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Competitive Radiative Decay and Metal-Metal Bond Cleavage from the Lowest Excited State of Triphenyltin- and Triphenylgermanium-Tricarbonyl(1,10-phenanthroline)rhenium

Sir:

The rate constants associated with dissociative excited-state processes in organometallic complexes have generally not been evaluated, despite the need for such measurements in directly assessing excited-state reactivity. There are now a number of reports of bimolecular excited-state reaction rate constants for electron and energy transfer.[1-7] In this communication we report the synthesis and electronic spectral and photochemical characterization of a set of complexes $Ph_3ERe(CO)_3L$ (E = Ge, Sn; L = 1,10-phenanthroline, 2,2′-bipyridine) where it is possible to evaluate k^*_{dissoc} associated with the excited-state dissociation (eq 1). This represents the first such determination for any metal-carbonyl complex, and, in particular, these results bear significantly on the now well-studied metal-metal bonded complexes.[8-15]

$$[\mathrm{E{-}Re}]^* \xrightarrow{k^*_{\mathrm{dissoc}}} \mathrm{E}\cdot + \mathrm{Re}\cdot \qquad (1)$$

Spectral properties for complexes studied are given in Table I; they are prepared by slow addition of a THF solution of Ph_3SnCl or Ph_3GeBr to a THF solution of the appropriate $[Re(CO)_3L]^-$ under Ar. $[Re(CO)_3L]^-$ is prepared by the 1% Na/Hg reduction of $ClRe(CO)_3L$ in THF solvent. The highly colored E-Re bonded complexes are formed in good yield (~50%) and can be purified by precipitation from concentrated CH_2Cl_2 solution by addition of isooctane. The complexes which have received detailed study to date are for E = Ge and Sn and L = 1,10-phenanthroline and these two substances have satisfactory elemental analyses (Alfred Bernhardt, West Germany). Anal. Calcd for $C_{33}H_{23}N_2O_3ReSn$ (found): C, 49.52 (49.34); H, 2.90 (2.92); N, 3.50 (3.26). Calcd for $C_{33}H_{23}N_2O_3ReGe$ (found): C, 52.54 (52.66); H, 3.07 (3.12); N, 3.71 (3.84).

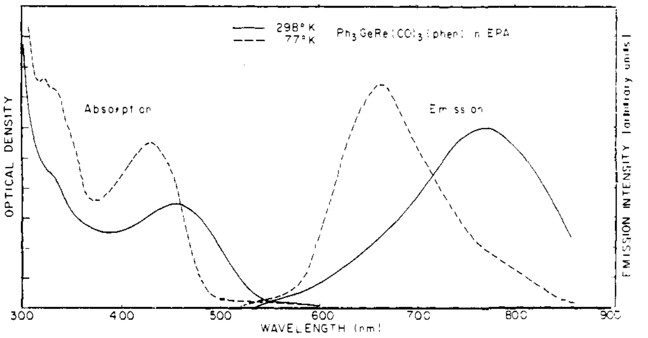

Figure 1. Absorption and emission of $Ph_3GeRe(CO)_3$(1,10-phenanthroline). The emission spectra are corrected for variation in detector sensitivity and are excited at 480 nm. The sensitivity for the 298 and 77 K emission is not the same, and the absorption spectral change from 298 to 77 K is not corrected for solvent contraction.

Table I. Spectral and Photochemical Properties of $Ph_3ERe(CO)_3$(1,10-phenanthroline) at 25 °C

E	IR bands, cm^{-1} (ϵ)[a]	$(E\text{-}Re)\sigma_b \rightarrow \pi^*L$, nm ($\epsilon$)[b]	emission max, nm (τ, μs)[c]	$\Phi \pm 10\%$ (λ, nm)[d]
Ge	2004 (4870)	450 (4940)	765 (2.6)	0.25 (313)
	1900 (3730)			0.30 (366)
				0.27 (436)
				0.26 (488)
				av 0.27
Sn	2004 (4700)	465 (4610)	750 (1.8)	0.26 (313)
	1903 (3840)			0.25 (366)
				0.22 (436)
				0.20 (488)
				av 0.23

[a] In CH_2Cl_2 with 0.5 M CCl_4 at 298 K measured with a PE 180 with matched path cells. [b] In CH_2Cl_2 with 0.5 M CCl_4 at 298 K measured using a Cary 17 ultraviolet-visible-near-infrared spectrophotometer. [c] Corrected emission maximum in CH_2Cl_2 with 0.5 M CCl_4 using a PE Model MPF44 exciting at 480 nm. The lifetime was measured using either a rhodamine dye laser (560 nm, ~5-ns pulse width) or a Xenon Corporation Model 437 nanopulser excitation source filtered to pass 436-nm light and the detection optics of a TRW decay time fluormeter with output to an oscilloscope. [d] Reaction quantum yield for disappearance of E-Re species is equal to the formation quantum yield for $ClRe(CO)_3$(1,10-phenanthroline) which exhibits IR absorptions, cm^{-1} (ϵ), in CH_2Cl_2-0.5 M CCl_4 at 2024 (4600), 1922 (3015), and 1898 (2600). All Φ values are in degassed CH_2Cl_2-0.5 M CCl_4 solutions at ~2 × 10^{-3} M E-Re species. Light intensities are ~3 × 10^{-7} einstein/min.

The UV-vis absorption spectra of the complexes (Figure 1 and Table I) are similar to those previously found[8d] for $(OC)_5Re\text{-}Re(CO)_3L$, except for the differences in the energetic position of the bands. We attribute the first absorption band to a metal-metal σ_b to $L\pi^*$ CT transition as in the previously studied Re-Re system. As usual,[6b,8d,16-18] for such metal carbonyl complexes the CT absorption depends markedly on the solvent; for example the first absorption maximum is at ~432 nm in CH_3CN and ~465 nm in benzene for E = Sn, L = 1,10-phenanthroline. $Ph_3ERe(CO)_5$ complexes absorb only at wavelengths <350 nm, ruling out a $\sigma_b \rightarrow \sigma^*$ type transition in the visible; $\sigma_b \rightarrow \sigma^*$ transitions are generally not too solvent sensitive.[8] The 2,2′-biquinoline complex has been prepared and, compared with the others, and the first band is at substantially lower energy in accord with the $(E\text{-}Re)\sigma_b \rightarrow L\pi^*$ CT assignment;[6b,8d] λ_{max} 560 nm for E = Sn, L = 2,2′-biquinoline in CH_2Cl_2.

What is novel is that some of the $Ph_3ERe(CO)_3L$ complexes exhibit detectable emission upon photoexcitation in fluid so-

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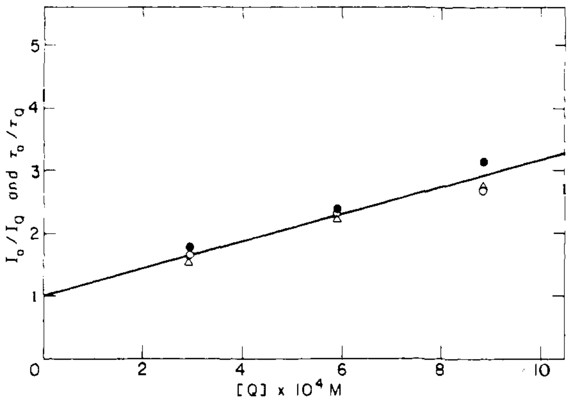

Figure 2. Stern-Volmer plots for anthracene quenching of emission intensity (○), emission lifetime (●), and reaction quantum yield (△) for 2×10^{-3} M $Ph_3GeRe(CO)_3$(1,10-phenanthroline) at 298 K in a degassed CH_2Cl_2 solution of 0.5 M CCl_4.

lution at 25 °C (Figure 1). The emission yield is fairly low ($\Phi \sim 10^{-3}$) and the complexes are very photosensitive ($\Phi \approx 0.25$), but the excitation spectrum for wavelengths longer than 300 nm shows that the emission efficiency is wavelength independent. The emission lifetime in degassed 0.5 M CCl_4-CH_2Cl_2 solution is 2.6 and 1.8 μs for $Ph_3GeRe(CO)_3$(1,10-phenanthroline) and $Ph_3SnRe(CO)_3$(1,10-phenanthroline), respectively, at 25 °C.

Photoexcitation of the complexes in degassed CH_2Cl_2-CCl_4 solutions results in photoreaction. $ClRe(CO)_3L$ is formed quantitatively chemically, and the reaction quantum yields for $Ph_3GeRe(CO)_3$(1,10-phenanthroline) and $Ph_3SnRe(CO)_3$(1,10-phenanthroline) are independent of the excitation wavelength (Table I). Thus, it appears that reaction and emission are detectable from the same lowest excited state. Consistently, the emission and reaction are quenched by the triplet quencher anthracene (E_T = 42 kcal/mol[19]). The quenching obeys Stern-Volmer kinetics[19] and the Stern-Volmer constant obtained is the same for emission, lifetime, and reaction quenching (Figure 2). This confirms that chemistry and emission result from the same excited state. The fate of the Ge- or Sn-centered fragments has not been quantitatively determined, but E-Cl bonded compounds have been identified as products upon irradiation in the chlorocarbon solutions.

Importantly, it appears that the reaction of the excited state is of the dissociative type and is not one where the excited state reacts bimolecularly with the chlorocarbon. The evidence for this is twofold. First, the complexes emit in benzene solution but concentrations of CCl_4 up to 1 M do not quench the emission, while irradiation in the presence of even 0.1 M CCl_4 gives clean generation of $ClRe(CO)_3L$. Second, irradiation of the reactive complexes in THF and other solvents yields efficient conversion into as yet unidentified products which do not have an E-Re bond as evidenced by bleaching of the low energy visible spectrum. The disappearance quantum yields are similar to those found in the presence of CCl_4.

Knowing the reaction quantum yield and the emission lifetime under the reaction conditions allows the evaluation of the rate constant (k^*_{dissoc}) for conversion of the excited state to product. For the Ge and Sn complexes studied here the values of k^*_{dissoc} are 1.0×10^5 and 1.3×10^5 s^{-1}, respectively.[20] Assuming that the excited state does not relax to a lower state which reacts very rapidly, these can be regarded as being associated with excited-state dissociation of the E-Re bond (eq 1). The excited-state rate of E-Re bond cleavage is very conservatively 10^{11} times the ground-state rate constant, since there is no detectable dark reaction over observation times of ~2 weeks under conditions where the excited-state rate constant is $\sim 10^5$ s^{-1}. Such tremendous enhancement in reaction rate constants is probably common upon excitation of organometallics, but rarely have we had the opportunity to measure the excited-state reaction rates. The (E-Re)$\sigma_b \rightarrow L\pi^*$ CT transition only reduces the σ-bond order by one half, in contrast to the situation in $Mn_2(CO)_{10}$ and related complexes where the $\sigma_b \rightarrow \sigma^*$ can reduce the Mn-Mn bond order to zero.[8] The k^*_{dissoc} values that we have measured are actually quite modest, but it is very likely that the k^*_{dissoc} for $\sigma_b \rightarrow \sigma^*$ type excited states would be several orders of magnitude higher than for the (E-Re)$\sigma_b \rightarrow L\pi^*$ CT excited states studied here.[21]

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