

- Acc. Chem. Res.*, in press.
- (15) C. A. Coulson, "Valence", 2nd Ed., Oxford University Press, London, 1961, pp 208-211.
- (16) (a) $^1J_{CH}$ correlates fairly well with the percent s character in the carbon orbital in hydrocarbons.^{17a,b} In other cases (e.g., the CH₄, CH₃Cl, CH₂Cl₂, CHCl₃ series) it correlates linearly with bond length.^{17c} In the latter series, if a bond length were 1.13 Å, $^1J_{CH}$ would be ~95 Hz. (b) Coulson¹⁵ predicts $k = 4.490 \times 10^{-5}$ dyn cm⁻¹ for a pure C(p)-H(s) bond; for a C(sp³)-H(s) bond $k = 5.387 \times 10^{-5}$ dyn cm⁻¹.
- (17) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York and London, 1972; (b) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959); (c) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).
- (18) (a) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 2935 (1975); (b) R. R. Schrock and P. R. Sharp, *ibid.*, **100**, 2389 (1978).
- (19) (a) K. Wade, "Electron Deficient Compounds", Appleton-Century-Crofts, New York, 1971; (b) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, 1963, p 172.
- (20) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976).
- (21) Green²² has "trapped" a methylene hydride complex with a tertiary phosphine. It now seems possible, however, that H₂ may never transfer "completely" from a methyl ligand to an electron-deficient metal to give an observable, *cis*-alkylidene-hydride complex.
- (22) N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 208, 761 (1974).
- (23) (a) F. A. Cotton and A. G. Stanislawski, *J. Am. Chem. Soc.*, **96**, 5074 (1974); (b) M. Brookhart, T. H. Whitesides, and J. M. Crockett, *Inorg. Chem.*, **15**, 1550 (1976); (c) S. D. Ittel, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, **100**, 1317 (1978); (d) R. B. Calvert and J. R. Shapley, *ibid.*, **99**, 5225 (1977); (e) G. A. Olah, G. Liang, and S. H. Yu, *J. Org. Chem.*, **41**, 2227 (1976).
- (24) In the neutron diffraction study²⁵ of [Fe[P(OMe)₃]₃(η³-C₈H₁₃)]⁺BF₄⁻,^{23c} the Fe-H distance is 1.879 (9) Å. In [Fe(CO)₃(η³-C₄H₇)]⁺ the J_{CH} value in the suggested^{23b} three-center, four-electron Fe-H-C bond was shown to be 74 Hz.^{23e}
- (25) J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, **100**, 7407 (1978).
- (26) (a) G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975), and references therein; (b) D. E. Webster, *Adv. Organomet. Chem.*, **15**, 147 (1977).
- (27) (a) Camille and Henry Dreyfus Teacher-Scholar, 1978. (b) PRF Predoctoral Fellow; (c) Halcon Fellow, 1978.

A. J. Schultz,* Jack M. Williams

Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

R. R. Schrock,*^{27a} G. A. Rupprecht,^{27b} J. D. Fellmann^{27c}

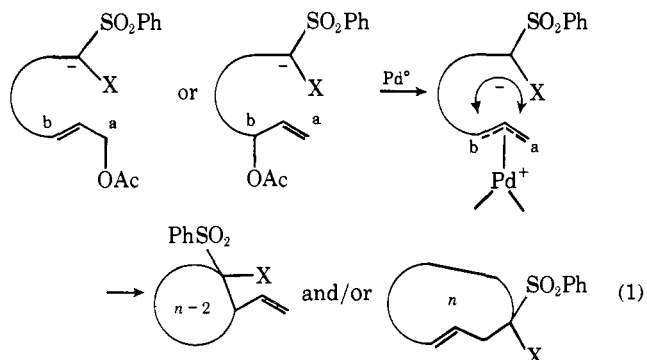
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received August 13, 1978

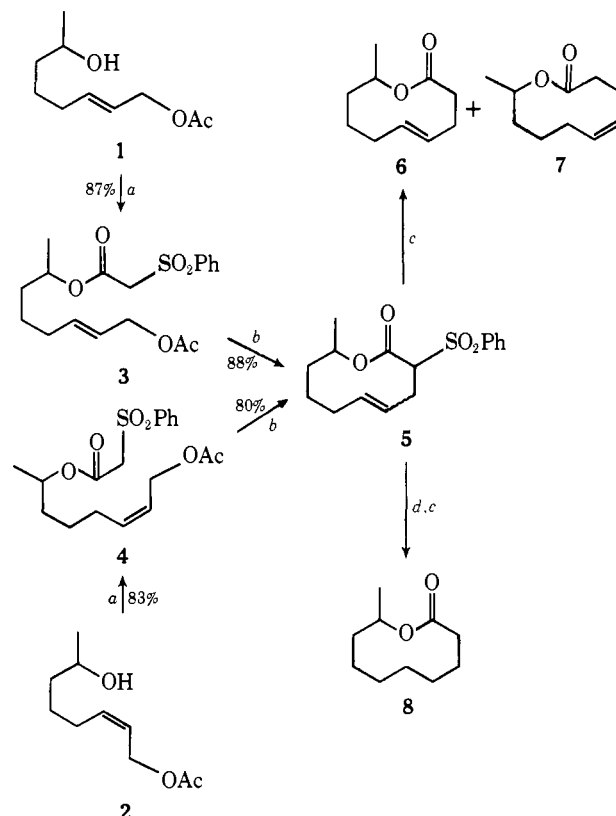
Influence of a Transition Metal on the Regiochemistry of Ring Closures. An Approach to Medium-Ring Compounds

Sir:

A basic tenet of cyclization is the great preference for formation of three-, five-, six-, and seven-membered rings over four-, eight-, nine-, and ten-membered rings. For example, a six-membered ring forms $>10^4$ faster than an eight-membered ring.¹ We report an unusual effect of palladium² on the rules for ring closure³ and the first examples of the preference for formation of eight- and nine-membered rings over competing six- and seven-membered rings. Growing interest in the syn-



Scheme I. Eight vs. Ten. Synthesis of Phoracantholides



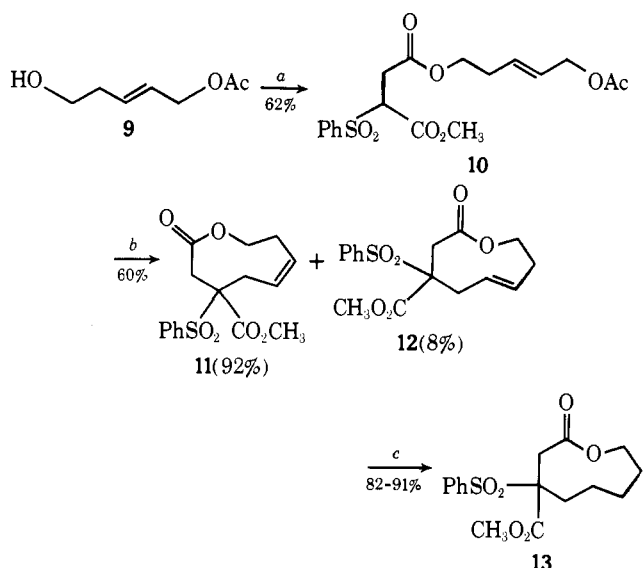
^a PhSO₂CH₂CO₂H, Ph₃P, C₂H₅O₂CN=NCO₂C₂H₅, PhCH₃, RT.

^b NaH, THF, 6 mol % (Ph₃P)₄Pd, 12 mol % diphos, reflux. ^c 6% Na (Hg), Na₂HPO₄, C₂H₅OH, -20 °C. ^d 5% Pd/BaCO₃, H₂, 2 atm, C₂H₅OH.

thesis of medium rings and the fact that medium-ring lactones are generally not accessible by lactonization⁴⁻⁶ methods highlight the potential importance of these observations.

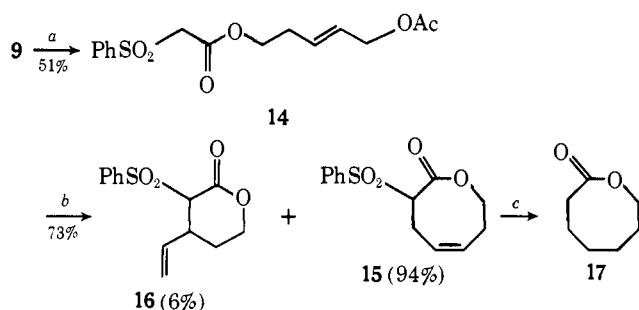
Equation 1 represents the general class of reaction that we have examined.^{2,3} The importance of ten-membered ring compounds in natural products and the fact that eight- and ten-membered ring formation occurs with almost equal facility¹ led us to compete an eight vs. ten (i.e., $n = 10$) directed to the phoracantholides as summarized in Scheme I. The hydroxyacetates **1**⁸ and **2**,⁸ whose olefin stereochemistry is established by the mode of synthesis⁷ and the 270-MHz NMR spectrum (**1**, δ 5.77 (dt, $J = 15.3, 6.3, 1$ Hz, 1 H), 5.56 (dt, $J = 15.3, 6.3, 1$ Hz, 1 H); **2**, δ 5.65 (dt, $J = 11, 7.3, 1.5$ Hz, 1 H), 5.53 (dt, $J = 11, 6.8, 1.5$ Hz, 1 H)), were esterified with benzenesulfonylacetic acid by the reverse activation procedure⁹ to give the cyclization substrates **3**⁸ and **4**.⁸ In both cases, treatment of the corresponding anions with a Pd(0) catalyst in the presence of diphos led to an isomeric mixture (*E,Z* and *R*,R**, and *R*,S**) of cyclization products **5**. The absence of absorptions at δ 5-5.5 for a monosubstituted olefin suggested the absence of eight-membered rings. Desulfonylation gave a mixture of *E* and *Z* ten-membered-ring lactones **6**⁸ and **7**,⁸ which were separated by VPC (20% DC710 on 60/80 Chromosorb W at 170 °C), the latter (phoracantholide J) isolated from the metasternal gland secretion of *Phoracantha synonyma*.^{6,10,11} NMR allows assignment of double-bond stereochemistry (**6**, δ 5.42 (ddd, $J = 15, 9.5, 4.5$ Hz), 5.28 (ddd, $J = 15, 10.5, 4$ Hz); **7**, 5.46 (tdd, $J = 11, 5.5, 2$ Hz), 5.35 (td, $J = 11, 4$ Hz)). The ratio of **6:7** was 85:15 from **3** and 65:35 from **4**. Thus, in contrast to the 12-membered-ring case, substantial loss of olefin geometry accompanied this cyclization. Further confirmation that the isomeric nature of **5** does not result from regioisomers arose in the catalytic hydrogenation

Scheme II. Seven vs. Nine. Synthesis of Octan-8-olides



a (i) BrCH_2COBr , $\text{C}_5\text{H}_5\text{N}$, CH_2Cl_2 , RT; (ii) NaH , $\text{PhSO}_2\text{CH}_2\text{CO}_2\text{CH}_3$, DMF, 0°C . *b* NaH , THF, 10 mol % $(\text{Ph}_3\text{P})_4\text{Pd}$, 10 mol % diphos, reflux. *c* 5% Pd/BaCO_3 , H_2 , 2 atm, $\text{C}_2\text{H}_5\text{OH}$.

Scheme III. Six vs. Eight. Synthesis of Heptan-7-olides



a $\text{PhSO}_2\text{CH}_2\text{CO}_2\text{H}$, Ph_3P , $\text{C}_2\text{H}_5\text{O}_2\text{CN}=\text{NCO}_2\text{C}_2\text{H}_5$, PhCH_3 , $0^\circ\text{C} \rightarrow \text{RT}$. *b* NaH , THF, 5 mol % $(\text{Ph}_3\text{P})_4\text{Pd}$, 10 mol % diphos, reflux. *c* (i) 5% Pd/BaCO_3 , H_2 , 2 atm, $\text{C}_2\text{H}_5\text{OH}$; (ii) 6% Na (Hg), HOAc, $\text{C}_2\text{H}_5\text{OH}$, -20°C .

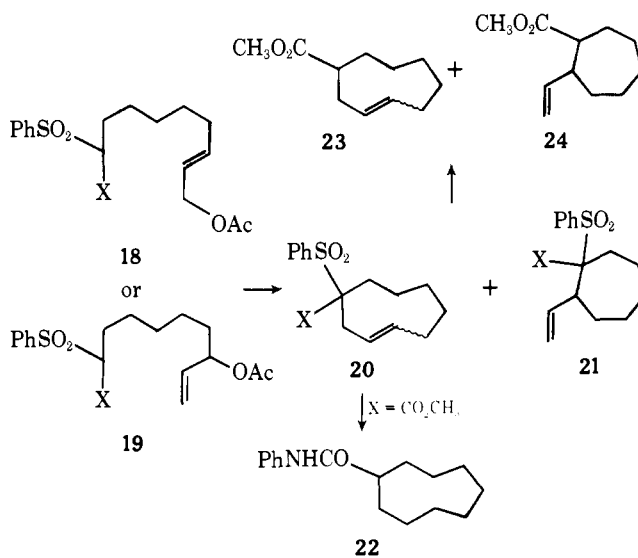
of the olefin followed by desulfonylation to give (\pm)-decan-9-olide (**8**, phoracantholide I) whose spectral properties agree with those of an authentic sample of the natural product.¹⁰

While palladium induced cyclization to give the ten-membered ring exclusively, in simple cyclizations such a competition does not lead to a great preference. On the other hand, a rate factor of 10^3 exists in favor of formation of a seven-membered compared with a nine-membered ring. Thus, the substrate **10**⁸ (see Scheme II), whose ease of synthesis as outlined illustrates one of the advantages of this method, was subjected to the usual cyclization conditions. Much to our surprise (and delight!) only nine-membered ring products **11**⁸ and **12**⁸ (*E:Z*, 8:92) were isolated and separated by TLC (25% $\text{C}_2\text{H}_5\text{OAc}$ in hexane; *E*, $R_f = 0.35$; *Z*, $R_f = 0.28$, mp $125\text{--}126^\circ\text{C}$). That the two compounds represent double-bond isomers was shown by their catalytic hydrogenation to give the same compound **13**.⁸ Olefin geometry is established by 270-MHz NMR: **11** (C_6D_6) δ 5.63 (dt, $J = 11, 8.6$), 5.38 (dt, $J = 11, 8.3, 1$ Hz); **12** (CDCl_3) δ 5.48 (ddd, $J = 15.8, 10, 5.9$ Hz), 5.41 (ddd, $J = 15.8, 10.4, 05.3$), 5.23 (ddd, $J = 15.8, 10.3, 4.5$ Hz), 5.12 (ddd, $J = 15.8, 11.2, 3.5$ Hz).

Scheme III illustrates a more severe test for cyclization preferences since a six-membered ring is favored kinetically by $>10^4$ over an eight-membered ring. Treatment of **14**⁸ under the usual cyclization conditions gave as the vastly major product the heptan-7-olide **15**,⁸ mp $87.5\text{--}89^\circ\text{C}$, with only a

trace of the six-membered ring **16**, the latter being detected in the crude reaction mixture by NMR signals for the mono-substituted olefin at δ 5.21 and 5.18. The shocking preference for formation of the eight-membered ring was confirmed by correlating **15** with the parent heptan-7-olide **17**, an authentic sample of which was independently synthesized.¹² The lability of the eight-membered ring lactone made desulfonylation rather tricky until we discovered that buffering the 6% Na (Hg) reaction medium with acetic acid solved the problem.

The preference for the larger ring in each case might be thought to reflect preferential reaction at a primary (site a in eq 1) vs. a secondary (site b in eq 1) carbon. This rationale was eliminated by cyclizing the all-carbon analogue **18**⁸ or **19**⁸ ($\text{X} = \text{CO}_2\text{CH}_3$) which gave a mixture of the nine- and seven-membered-ring compounds in which the latter predominated (for $\text{X} = \text{CO}_2\text{CH}_3$, 30:70 **20:21** from **18** ($\text{X} = \text{CO}_2\text{CH}_3$) and 37:63 from **19** ($\text{X} = \text{CO}_2\text{CH}_3$) in the presence of diphos and



7:93 in the absence of diphos). On the other hand, when **19** ($\text{X} = \text{PhSO}_2$) is cyclized, the ratio of **20:21** ($\text{X} = \text{PhSO}_2$) is $\sim 73:27$, i.e., the nine-membered ring predominates. The structure of **20** was confirmed by converting it into the known anilide **22** (mp $138.5\text{--}140^\circ\text{C}$).

The results show that chain conformation, as well as the nature of the cyclization initiator (i.e., the allylpalladium cationic moiety), are combining to overwhelm the normal preferences for ring closure. Synthetically, the results clearly point to the unique role that the transition metal catalyst can play in changing the usual rules in organic reactivity and make this type of approach particularly attractive to the difficult class of medium-ring compounds. Furthermore, by manipulating the substitution of the chain, the nucleophile, and the ligands, either cyclization mode appears feasible.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of our programs. We thank Engelhardt Industries for a generous gift of palladium chloride.

Microfilm Material Available: A listing of spectral data for **3**, **4**, **6**, **7**, and **10–15** (3 pages). Ordering information is given on any current masthead page.

References and Notes

- Galli, C.; Illuminati, G.; Mandolini, L.; Tamborra, P. *J. Am. Chem. Soc.* **1977**, *99*, 2591. Illuminati, G.; Mandolini, L.; Masci, B. *ibid.* **1975**, *97*, 4960.
- For a review see Trost, B. M., *Tetrahedron* **1977**, *33*, 2615.
- Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1977**, *99*, 3867. Kitagawa, Y.; Itoh, A.; Hashimoto, S.; Yamamoto, H.; Nozaki, H. *ibid.* **1977**, *99*, 3864.
- For a review see Nicolaou, K. C. *Tetrahedron* **1977**, *33*, 683.

- (5) Lactonization to eight- and nine-membered rings is reported to occur in 0–13% yields. Vorbrüggen, H.; Krolkiewicz, K. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 876. Mukaiyama, T.; Narasaka, K.; Kikuchi, K. *Chem. Lett.* **1977**, 441. Mukaiyama, T.; Usai, M.; Saigo, K. *ibid.* **1976**, 49. Kurihara, T.; Nakajima, Y.; Mitsunobu, O. *Tetrahedron Lett.* **1976**, 2455. Corey, E. J.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1974**, *96*, 5614. For a successful lactonization to a ten-membered ring, see Gerlach, H.; Krinzler, P.; Oertle, K. *Helv. Chim. Acta* **1978**, *61*, 1226.
- (6) It should be recalled that these palladium reactions involve attack of the nucleophile on the face of the allyl unit opposite palladium. Thus, an analogy can be made to normal S_N2 reactions in which the palladium functions as a leaving group. Such a process is not comparable with allyl–allyl couplings in which both partners are bound to the metal and for which the metal can play a more obvious role. For a review in the area of nickel chemistry, see Jolly, P.W.; Willie, G. "The Organic Chemistry of Nickel", Academic Press: New York, 1974; Vol. 1.
- (7) (a) The *E* olefin is established by a Emmons–Wadsworth–Horner olefination and the *Z* olefin by an olefin inversion sequence from the *E* isomer. (b) Verhoeven, T. R., Ph.D. Thesis, University of Wisconsin, 1979.
- (8) This compound has been fully characterized by spectroscopic data and elemental composition. For a listing of spectral data see the appendix which appears in the microfilm version.
- (9) Mitsunobu, O.; Eguchi, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3427. Bose, A. K.; Lal, B.; Hoffman, W. A.; Manhas, M. S. *Tetrahedron Lett.* **1973**, 1619. Loibner, H. J.; Zbiral, E. *Helv. Chim. Acta* **1976**, *59*, 2100. Mitsunobu, O.; Kimura, J.; Iizumi, K.; Yanagida, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 510.
- (10) Moore, B. P.; Brown, W. V. *Aust. J. Chem.* **1976**, *29*, 1365. We thank Dr. B. P. Moore for spectral data from the authentic sample.
- (11) A sample of (*E*)-4-decen-9-olide was sent to Dr. B. P. Moore, CSIRO, Division of Entomology, Canberra, who informed us that it is absent from the metasternal secretion.
- (12) Huisgen, R.; Ott, H. *Angew. Chem.* **1958**, *70*, 312. Friess, S. L.; Frankeenburg, P. E. *J. Am. Chem. Soc.* **1952**, *74*, 2679.

Barry M. Trost,* Thomas R. Verhoeven

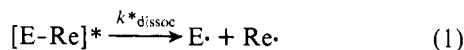
Samuel M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin—Madison
Madison, Wisconsin 53706

Received November 14, 1978

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 $\text{Ph}_3\text{ERe}(\text{CO})_3\text{L}$ (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}



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 $[\text{Re}(\text{CO})_3\text{L}]^-$ under Ar. $[\text{Re}(\text{CO})_3\text{L}]^-$ is prepared by the 1% Na/Hg reduction of $\text{ClRe}(\text{CO})_3\text{L}$ 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 isoctane. 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 $\text{C}_{33}\text{H}_{23}\text{N}_2\text{O}_3\text{ReSn}$ (found): C,

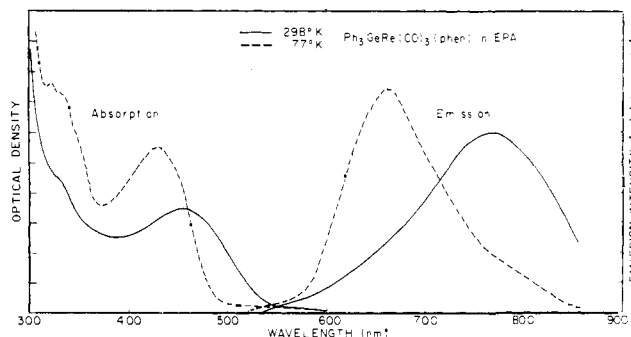


Figure 1. Absorption and emission of $\text{Ph}_3\text{GeRe}(\text{CO})_3(1,10\text{-phenanthroline})$. The emission spectra are corrected for variation in detector sensitivity and are excited at 480 nm. The sensitivity for the 298 and 77 K emission is not the same, and the absorption spectral change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

Table I. Spectral and Photochemical Properties of $\text{Ph}_3\text{ERe}(\text{CO})_3(1,10\text{-phenanthroline})$ at 25 °C

E	IR bands, cm^{-1} (ϵ) ^a	(E–Re) $\sigma_b \rightarrow \pi^*L$, nm (ϵ) ^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 fluorimeter with output to an oscilloscope. ^d Reaction quantum yield for disappearance of E–Re species is equal to the formation quantum yield for $\text{ClRe}(\text{CO})_3(1,10\text{-phenanthroline})$ 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 $\sim 2 \times 10^{-3}$ M E–Re species. Light intensities are $\sim 3 \times 10^{-7}$ einstein/min.

49.52 (49.34); H, 2.90 (2.92); N, 3.50 (3.26). Calcd for $\text{C}_{33}\text{H}_{23}\text{N}_2\text{O}_3\text{ReGe}$ (found): C, 52.54 (52.66); H, 3.07 (3.12); N, 3.71 (3.84).

The UV–vis absorption spectra of the complexes (Figure 1 and Table I) are similar to those previously found^{8d} for $(\text{OC})_5\text{Re-Re}(\text{CO})_3\text{L}$, 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,^{16b,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. $\text{Ph}_3\text{ERe}(\text{CO})_3$ 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–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 $\text{Ph}_3\text{ERe}(\text{CO})_3\text{L}$ complexes exhibit detectable emission upon photoexcitation in fluid so-