where R is any conveniently generated free radical. When reactions were tried with lead vapor and plasma-produced trifluoromethyl radicals in the apparatus described,[1] no significant quantity of tetrakis(trifluoromethyl)lead was produced.

Lead trifluoromethyl compounds were unknown until 1978,[2] when the compounds tris(trifluoromethyl)methyllead and bis(trifluoromethyl)dimethyllead were prepared in our laboratory by a series of transfer reactions with bis(trifluoromethyl)mercury.[3] The synthesis of tetrakis(trifluoromethyl)lead, $Pb(CF_3)_4$, has now been accomplished in low yields by cocondensation of lead dichloride with trifluoromethyl radicals generated from a hexafluoroethane plasma source:

$$C_2F_6 \xrightarrow[100\ \mathrm{W,\ 14\ MHz}]{\mathrm{rf}} 2CF_3^{\bullet}$$

$$PbCl_2(g) + 4CF_3^{\bullet} \xrightarrow{-196\ ^{\circ}C} Pb(CF_3)_4 + Cl_2$$

This is the first successful synthesis of tetrakis(trifluoromethyl)lead.

The reactor used in this work has been illustrated elsewhere.[1] In a typical reaction, 1 g of dry lead dichloride was placed in a quartz crucible, which was then placed inside a resistively heated crucible heater. The radio frequency signal was supplied by a 100-W, 1356-MHz radio frequency generator, which was capacitively coupled to the reactor. The hexafluoroethane flow rate was set between 1 and 2 mmol/min, and the total pressure was maintained at less than 2 Torr. After completion of the reaction, the volatile products were vacuum distilled through a −110 °C trap to remove the excess hexafluoroethane and chlorine produced in the reaction. Care must be taken to minimize the exposure of the less volatile products to the chlorine produced or otherwise no trifluoromethyl-substituted lead compounds will be detected. If such care is taken, nearly all of the trifluoromethyllead compound is $Pb(CF_3)_4$, according to fluorine NMR spectra.

If the products are exposed to chlorine, several small NMR and GLC peaks appear of partially chlorinated lead trifluoromethyl compounds. If $PbBr_2$ or PbI_2 is used as a precursor, separation and removal of the halogen is more difficult owing to the more similar volatility of the minor products compared to that of $Pb(CF_3)_4$, and lower yields result.

The products of five reactions were collected at −110 °C, combined, and vacuum distilled. The fraction containing virtually all of the trifluoromethyllead compound very slowly passed a −78 °C trap. This fraction was then separated on a gas chromatograph (10% SE-30 on Chromosorb P) from the fluorocarbon catenation products also produced in the plasma. All of the product was placed in a preweighed capillary, sealed under vacuum, and weighed [21.4 mg of $Pb(CF_3)_4$]. A gas-phase weight determination gave 480 g/mol. (The calculated value is 483 g/mol.) The yield of tetrakis(trifluoromethyl)lead was between 1 and 2 mg/h.

Tetrakis(trifluoromethyl)lead is a colorless liquid that hydrolyzes in water to form fluoroform. With the mass spectrometer cooled to room temperature, the mass spectrum consisted of $Pb(CF_3)_n^+$ species and fluorocarbon fragments. The following lead species were observed (each envelope had the isotopically correct pattern but is given here in terms of ^{208}Pb isotopes only): *m/e* 208, Pb^+ (82%); *m/e* 227, PbF^+ (61%); *m/e* 277, $Pb(CF_3)^+$ (75%); *m/e* 346, $Pb(CF_3)_2^+$ (18%); *m/e* 415, $Pb(CF_3)_3^+$ (100%); *m/e* 465, $Pb(CF_3)_3CF_2^+$ (less than 1%). The fluorine NMR spectrum, taken on a neat liquid in a capillary, gave a singlet at −41 ppm from $CFCl_3$; $J(^{207}Pb–F) = 808$ Hz. The gas-phase infrared spectrum contains absorptions at 1240 (m), 1150 (vs), 1105 (w), 1065 (s), 1030 (w), and 720 cm^{-1} (m).

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Registry No. $Pb(CF_3)_4$, 4556-29-0; $PbCl_2$, 7758-95-4; C_2F_6, 76-16-4.

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[1] Juhlke, T. J.; Braun, R. W.; Bierschenk, T. R.; Lagow, R. J. *J. Am. Chem. Soc.* **1978**, *101*, 3229.

[2] Some higher lead alkyls were prepared by Stone and co-workers using conventional synthetic methods: Stone, G.; et al. *Chem. Ind.* **1959**, 1409.

[3] Lagow, R. J.; Eujen, E. *J. Chem. Soc., Dalton Trans.* **1978**, 541.

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Time-Dependent Photoselection Results for Ruthenium(II) Diimine Complexes

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Krausz[1] has reported that our time-dependent excitation polarization results[2] for $Ru(bpy)_3^{2+}$ in glassy solution at 77 K could not be verified in his laboratory. While, in general, a negative result as he has reported must be viewed with caution, the confusion created by his report and the importance of this time-dependent result to establishing the correct mechanism for localization of the emitting triplet of the $Ru(bpy)^{2+}$ species necessitates a response.

In our work,[2] we pointed out that the decrease of the maximum excitation polarization from a value as high as $P_{max} \sim 0.4$ at short times (5–10 ns) to the steady-state $P_{max} \sim 0.23$ for those glassy solvents meant that the mechanism of localization necessarily was *intrinsic*, not *environmental* (solvent driven) as suggested by Krausz on the basis of excited-state resonance Raman[3] and emission measurements at the melting point of the glassy solvent.[4] This conclusion of intrinsic localization necessarily derived from the earlier excitation polarization result of Carlin and De Armond,[5] which was obtained in glassy solution at *77 K*, where solvent motion is not expected. Recent excited-state resonance Raman results by Brus and Carroll[6] concur with our conclusion that the localization is intrinsic.

Most recently, we have, in a detailed paper,[7] presented a model for the rationale of the magnitude of the steady-state excitation *P* in a variety of Ru(II) diimine complexes. The model describes the potential surfaces of the excited MLCT singlet and the emitting triplet states, noting that the singlet state consists of localized and delocalized regions and it is for this reason that the anomalous P_{max} magnitude is observed for Ru(II) tris- and bis(diimine) complexes.

Concurrently, we did report time-resolved P_{max} data for a number of tris(diimine) complexes, including the mixed-ligand complexes $[Ru(bpy)_2(phen)]^{2+}$ and $[Ru(phen)_2(bpy)]^{2+}$, for which P_{max} at 0–5 ns was found to be 0.43 in pure ethanol glass. Other complexes, including $[Ru(phen)_3]^{2+}$, $[Ru(bpz)_3]^{2+}$, and $[Ru(pq)_3]^{2+}$ (bpz = 2,2′-bipyrazine and pq = 2,2′-pyridylquinoline) as the original $[Ru(bpy)_3]^{2+}$, evidence solvent dependence in the decay of the polarization value (*P*).

We have pointed out that the original interpretation[2] of the time-dependent P_{max} as resulting from exciton hopping between the chelate rings is incorrect and that this fast decrease of *P* results from the spin–lattice relaxation (SLR) between the closely spaced spin states of this emitting triplet. While the details of the phonon spectrum for glassy solution are not well-known, the data for crystalline systems would suggest that at 77 K in glassy solution saturation of the lattice phonon modes would not be likely, since a large number of phonon modes would exist at this temperature. Thus, the suggestion by Krausz that our experimental laser intensity affects the equilibration of the spin state and could give rise to artifactually high *P* values seems unlikely. Further, in our measurement technique using a Molectron dye laser system as the excitation source, the laser beam was focused to a tight spot and also defocused to give low signal intensity. No difference in

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[1] Krausz, E. *Inorg. Chem.* **1988**, *27*, 2392.

[2] Myrick, M. L.; Blakley, R. L.; De Armond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 2841.

[3] Krausz, E. *Chem. Phys. Lett.* **1985**, *116*, 501.

[4] Ferguson, J.; Krausz, E. *Chem. Phys. Lett.* **1986**, *127*, 551.

[5] Carlin, C. M.; De Armond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297.

[6] Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 7613.

[7] Myrick, M. L.; Blakley, R. L.; De Armond, M. K.; Arthur, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 1325.

0020-1669/89/1328-0981$01.50/0

the time dependence of P_{max} could be observed for these excitation techniques. This fact, the solvent dependence observed for the P_{max} decay, and the existence of complexes that do not exhibit the time-dependent decay make unlikely that the time dependence of P results from an artifact such as sample heating.

The origin of the Krausz measurement problem is difficult to ascertain as was the case of our earlier rebuttal[8] to his "correction"[9] of our P_{max} data. Most likely, the problem is that the Krausz experimental system does not have an adequately fast response time. Note also that for our data the highest P occurs in 0–5-ns time delay of the Boxcar Integrator and that the steady-state P_{max} is obtained after ~20 ns, not 300 ns as suggested by Krausz. Indeed, Krausz has incorrectly reproduced our data in his Figure 2.

Finally, his suggestion in the last paragraph of his note that the origin of the deviation of the P_{max} from the 0.14 expected for a planar emitter–planar absorber is due to a "small amount of in-plane anisotropy due to environmental effects", a "red edge" effect, has been shown inconsistent[5,8] with the solvent dependence of P_{max}.

In summary, our time-resolved P_{max} for a number of different complexes, in a variety of different solvents and under different excitation intensity conditions, cannot be argued away. Further independent excited-state resonance Raman results[6] at various temperatures argue that the localization is intrinsic, consistent with the results of our time-resolved P measurement.[2,7]

Our most recent experimental results[10] at 7 K do demonstrate that slow spin-lattice relaxation can alter the emission decay characteristics for $Ru(bpy)_3^{2+}$ at this temperature such that a rise time can be measured. Subsequent analysis of these data and temperature-dependent (7–77 K) photoselection data[11] make apparent that the emitting state of the $Ru(bpy)_3^{2+}$ species (glassy solution, dilute crystal) at *all temperatures* is a spin triplet with levels closely spaced (~0.1 cm^{-1}) as found in most π-electron organic heterocycles.

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(8) Blakley, R. L.; Myrick, M. L.; De Armond, M. K. *Inorg. Chem.* **1988**, *27*, 589.
(9) Ferguson, J.; Krausz, E. *Inorg. Chem.* **1987**, *26*, 1383.
(10) Myrick, M. L.; Blakley, R. L.; De Armond, M. K. *Chem. Phys. Lett.*, in press.
(11) Myrick, M. L.; Blakley, R. L.; De Armond, M. K. *Chem. Phys. Lett.*, in press.

Additions and Corrections

1985, Volume 24

Stuart Bristow, John H. Enemark,* C. David Garner,* Martin Minelli, Gareth A. Morris, and Richard B. Ortega: Synthesis of (1,2-Benzenediolato(2−)-*O,O'*)oxobis(1-piperidinolato(1−)-*O,N*)molybdenum(VI), $[MoO(C_5H_{10}NO)_2(C_6H_4O_2)]$, and Structure Determination by Correlated ^1H–^{13}C Two-Dimensional NMR Spectroscopy and X-ray Crystallography.

Page 4074. In Table III, the chemical shift of $[MoO(C_5H_{10}NO)_2$-(3,5-*t*-Bu$_2$-cat)] should be +20 ppm. We thank W. E. Newton et al. (*Inorg. Chem.* **1988**, *27*, 359) for bringing the error in the sign of the chemical shift to our attention.—John H. Enemark