the mutual luminescence quenching of these complexes. This system is remarkable in the fact that the same pair of high-energy products is obtained irrespective of the absorbing species. Actually, the reaction uses a wide spectral region of the exciting light and is efficient over a wide range of relative concentrations of the reactants.

The results described here show that the metal-centered doublet state of $\mathrm{Cr(bpy)_3}^{3+}$ can act as a strong oxidizing agent. The extension of studies on excited-state electron-transfer process of coordination compounds by flash techniques seems to be worthwhile, especially in view of the relevance of these systems as catalysts in solar energy conversion.[18,19] In this regard, it might be pointed out that the $\mathrm{Cr(bpy)_3}^{3+}/\mathrm{Ru(bpy)_3}^{2+}$ system is capable of converting a considerable fraction of the absorbed light energy (Figure 1). It might also be interesting to notice that both of the primary photoproducts of this system have been independently found to cause decomposition of water, either by reduction ($\mathrm{Cr(bpy)_3}^{2+}$)[20] or by oxidation ($\mathrm{Ru(bpy)_3}^{3+}$).[18]

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Tri-μ_2-carbonyl-tris(η^5-cyclopentadienyl)-*triangulo*-trirhodium. A New, Improved Preparation and Some Observations on Its Dynamic Properties[1]

Sir:

Two isomers of $\mathrm{Cp_3Rh_3(CO)_3}$ (Cp = η^5-$\mathrm{C_5H_5}$), isolated after prolonged photolysis of $\mathrm{CpRh(CO)_2}$, were shown by single-crystal x-ray diffraction to have structures **1**[2a] and **2**.[2b] These structures have figured prominently in discussions of trimetallic carbonyl clusters as models for solution structures[3] or for intermediates in carbonyl scrambling processes.[4,5] However, little information has been available concerning whether the rhodium trimers maintain the same structures in solution, whether they are fluxional, or to what extent they interconvert.[4,6,7] We have discovered a new preparation of $\mathrm{Cp_3Rh_3(\mu_2\text{-}CO)_3}$ (isomer **1**) that, in providing **1** in convenient

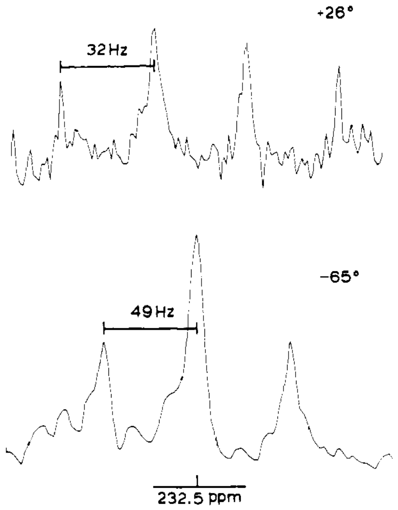
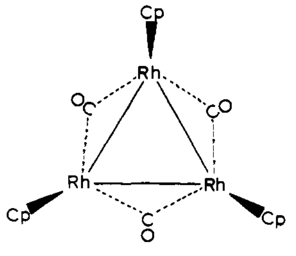
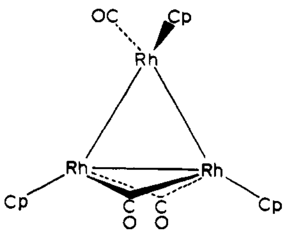


Figure 1. Carbonyl ^{13}C NMR spectra for $Cp_3Rh_3(\mu_2\text{-}CO)_3$ (1) in the slow-exchange (−65 °C) and fast-exchange (26 °C) limits.

quantities, has allowed examination of its solution structure and dynamics.



1



2

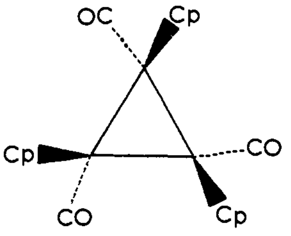
Shvo and Hazum recently reported that Me_3NO strongly facilitates formation of (diene)$Fe(CO)_3$ complexes from $Fe(CO)_5$.[8] This result suggested that such an oxidative decarbonylation reaction might provide a general means of producing unsaturated intermediates (eq 1).[9]

$$L_nMCO + Me_3N^+O^- \rightarrow L_nM + CO_2 + Me_3N \quad (1)$$

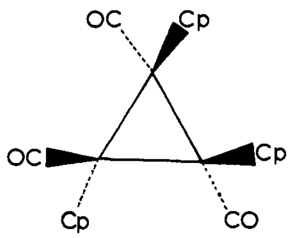
In the absence of added ligand the unsaturated species could interact with its saturated precursor to form a metal–metal bond. We have found the interaction of $CpRh(CO)_2$ with Me_3NO to provide an efficient route to isomer **1** together with the known dimer $Cp_2Rh_2(CO)_3$[7,10] (**3**) and a new tetrameric compound $Cp_4Rh_4(CO)_2$ (**4**). Thus, refluxing a mixture of $CpRh(CO)_2$ and hydrated Me_3NO (ca. 1 equiv) in benzene for 1–2 h followed by preparative TLC affords green **1** (30–60%), red **3** (10–25%), and black **4** (∼5%) together with smaller amounts of presently unidentified products.[11] The formulation of **4** follows from its field-desorption mass spectrum (*m/e* 728 M^+), and infrared and NMR data[13] support a carbonyl face-bridged structure analogous to that recently proposed for $Cp_4Co_4(CO)_2$.[14]

The field-desorption mass spectrum (*m/e* 588, M^+) of the green product together with its solid state IR data (ν_{CO}, KBr, 1827 s, 1783 m, 1766 s; lit.,[2b] 1820 vs, 1776 sh, 1761 vs, 1740 sh, 1715 sh) establish it as isomer **1**. Furthermore, its solution IR (ν_{CO}, CH_2Cl_2, 1849, 1793 cm^{-1}) and ^1H NMR (τ 4.47, singlet at 28 and −50 °C) spectra suggest adoption of structure **1** in solution as well. Confirmation of this suggestion comes from the ^{13}C NMR spectrum (see Figure 1) of 50% ^{13}CO-enriched material (prepared from enriched $CpRh(CO)_2$), which consists at −65 °C of a triplet ($J_{Rh\text{-}C}$ = 49 Hz) centered 232.5 ppm downfield of Me_4Si. At 26 °C the spectrum is a quartet ($J_{Rh\text{-}C}$ = 32 Hz),[16] which establishes complete scrambling of the CO ligands over the Rh_3 framework.

We have not observed isomer **2** in any of our preparations, nor is there any evidence in the IR or NMR spectra of **1** for the presence of small amounts of **2**. It has been suggested that carbonyl site exchange in the two isomers must be slow or else they could not have been separately isolated.[7] However, examination of their structures shows that symmetrical movement of the bridging carbonyls to terminal positions does not generate identical intermediates. On the contrary, each idealized intermediate preserves the symmetry, C_{3v} or C_s, of its precursor. The C_{3v} intermediate generated from **1** has three carbonyls on one side of the Rh_3 triangle, whereas the C_s species formed from **2** has two carbonyls on one side of the triangle and one on the other. Interconversion of the two intermediates would require a localized 180° rotation of one entire Rh(CO)Cp unit. Re-formation of triply bridged **1** from the C_{3v} intermediate ultimately allows each CO ligand to visit each rhodium atom. Significantly, the carbonyls in the C_s intermediate are appropriately aligned for re-formation of the double bridge in **2** along a new edge of the triangle.[17] Repetition of this process also allows each CO ligand to visit all three rhodium atoms, but carbonyls on opposite sides of the triangle are not equilibrated, and a 2:1 pattern of quartets is predicted for the fast exchange limit.[19] Thus, carbonyl scrambling is possible for both isomers of $Cp_3Rh_3(CO)_3$, even though they are not readily interconverted. Verification of the behavior predicted for isomer **2** is being sought.



C_{3v}



C_s

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(11) Conducting the reaction at room temperature in acetone affords a higher yield of dimer **3**. Experiments in the absence of Me_3NO establish (i) that **3** decomposes to 1 plus some **4** after ca. 2 h in refluxing benzene, (ii) that prolonged reflux of $CpRh(CO)_2$ in toluene produces 1 with **4** and some **3** in low total yield, (iii) that 1 is converted to **4** slowly in refluxing toluene but more quickly in refluxing xylene, and (iv) that interaction of 1 with diphenylacetylene in refluxing toluene provides the known compound $Cp_3Rh_3(CO)(C_2Ph_2)$.[12] These and other transformations involved in the formation, interconversion, and reactions of 1, **3**, and **4** will be discussed in a full paper.

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(13) IR, ν_{CO}, CH_2Cl_2: 1700, 1671 cm^{-1}; ^1H NMR, τ, $CDCl_3$, 4.48 (s, 10 H), 4.59 (s, 10 H) at −50 °C; ^{13}C NMR, δ_C, CH_2Cl_2, 235.6 dt (J_{Rh-C} = 49 Hz, J_{Rh-C} = 35 Hz) at −63°. Compound **4** displays fluxionality below room temperature, in contrast to its cobalt analogue.[14] The dynamic behavior of **4** will be discussed separately.

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(15) The electron-impact mass spectrum of 1 is complex and shows evidence for $Cp_4Rh_4(CO)_2^+$ (*m/e* 728), as previously reported.[2a] In our hands (170 °C, 70 eV) the intensity ratio (588/728) was ca. 3/1. We attribute the appearance of tetramer peaks to thermal decomposition of 1 in the probe (see footnote 11). In contrast, the field-desorption spectra of 1 and **4**, with ionization at room temperature, show only the molecular ions for each compound.

(16) Spectra were obtained on a Jeol Fx-60 spectrometer at 15.03 MHz, accumulating ca. 20 000 pulses for each spectrum. Solutions (CH_2Cl_2/CD_2Cl_2 or $CH_2Cl_2/(CD_3)_2CO$) were saturated in 1 and ca. 0.015 M in $Cr(acac)_3$.

(17) A similar process has been suggested for carbonyl scrambling in $Fe_3(CO)_{12}$[18a] which apparently occurs with a very low activation barrier.[18b] See also ref 6.

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(19) However, only one Cp resonance should be observed. Similar patterns of equilibration (incomplete for the carbonyls) should obtain for $Cp_3Co_3(CO)_3$, which apparently adopts solution structures related to **2**.[20]

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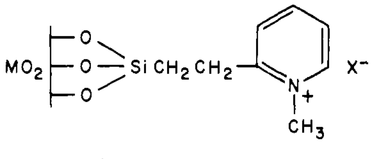
Chemically Modified Electrodes. 3. SnO_2 and TiO_2 Electrodes Bearing an Electroactive Reagent

Sir:

In an emerging new approach to electrochemistry, the surfaces of carbon[1,2] and tin oxide[3,4] electrodes have been chemically modified with several covalently attached reagents. The electrode surfaces exhibit the reagents' properties, such as inducing chirality in electrochemical processes[1] and surface base protonation equilibria.[2,3] We report here the first examples of chemically modified electrode surfaces which bear a covalently anchored[5] *electroactive* reagent. Such chemically modified electrodes present opportunities for fundamentally new approaches to the study of electrochemical reactions and to the tailoring of electrode surfaces for specific electrocatalytic properties.

The electrode materials employed are F-doped SnO_2 films (~5000 Å, 5 Ω square) on glass,[3] and TiO_2 films (est. 1000 Å) on titanium prepared by anodization (15% H_2SO_4, 20% NaH_2PO_4, 50 V) of polished titanium[7,8] followed by heating in 10% H_2 (in N_2, 400 °C) for several hours.[9] The surfaces of both electrodes were reacted with β-trichlorosilyl(2-ethyl) pyridine in benzene under anhydrous conditions[10] and then with refluxing neat CH_3I. The surface molecule sought is



I

The silanization of SnO_2 electrodes has been demonstrated;[3] chemical modification of TiO_2 electrode surfaces has not been previously reported. We will refer to the chemically modified electrodes I as $TiO_2/py(CH_3)^+$ and $SnO_2/py(CH_3)^+$.

Figure 1 shows N 1s ESCA spectra of various TiO_2 electrodes. Following silanization (curve B), pyridine N 1s appears at 400.0 eV. Methylation (curve D) produces a new band with binding energy (401.5 eV) quite close to that of N 1s in authentic methylpyridinium iodide (curve C). An analogous set of ESCA N 1s spectra is obtained for SnO_2 electrodes. The methylation reaction is not quantitative on either electrode (~50% on TiO_2, ~70% on SnO_2). ESCA spectra of the surface counterion X^- after exposure of the electrode to solutions of various anions (I^-, Br^-, Cl^-, ClO_4^-, BF_4^-) show that X^- is readily exchangeable. The ESCA results are consistent with the expectations of I above, except that the actual number of MOSi bonds is undetermined.

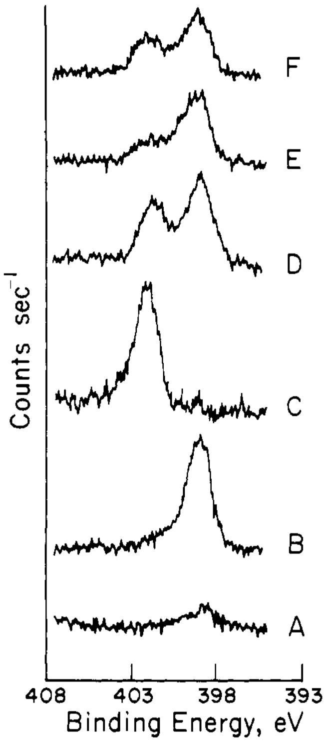


Figure 1. ESCA N 1s spectra of chemically modified TiO_2 electrodes. Binding energies are referenced to C 1s at 285 eV. Curve A is blank TiO_2.

Alkylpyridinium ions are electroreducible[12] but have not been studied in CH_3CN solvent. The initial (one electron) reduction product is thought to undergo dimerization. Figure 2 illustrates cyclic voltammograms in CH_3CN of free $py(CH_3)^+$ and of the surface molecule I. On a Pt electrode (curve A) free $py(CH_3)^+$ shows an irreversible current peak −1.32 v vs. SCE and shows a reoxidation wave at −0.15 V. Exhaustive reduction (coulometric $n \approx 1$) of free $py(CH_3)^+$ enhances the −0.15 V wave; reoxidation of the product solution, presumably the mentioned dimer, regenerates ~80% of the original cation wave. On an unmodified TiO_2 film electrode (curve B), the irreversible free $py(CH_3)^+$ wave appears at −1.56 V. No reoxidation wave is seen, unsurprisingly, since its potential (on Pt) lies anodic of the flat band potential of the n-type TiO_2 semiconductor electrode.[13,14]

A fresh $TiO_2/py(CH_3)^+$ electrode exhibits an irreversible reduction wave (curve C, Figure 2) at a potential (−1.35 ± 0.04 V) close to free $py(CH_3)^+$ on Pt. An immediate repeat scan yields a current envelope (curve D) identical with a background scan[15] on an unmodified TiO_2 electrode. Potentiostatting a reduced $TiO_2/py(CH_3)^+$ electrode at 0.0 V for a few minutes, however, regenerates reproducibly ~30% of the original surface wave as seen on the cathodic sweep, curve E. These results indicate that on TiO_2 the surface species I is indeed electroreducible, and that its reduction product remains bound to the electrode and can be reoxidized. ESCA data support this view. Curve E of Figure 1 shows that the 401.5 eV quaternary nitrogen band is substantially eliminated on a $TiO_2/py(CH_3)^+$ electrode reduced at −1.8 V. Curve F shows a $TiO_2/py(CH_3)^+$ electrode first reduced, then reoxidized at 0.0 V; the pyridinium N 1s band returns to an extent consistent with the electrochemistry. That the reoxidizable surface species is actually the 4,4′ dimer of I is consistent with (but not proven