1 may induce the facile β cleavage[18,22,23] of the neighboring C–N bond shown by the dotted line and prevents the chain propagation process demonstrated in the decomposition reaction of *tert*-butyl hydroperoxide. This facile cleavage of **1** gives rise to carbonyl compound and hydroxyl radical in good yield.

tert-Butyl hydroperoxide reacts with benzene, for example, in the presence of a Lewis acid to give phenol.[20,24] In the presence of aluminum chloride, *tert*-butoxy cation formed from the hydroperoxide by treatment with aluminum chloride reacts with benzene to give *tert*-butyl phenyl ether, which in turn affords phenol upon hydrolysis.[24] For comparison, the reaction of α-azohydroperoxide **1a** with benzene in the presence of aluminum chloride was examined. However, only a small amount of phenol (<4%) was obtained by this reaction.

Although mechanistic details of the reaction with the α-azohydroperoxide found by this study have to be elucidated by further studies, we would like to stress that the α-azohydroperoxide exhibits interesting chemical reactivities differing from those of the alkyl hydroperoxide, generating hydroxyl radical which hydroxylates aromatic molecules under anhydrous condition without any catalyst. The reaction of α-azohydroperoxide with organic substrates can be achieved even by using longer wavelength light at low temperature.

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Multiple Emissions from Rhenium(I) Complexes: Intraligand and Charge-Transfer Emission from Substituted Metal Carbonyl Cations

Sir:

Transition metal complexes that exhibit optically excited emission from two, non-equilibrated excited states are known,[1–5] but factors controlling this important phenomena are not well understood. We report the synthesis and characterization of a set of Re(I) complexes where two emissions obtain and where systematic variation in charge density on Re(I) results in systematic variation in the energy of the ReLCT emissive state. Importantly, significant variation in charge density on Re(I) can be effected by variations in N-donor ligands other than L. The relative importance of ReLCT and intraligand, $^3(\pi\text{-}\pi^*)$ emission can be manipulated in a controlled manner, depending on the energetic separation of the ReLCT and $^3(\pi\text{-}\pi^*)$ states.

The Re(I) complexes studied were prepared according to

$$fac\text{-}[\mathrm{ClRe(CO)_3L}] \xrightarrow[\substack{\mathrm{THF}\ or\ \mathrm{CH_3CN,\ S} \\ \mathrm{AgCF_3SO_3}}]{\Delta,\ 80\ ^\circ\mathrm{C}} fac\text{-}[\mathrm{SRe(CO)_3L}]^+(\mathrm{CF_3SO_3})^- + \mathrm{AgCl} \qquad (1)$$

$S = CH_3CN$, PhCN, pyridine, piperidine
$L =$ 2,2′-biquinoline, 1,10-phenanthroline

fac-[ClRe(CO)$_3$L] complexes were synthesized according to published procedures.[1,6] Products are isolated as the $CF_3SO_3^-$ salt by first filtering to remove the AgCl; solvent is removed by rotary evaporation. Products can be purified by crystallization from CH_3CN by addition of ether/*n*-pentane solution. Re(I) cations exhibit two bands in the CO stretching region of the IR, Table I, and ^{1}H NMR spectra for the complexes are consistent with the formulation *fac*-[SRe(CO)$_3$L]$^+$. Elemental analysis (Alfred Bernhardt, West Germany) for $S = CH_3CN$ or piperidine is satisfactory. Calcd for $S = CH_3CN$ (found): C, 33.75 (33.92); H, 1.72 (1.87); N, 6.56 (6.40). Calcd for S = piperidine (found): C, 36.81 (36.74); H, 2.77 (2.75); N, 6.13 (6.29). Table I includes spectral data for the previously characterized[6] neutral complexes *fac*-[ClRe(CO)$_3$L], for comparison.

The Re(I) cations exhibit detectable optical emission at 298 or 77 K in solution, Table I. Solution lifetimes at 298 K are $\sim 10^{-6}$ s, and the emission spectra are featureless and independent of the excitation wavelength (230–410 nm). The emission maximum for L = 2,2′-biquinoline is at lower energy than that for L = 1,10-phenanthroline, consistent with a CT emission associated with Re → L direction in absorption. This ordering of energy is consistent with the previous assignments of MLCT bands.[6,7] The difference in 2,2-biquinoline and 1,10-phenanthroline rules out a ligand field assignment; the ligand field states would be at the same energy for these complexes, since the donor sphere is invariant. Consistent with a CT assignment, the emission maximums for the four cations for L = 1,10-phenanthroline are ordered as predicted from the CO stretching frequencies: $CH_3CN \sim PhCN >$ pyridine > piperidine; that is, the complex exhibiting the lowest electron density (highest CO stretching frequency) on Re has the highest energy CT state, confirming the direction of the CT.

The emission of the various Re(I) species undergoes substantial changes upon cooling solutions of the complexes to 77 K. Generally, and as has been reported previously,[1,6,8] the emission blue shifts and intensifies. For *fac*-[(CH$_3$CN)-Re(CO)$_3$(2,2′-biquinoline)]$^+$ the featureless CT emission moves smoothly to the blue and intensifies as found[6] for *fac*-[ClRe(CO)$_3$(1,10-phenanthroline)]. Except for *fac*-

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Table I. Spectral Data for Rhenium Complexes

complex[a]	IR, $\mathrm{cm^{-1}}$ [b] (ϵ, $\mathrm{M^{-1}\,cm^{-1}}$)	Re → LCT abs, $\mathrm{cm^{-1}}$ (ϵ, $\mathrm{M^{-1}\,cm^{-1}}$)[c]	emission maxima, $\mathrm{cm^{-1}}$ (lifetime, μs)[d]	
			298 K	77 K[e]
fac-$[(CH_3CN)Re(CO)_3phen]^+$	2041 (4620), 1938 (3970)	~27 780 (6410), sh	18 800 (0.80)	total: 21 980, 20 530, 19 340 (11 + 75) long lived (70[f]): 22 120, 20 750, 19 340 (75)
fac-$[(PhCN)Re(CO)_3phen]^+$	2041 (1.13), 1937 (1)	~27 780 (5920), sh	18 700 (0.70)	total: 21 980; 20 530, 19 270 (9 + 95) long lived (80): 22 000, 20 510, 19 210 (95)
fac-$[(py)Re(CO)_3phen]^+$	2036 (1.25), 1931 (1)	~27 400 (4780), sh	18 120 (0.80)	total: 21 320, 20 410 (11 + ~50) long lived (30): 21 740, 20 410, 19 230 (~50)
fac-$[(pip)Re(CO)_3phen]^+$	2032 (1.01), 1921 (1)	~27 250 (4760), sh	17 890 (0.80)	total: 21 830, 21 140, 19 610 (9 + ~50) long lived (10): 21 880, 20 580, 19 280 (~50)
fac-$[ClRe(CO)_3phen]$	2024 (4600), 1920 (3015), 1898 (2600)	~26 450 (3400)	17 200 (0.85)	total: 18 690 (9.0) long lived (0): none detectable
fac-$[(CH_3CN)Re(CO)_3biquin]^+$	2040 (4050), 1938 (3630)	~23 260 (2900), sh	15 900 (0.75)	total: 16 290 (2.4) long lived (0): none detectable
fac-$[ClRe(CO)_3(biquin)]$	2023 (3880), 1920 (2210), 1899 (2410)	22 420 (3470)	none detectable	total: 15 760 (0.75) long lived (0): none detectable

[a] All cations were measured as the $CF_3SO_3^-$ salt; phen ≡ 1,10-phenanthroline; py ≡ pyridine; pip ≡ piperidine; biquin ≡ 2,2′-biquinoline. [b] All data were for CH_3CN solutions ± 1 $\mathrm{cm^{-1}}$; recorded using PE 180 IR spectrometer. [c] All data were for CH_3CN solutions; recorded using Cary 17 UV-vis-near-IR spectrophotometer; sh ≡ shoulder. [d] All data were for EPA solutions; 298 and 77 K total spectra were recorded using a Hitachi Perkin-Elmer MPF-44 spectrophotofluorometer and long-lived 77 K spectra using phosphoroscope attachment on an Aminco-Bowman SPF-2 spectrophotofluorometer. All spectral maxima represent raw data; the detector sensitivity varies by less than a factor of 2 over the wavelength, but the 77 K emission is dependent on excitation wavelength (see text). [e] The ratio of long-lived to short-lived emission depends on S and excitation wavelength (see text). Numbers in parentheses after "long lived" give the fraction (±20%) of the emission which is long lived, excited at 325 nm. Lifetimes are ±20% and perhaps somewhat less certain for the long-lived component of the py and pip complexes. [f] Percent.

$[SRe(CO)_3(1,10\text{-phenanthroline})]^+$ the 77 K emission is an excitation wavelength dependent mixture of two emissions: ReLCT and IL, Figure 1. The telltale feature is that the usual blue shift and increase in intensity of the emission at 77 K compared to 298 K is accompanied by the development of structure on the spectrum. That two, nonequilibrated states are emitting is evidenced by the fact that the spectrum obtained using the phosphoroscope attachment of the emission spectrophotometer is significantly different from the total emission spectrum. The phosphoroscope only allows the observation of long-lived emission (>50 μs); when the phosphoroscope is used the short-lived (~10 μs) emission of neither the *fac*-$[(CH_3CN)Re(CO)_3\text{-}(2,2'\text{-biquinoline})]^+$ nor *fac*-$[ClRe(CO)_3L]$ is observable, for example. The vibrational structure of the long-lived component of the emission of *fac*-$[SRe(CO)_3(1,10\text{-phenanthroline})]^+$ is similar, but not identical, with that for 1,10-phenanthroline. We therefore assign the long-lived emission to a perturbed 1,10-phenanthroline π-π^* triplet state. The featureless, short-lived emission at 77 K is associated with the ReLCT state. These data are essentially like those for *fac*-$[XRe(CO)_3(3\text{-benzoylpyridine})_2]$ (X = Cl, Br, I) which we recently showed[1] to exhibit emission from a ReLCT state and from a slightly perturbed 3-benzoylpyridine $^3(n$-$\pi^*)$ state.

For L = 1,10-phenanthroline complexes, variation in the ligand S controls the energy of the ReLCT state; for the higher energy ReLCT the relative importance of the $^3(\pi$-$\pi^*)$ emission becomes greater. Correlating with the CO stretching frequencies and room temperature emission maxima, the relative importance of the $^3(\pi$-$\pi^*)$ emission is ordered according to S as follows: CH_3CN ~ PhCN > pyridine > piperidine, Table I. *fac*-$[ClRe(CO)_3(1,10\text{-phenanthroline})]$ exhibits an even lower energy ReLCT 298 K emission and gives no detectable $^3(\pi$-$\pi^*)$ emission. Generally, whether one or two emissions is detectable will depend on the rate at which the upper emissive state decays to the lower emissive state compared to radiative decay rates. The internal conversion rate from the $^3(\pi$-$\pi^*)$ state to the ReLCT state is controlled by the electronic and vibronic coupling of the two states. Along with a low density of states resulting in weak vibronic coupling, the geometrical difference of the two states likely contributes to the slow rate of internal conversion when the two states are close in energy. The internal conversion rate is apparently slow, despite the fact that electronic coupling is greatest when the separation of the states is smallest. As the energetic separation between $^3(\pi$-$\pi^*)$ and ReLCT increases, electronic coupling weakens, while the vibronic coupling strengthens owing to a greater density of states. The increased vibronic coupling results in sufficiently fast internal conversion that only ReLCT emission is observed when ReLCT is sufficiently lower than $^3(\pi$-$\pi^*)$. For a number of rigid aromatic hydrocarbons internal conversion from the singlet to the triplet state becomes slower as the singlet-triplet energy separation increases,[9] indicating a different balance of factors controlling internal conversion compared to the Re(I) complexes reported here.

Finally, the relative importance of $^3(\pi$-$\pi^*)$ and ReLCT emission can be varied by variation in the excitation wavelength in the vicinity of the *onset* of the absorption/excitation spectrum. At the lowest excitation energies (~410 nm) the emission is dominated by the broad, featureless, short-lived (~10 μs) emission which we attribute to the ReLCT state. Except for the bulk of the excitation spectrum (<350 nm) the ratio of $^3(\pi$-$\pi^*)$ and ReLCT emission is essentially invariant. A reexamination of the excitation of *fac*-$[XRe(CO)_3(3\text{-benzoylpyridine})_2]$ shows that it too exhibits somewhat more ReLCT emission if the excitation energy is low enough, in contrast to our earlier claim[1] using a less sensitive emission spectrometer where we were unable to use such low energy

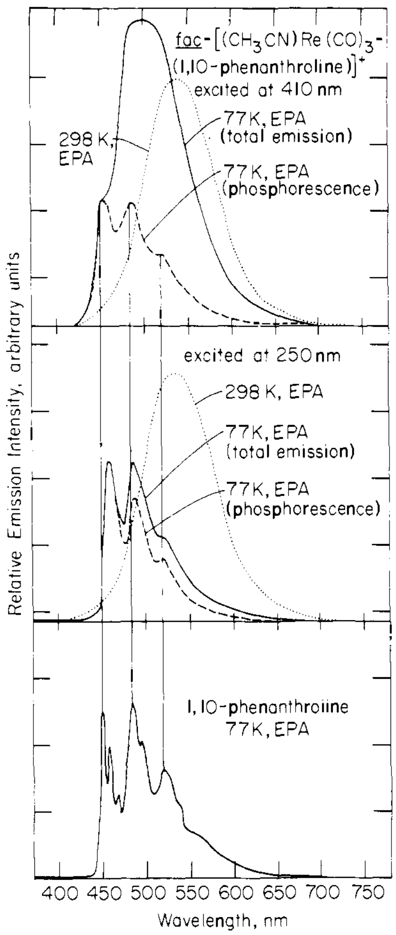

Figure 1. Emission spectra excited at 410 nm (top) and 250 nm (middle) for $\sim 10^{-4}$ M EPA solutions. The total emission of 1,10-phenanthroline (bottom) is shown for comparison. The spectra are not shown at the same sensitivity. All spectra are total emission spectra except the two marked "phosphorescence" which were recorded with the phosphoroscope attachment in place. The phosphoroscope only allows the detection of emissions longer than ~ 50 μs.

excitations. The conclusion from this absorption edge excitation is that, while the ReLCT state may be close in energy to the $^3(\pi$-$\pi^*)$, the ReLCT is lower for the systems examined thus far.[10]

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(10) We are well aware that emissive impurities may well give rise to multiple emissions. However, we have successfully repeated the experimental data found in Table I for several solvents and for different synthetic material prepared independently by two different workers. Free ligand 1,10-phenanthroline impurity emission is ruled out by the data in Figure 1; adding $AgCF_3SO_3$ in small amounts does not alter the emission properties; the complexes are "pure" by elemental analysis and ^{1}H NMR and by IR immediately prior to and after emission spectroscopy measurements. None of the solvents or reagents used in synthesis, workup, or purification exhibits emission like that (lifetime, energy) found for the four cations for L = 1,10-phenanthroline. All sources of "impurity" emission are thus ruled out; the essential results detailed in Table I and Figure 1 are also independent of concentration in the range 10^{-4}–10^{-5} M.

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Homogeneous Carbon Monoxide Hydrogenation on Multiple Sites: A Dissociative Pathway to Oxygenates

Sir:

Transition metal cluster complexes offer the prospect of a new class of selective homogeneous Fischer–Tropsch catalysts by virtue of the proximity of multiple reaction sites on the faces or edges of the cluster, a factor which may have special significance in carbon monoxide hydrogenation catalysis.[1] However, in contrast to the large and increasing number of organo cluster molecules containing hydrocarbon ligands derived from olefins, acetylenes, etc.,[2] there are no examples of organometallic clusters in which the organic moiety was derived solely from CO and H_2, and, in those cases where CO hydrogenation has been reported to be catalyzed by polynuclear complexes,[3] no cluster-bound intermediates have been detected.

We report here the synthesis and characterization of the first member of a new class of organometallic clusters which owe their formation to the reactivity of the encapsulated carbon atom found in the carbidocarbonyl cluster $Fe_6C(CO)_{16}^{2-}$.[4] When suitably exposed (in this case by oxidation of the cluster), the isolated carbon atom, which has no counterpart in mononuclear systems, exhibits a chemistry conducive to carbon–carbon bond formation by reaction with carbon monoxide. A cluster-bound organic fragment is thus built up from CO in a manner unique to cluster chemistry.

A deep red solution of $(Et_4N)_2[Fe_6C(CO)_{16}]$ (I, 3.0 g), in methanol (200 mL) was treated dropwise with a solution of tropylium bromide[5] (3.0 g) in methanol (30 mL), under nitrogen, until the color had changed to green-black, and the infrared absorptions of I at 2028, 1964, 1931, and 1772 cm^{-1} in methylene chloride solutions of evaporated aliquots of the reaction mixture were replaced by new bands at 2024 (s), 1998 (s), 1980 (sh), 1970 (sh), 1925 (m), and 1650 cm^{-1} (w). The product, II, was isolated by evaporation of the methanol, washing with pentane (to remove bitropyl), extraction into methylene chloride, and crystallization as black prisms (1.8 g) from methylene chloride–butanol. ^{1}H NMR (100 MHz, CD_2Cl_2) showed only a sharp singlet at δ 3.35 (3 H) in addition to cation resonances at 3.05 (8 H) and 1.20 (12 H). ^{13}C NMR (20 MHz, CD_2Cl_2, $\sim 30\%$ ^{13}C enriched)[6]: 237, 214, 175 ppm (Me_4Si) in approximate intensity ratio 1:12:1. These data, together with elemental analysis, supported the formulation of II as $(Et_4N)[Fe_4C(CO)_{12}\cdot CO_2CH_3]$. In view of the novelty of a tetranuclear cluster containing a lone carbon atom, an X-ray crystallographic study was performed.[7]

Crystals of II were grown from methylene chloride–butanol. The molecule crystallizes in the orthorhombic space group P_{bca} ($D_{2h}{}^{15}$, No. 61) with a = 12.099 (3), b = 17.889 (6), c =

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