# Rhodamine Complexes. Preparation, Photophysical Properties, and the Structure of $[Rh(rhodamine)(CO)(P(tol)_3)_2][SbF_6]^{\dagger}$

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The fluorescent dye rhodamine B has been used as a ligand, binding through its carboxylate group, in complexes of Rh(I), Ir(I), Ir(I), and Pt(II). Slight alteration in the absorption spectrum of the rhodamine chromophore results from its coordination, but profound changes are observed in the luminescence intensity of the coordinated chromophore. In compounds where the rhodamine is bound to a readily oxidized metal center (Rh(I), Ir(I), H<sub>2</sub>Ir(III)) its fluorescence is strongly quenched, but when it is bound to a less easily oxidized metal center (Ir(III)) the rhodamine fluorescence remains intense. From these and other observations we propose electron transfer as the excited-state quenching mechanism. The structure of the title compound reveals an unexpected packing arrangement, best described as linear chains of Rh-rhodamine cations held together by rhodamine-rhodamine interactions.

# Introduction

The photophysical behavior of organic dye molecules in the presence of metal compounds has been an issue of interest, with particular emphasis on the mechanism(s) by which the metal compounds quench luminescent excited states of the dye molecules.<sup>1</sup> Important mechanisms include metal-induced intersystem crossing to nonemissive triplet excited states, energy transfer from the excited dye molecules to low-lying excited states of the metal complexes, and electron transfer between the dye molecules and metal centers.<sup>2</sup> Electron transfer between dyes and delocalized electronic states of metal compounds is especially important in photographic sensitization of silver halide grains by organic dyes.<sup>3</sup>

While there are a number of studies of the quenching of excited states of dyes by metal ions in solution,<sup>2</sup> detailed studies of photophysical properties of dyes chemically bound to a metal center have tended to concentrate on three particular classes of compounds, namely, transition-metal compounds bearing bipyridyl and/or phenanthrenyl ligands, rare-earth compounds with chelating organic ligands, and dye molecules bearing crown ether or cryptand substituents, capable of binding metal ions.<sup>4,5</sup> We decided to explore other types of compounds and have examined the behavior of selected organic dye molecules attached to several selected organo-transition-metal centers. We wished to see what effect each metal center might have on the dyes' excited states and to incorporate our observations into the larger body of (metal)-(excited organic chromophore) interactions. In this article we describe the syntheses of organorhodium, -iridium, and -platinum complexes 1-8 (Chart I) bearing the rhodamine chromophore, aspects of the photophysical behavior of these materials, and the crystal and molecular structure of the rhodium-rhodamine compound **1a**. In all cases we use "rhodamine" to refer to the well-known xanthene dye rhodamine B, which is frequently used in laser and biological staining applications.

## **Results and Discussion**

Preparation and Handling. We were able to isolate the square-planar Rh(I), Ir(I), and Pt(II) compounds 1-4 as microcrystalline materials. Syntheses were attempted of a number of other isoelectronic Rh, Ir, and Pt compounds, particularly compounds containing other phosphine ligands, but at best only impure products, unsuitable for spectroscopic/photophysical studies, could be isolated. The particular Pt(II) compound 2 was



prepared because we hoped its very close resemblance to the Rh/Ir compounds 1 would allow comparison of their respective photo-

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physical properties. But in solution, compound 2 appears to undergo partial isomerization to the cis compound, which inhibits a meaningful interpretation and comparison of the emission data. Therefore we prepared the Pt(II) compounds 3 and 4 bearing chelating phosphine ligands, which should not isomerize. We also prepared the Ir(III) compounds 5-8 to assess the effects of the higher formal oxidation state and chelating vs monodentate dye coordination. All compounds were characterized by conventional NMR and IR spectroscopy. The sensitivity of these compounds, combined with a tendency for most of these compounds to cocrystallize with volatile solvent molecules, has made it troublesome to obtain elementally pure samples, but for compound 6 satisfactory C, H, N analysis was obtained. For all other compounds we were able to prepare samples that had no impurities discernible by <sup>1</sup>H NMR (>97% pure, excluding cocrystallized solvent).

The simplest synthetic method, applicable to all these compounds except 8, is room-temperature reaction of the leuco form of "free-base" rhodamine B (9) with an appropriate precursor metal complex containing an extremely labile ligand, as in eq 1 (Ln = ligand). Details are given in the Experimental Section.



In all these compounds the rhodamine dye molecule is bound through one or both carboxylate oxygen atoms, as found in the crystal structure of 1a (see Figure 1). We believe each compound is formed by direct attack of the precursor metal complex, functioning here as a ring-opening Lewis acid, on a lactone oxygen atom of the leuco rhodamine reagent 9. Even so, the transition-metal centers employed in this study do not have great affinity for carboxylate groups, so the rhodamine compounds tend to be fragile and susceptible to acidolysis and hydrolysis. Ligand substitution is also important, and several of the compounds will undergo the reverse reaction of eq 1 when exposed to modestlystrongly binding ligands L' (halide ions, phosphines, pyridine, even acetonitrile). For these reasons we have had to be scrupulously careful in preparing spectroscopic samples, but still we occasionally observed irreproducible phenomena that we ascribe to sample decomposition.

Absorption and Emission Spectroscopy. Owing to the above-mentioned reactivity of these ionic compounds with coordinating solvents and OH bonds, the solvent we chose for spectroscopy was dichloromethane. In concentrated  $CD_2Cl_2$  solutions (0.1-1 M) these compounds are thermally and photochemically stable (<sup>1</sup>H NMR analysis), but in the much more dilute solutions required for optical spectroscopy several of the compounds undergo changes. For instance, the optical density (OD) of a solution of compound **1a** in CH<sub>2</sub>Cl<sub>2</sub> changed from 0.178 to 0.148 when placed in a spectrophotometer and scanned repeatedly over a 3-h period. However, the OD of solutions of **6** and of **10** did not change significantly under comparable conditions. For quantitative absorption and emission studies, solutions were freshly prepared by

TABLE I: Absorption and Emission Data for Compounds 1-9

compd	abs max," nm	10 <sup>-5</sup> € <sup>b</sup>	emission max, <sup>c</sup> nm	rel emission int, <sup>d</sup> %
1a	541	1.05	580	8
1b-SbF6	543	1.11	577	9
1b-SO <sub>3</sub> CF <sub>3</sub>	545	1.00	577	12
2 <sup>e</sup>	541	0.73	572	18
3	547	0.80	571	100
4	546	1.03	577	13
5	542	1.13	566	170
6	565	1.2	583	118/3
7	552	1.10	579	24
8	542	1.13	564	104
9 (leuco rhodamine)	317	0.18	500	h
10 (Me <sub>3</sub> Si-rhodamine SO <sub>3</sub> CF <sub>3</sub> )	557	1.31	579	100.0 <sup>d</sup>

<sup>a</sup>All measurements in CH<sub>2</sub>Cl<sub>2</sub> solution, OD in the range 0.1–0.4, at room temperature. <sup>b</sup>Determined by comparison of OD before and after treatment with ClSiMe<sub>3</sub>, except for compounds 6, 9, and 10 (determined directly). <sup>c</sup>Excitation at wavelength of maximum absorbance. <sup>d</sup>See Experimental Section. Values are relative to compound 10 = 100% and expected relative errors are of the order  $\pm 10\%$ . <sup>c</sup>Contains some cis isomer; see text. Observed emission intensities vary. <sup>f</sup>Does not react cleanly with ClSiMe<sub>3</sub>.  $\epsilon$  determined directly,  $\pm 10\%$ . <sup>g</sup>Could not be compared with silylated material. Expected emission calculated as in Experimental Section. <sup>h</sup>Intensity increases dramatically with continued illumination at 317 nm.

using compounds pure by NMR and freshly recrystallized whenever possible and were handled in the dark.

Absorption and emission data for the compounds are presented in Table I. In each case the rhodamine chromophore exhibits its intrinsic absorption spectrum with little perturbation in shape but with some shift in position and considerable variation in intensity, relative to the spectrum of compound 10 (which we have chosen as our reference compound). The observed variation of intensity concerns us, even though many chromophores show environment-sensitive absorption intensities, because it may be indicating varying amounts of ion pairing and/or aggregation or sample decomposition by the reverse of reaction 1. We have been unable to address this issue satisfactorily because the compounds are fragile, and we simply cannot be certain what species are present in extremely dilute solution (OD ca. 0.1). We have compared the thickness-compensated absorption spectra of several samples with OD varying from 0.15 to 1.5 and have seen shifts no larger than  $\pm 2$  nm in position and  $\pm 5\%$  in intensity. But undisturbed samples can exhibit similar intensity variations resulting from elapsed time alone (see above), so dilution studies neither confirm nor disprove tendencies for ion pairing or aggregation. However, a very recent study<sup>6</sup> of rhodamine B (acid form, chloride salt) in alcohol solutions of varying pH found that absorption intensities diminished by ca. 13% on deprotonation. To some extent, then, rhodamine bound to the metal centers in compounds 1-8 may resemble its deprotonated form.

Another complication that confronts us is our inability to prepare pure salts of all compounds with the same counterion. Synthetic constraints oblige us to compare/contrast  $SO_3CF_3$  salts of some compounds with  $SbF_6$  salts of others, and assume that cation-anion interactions are less important than intracation rhodamine-metal interactions. We were able to prepare the  $SO_3CF_3$  as well as the  $SbF_6$  salts of compound **1b** and found them sufficiently similar (Table I) to support the general observations and conclusions we draw in this article.

Despite these complications, we believe the shifts in the wavelength of the absorption maximum can be rationalized by charge and structural effects within the metal-rhodamine cation alone: Hückel calculations suggest that the excited state of the rhodamine chromophore has greater electron density (less positive charge) in the central ring, and especially at the unique carbon atom, than does the ground state, so a stronger positive charge

<sup>(4) (</sup>a) See: Lohr, H.-G.; Vogtle, F. Acc. Chem. Res. 1985, 18, 65-72 and references therein. (b) Konopelski, J. P.; Kotzyba-Hibert, F.; Lehn, J.-M.; Desvergne, J.-P.; Fages, F.; Castellan, A.; Bouas-Laurent, H. J. Chem. Soc., Chem. Commun. 1985, 433-436. (c) de Silva, A. P.; de Silva, S. A. Ibid. 1986, 1709-1710. (d) Guinand, G.; Marsau, P.; Lehn, J. M.; Kotzyba-Hibert, F.; Konopelski, J. P.; Desvergne, J. P.; Fages, F.; Castellan, A.; Bouas-Laurent, H. Acta Crystallogr. Sect. C 1986, C42, 715-719. (e) Guinand, G.; Marsau, P.; Bouas-Laurent, H.; Castellan, A.; Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lamotte, M. Ibid. 1987, C43, 857-860. (g) Mau, A. W.-H.; Sasse, W. H. F.; Creaser, I. I.; Sargeson, A. M. Nouv. J. Chim. 1986, 10, 589-592. (h) Ghosh, S.; Petrin, M.; Maki, A. H.; Sousa, L. R. J. Chem. Phys. 1987, 87, 4315-4343 and references therein.

<sup>(5)</sup> Transition-metal complexes of several biologically important chromophores have been reported: Burgmayer, S. J. N.; Stiefel, E. I. J. Am. Chem. Soc. 1986, 108, 8310-8311 and references therein.

<sup>(6)</sup> Arbeloa, I. L.; Rohatgi-Mukherjee, K. K. Chem. Phys. Lett. 1986, 128, 474-479.

in the vicinity of the unique carbon atom should cause a red shift in the position of the rhodamine absorption and emission. Thus the position of the rhodamine absorption is sensitive to both the actual charge of the attached metal center, which varies from complex to complex, and to the physical distance between the metal center and the central ring of the chromophore, which falls into one of two ranges. In the monodentate compounds 1-5 and 8 the distance from the metal atom to the unique carbon atom of the rhodamine should be comparable to the distance found in compound 1a (5.8 Å); in the bidentate compounds 6 and 7 this distance should be approximately 4.8 Å. It is not surprising, then, that the compound showing the lowest excited-state energy (the "reddest" spectra), compound 6, has both bidentate rhodamine and the greatest formal charge. However, the rhodamine absorption is also quite sensitive to the distance and extent of residual bonding between the carboxylate oxygen atom and the unique carbon atom (which are formally covalently bonded in the starting leuco compound 9). These factors will be convolved with the effects of the charge and distance of the bound metal atom-and also with any ion pairing or aggregation effects.

The emission spectra of compounds 1-8 follow the trends established by the absorption spectra; that is, immaterially different in shape from the reference compound 10 although tending to redor blue-shift in the same directions as the corresponding absorption spectra. But while emission spectra resemble that of the reference compound, relative emission intensities are quite different (see Table I and Experimental Section). To summarize the trends established by this data: The emission from square-planar trans-biphosphine Rh, Ir, Pt compounds 1 and 2 is appreciably quenched while emission from cis-bisphosphine Pt compound 3 is intense; emission from the ferrocenylphosphine compound 4 is again appreciably quenched; emission from the octahedral methyl-Ir(III) compounds 5 and 6 is intense; and emission from the dihydrido-Ir(III) compound 7 is significantly quenched while emission from the dihydridocarbonyl-Ir(III) compound 8 is intense. We have established that the quenching process(es) is (are) intramolecular in compounds 1, 2, 4, and 7 by the following experimental procedure: A freshly prepared solution of each compound, after its luminescence was recorded, was treated with excess ClSiMe<sub>3</sub>, and the luminescence of the resulting solution was measured again (see Experimental Section). The reaction of ClSiMe<sub>3</sub> with monodentate rhodamine compounds 1-5 and 8 proceeds rapidly and cleanly according to eq 2, and the rhodamine



is liberated as its trimethylsilyl ester—which is the reference compound 10. (Compound 6 reacts only very slowly with ClSiMe<sub>3</sub> to form several unidentified compounds.) Solutions treated with ClSiMe<sub>3</sub> in this fashion exhibited luminescence spectra and intensities indistinguishable from those of the reference solution of pure 10. Certainly the concurrently formed chloro-metal compounds could effect bimolecular quenching of the liberated (trimethylsilyl)rhodamine, but at the concentrations present in these experiments (on the order of  $10^{-6}$  M for each species) bimolecular quenching of the rhodamine singlet excited state (lifetime of compound 10 is 4.5 ns) is insignificant.

One peculiar feature of the emission spectra of the feebly emitting compounds 1, 2, and 4 is that the emission maxima are only slightly blue-shifted (0-7 nm) from that of the reference rhodamine compound 10. Since the absorption maxima are significantly blue-shifted (11-16 nm), we must be concerned that it may be a small amount of liberated (photochemically or by decomposition) rhodamine that is actually responsible for the observed emission and that bound rhodamine may be entirely quenched. We believe that some and perhaps most of the emission does arise from bound rhodamine, but the questions of sample decomposition cannot be answered with complete satisfaction for these fragile rhodamine compounds. Fortunately, the Ir(III) compounds 5 and 6 are much more robust; the  $\eta^2$  compound 6 even survives for several hours in the presence of ClSiMe<sub>3</sub> (whereas compound 7 and all the  $\eta^1$  compounds react essentially immediately according to eq 2). Compound 6 exhibits absorption and emission spectra that are significantly red-shifted relative to liberated rhodamine (10), and compounds 5 and 8 exhibit markedly blue-shifted spectra. Thus we are confident that, at least for compounds 5, 6, and 8, decomposition is negligible and the intense fluorescence emanates entirely from bound chromophore. In the case of the Pt compounds 3 and 4, the ferrocenyl compound 4 allows us to explore the decomposition issue in another context (see below). Incidentally, given the close structural relationship between compounds 5 and 8 one would expect comparable blue shifts, and the observed similarity is very reassuring.

Quenching Mechanism. Of the three most common mechanisms for quenching—energy transfer, electron transfer, and intersystem crossing—we believe electron transfer (eq 3) is the



dominant quenching mechanism for all the compounds described in this article. We recognize that structural similarities among closely related compounds do not guarantee a common single quenching mechanism, but the present family of compounds exhibits a remarkably consistent trend supporting electron transfer.

From the emission data for the series of compounds, the trend is that the compounds with easily oxidized metal centers (e.g., 1) show less emission (excited states are significantly quenched) and compounds with less easily oxidized metal centers are more emissive. To attempt a more quantitative discussion, we note that the reported  $E_{1/2}$  values for oxidation and reduction of rhodamine B (chloride salt of the protonated form) in acetonitrile solution are 1.07 and -0.94 V vs SCE, respectively, with some evidence hinted that reduction is a multielectron process.7a Values reported in ethanol solution are +1.2 (oxidation) and -0.8 V (reduction).7b Redox potentials for representative metal compounds are difficult to obtain owing to the complicated electrochemical reactions they undergo,<sup>8</sup> but reported  $E_{1/2}$  potentials for IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> in dichloromethane solution are  $E_{ox} = 1.12$  V vs SCE<sup>9</sup> and  $E_{red} = -2.30$  V vs SCE.<sup>10</sup> Combining these values with an excited state energy of 2.18 eV (568 nm), we obtain the data in Table II. From these data the excited-state electron-transfer process rhodamine\* +  $IrCl(CO)(PPh_3)_2 \rightarrow rhodamine^{-} + [Ir(II)Cl(CO)(PPh_3)_2]^+$  is exergonic by 0.12 V, clearly consistent with the postulate of rapid electron transfer for compound 1b (eq 3). A better model for the

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<sup>(9)</sup> Vecernik, J.; Masek, J.; Vieck, A. A. J. Chem. Soc., Chem. Commun. 1975, 736–737.

<sup>(10)</sup> DeMontauzon, D.; Poilblanc, R. J. Organomet. Chem. 1975, 93, 397-404.

**TABLE II: Energies of Electron-Transfer Reactions** 

species	energy, V
$IrCl(CO)(PPh_3)_2 + rhodamine$	0.00
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> + [rhodamine]*	2.18 <sup>a</sup>
$[IrCl(CO)(PPh_3)_2]^+ + [rhodamine]^-$	2.06 <sup>b</sup>
$[IrCl(CO)(PPh_3)_2]^- + [rhodamine]^+$	3.37 <sup>b</sup>

<sup>a</sup>Assuming excited state at 568 nm (average of emission and absorption maxima for compound 10). <sup>b</sup>Based on literature values for redox potentials; see text.

Ir center of compound **1b** is Ir(4-methylbenzoate)(CO)(P(tol)<sub>3</sub>)<sub>2</sub>, which exhibits irreversible oxidation at 0.34 V relative to ferrocene in CH<sub>2</sub>Cl<sub>2</sub> (ca. 0.74 V vs SCE). With this value, the electrontransfer process of eq 3 is exergonic by 0.5 V. If oxidizing the metal center requires more than about 1.3–1.4 V vs SCE,<sup>7</sup> or about 0.2–0.3 V more than IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, rhodamine fluorescence should be largely unquenched.

Platinum(II) compounds can also be relatively easily oxidized; from literature data on Pt(aryl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> compounds, oxidation occurs at ca. 1.1-1.4 V vs SCE (depending upon the substituents in the aryl group).<sup>11a</sup> This hovers around the limit of possible exergonic electron transfer to excited rhodamine. Better models for the methyl-Pt(II) compounds 2 and 3 are the corresponding phosphine-platinum-methyl-chloro compounds, but unfortunately they did not exhibit well-defined redox activity. For Pt(diphos)Cl(CH<sub>3</sub>), an ill-behaved oxidation wave could be detected at +0.96 V relative to ferrocene in CH<sub>2</sub>Cl<sub>2</sub> (ca. 1.4 V relative to SCE). This is the upper limit, given above, for thermodynamically accessible excited-state electron transfer in rhodamine compounds. Of course, solution electrochemical measurements even of ideally well-behaved compounds are only approximate indications of potentials for intramolecular excited-state electron transfer. But this estimated electron-transfer potential, together with the relative emission intensities of compounds 2 and 3, support the conclusion that the excited-state electron-transfer potential is very delicately poised and may be slightly exergonic for 2 and endergonic for 3. We reconsider compound 3 at a later point.

A complication peculiar to compound 2 is its tendency to undergo trans-cis isomerization. From NMR spectra (see Experimental Section) the material is initially predominantly the trans isomer, but a slow isomerization converts some of the material to what we believe is the cis isomer. We also note that luminescence from "compound 2" is extremely variable, with aged spectroscopic solutions of compound 2 (or freshly prepared spectroscopic solutions of aged compound 2) being strikingly more luminescent (relative emission intensity, Table I, 40-90%) than freshly prepared spectroscopic solutions of freshly prepared compound 2 (relative emission intensity ca. 18%). The exact processes occurring in dilute solution cannot be determined, but we propose that the cis isomer-present in significant amounts only in aged solutions/material-is intrinsically more emissive than the trans isomer. This in turn could be the result of structural or steric differences between the two isomeric forms. But there are also electronic differences between, for instance, cis and trans isomers of dihalobis(phosphine)platinum(II) compounds;11b cis isomers tend to be colorless and trans isomers yellow, and photochemically interconvertable. If for whatever reason metal-rhodamine electron transfer was slightly less favorable in the cis than in the trans isomer, the observed emission intensity trends can be accounted for. This underscores the notion that these Pt(II) compounds are very delicately poised on the threshold of energetically allowed excited state electron transfer.

It would be very useful to have actual measurements of excited-state lifetimes for these compounds. But after a few attempts at determining excited-state lifetimes, we were overwhelmed by difficulties that appear to be inherent in the compounds themselves. The tendency for at least some of the rhodamine to detach itself from the transition-metal centers, combined with time-dependent changes in absorption and emission intensities, makes it nearly impossible to deconvolve photon-counting data into meaningful excited-state lifetimes. Longer data collection times make the difficulties especially acute for the feebly emitting compounds 1, 2, 4, and 7. In future work we may study emission from these compounds in low-temperature glasses, which could suppress decomposition and allow a more meaningful determination of lifetimes and rates of quenching processes.

According to electron-transfer theory, we expect the rhodamine complex of a more easily oxidized metal center to exhibit less emission. But without reasonable estimates of quenching rates. any attempt to draw even a semiquantitative correlation from the results reported here would be foolhardy. We must be content with the much more general, qualitative conclusion that emission from more easily oxidized compounds 1 should be more strongly quenched than emission from the less easily oxidized compound 2, while emission from still less easily oxidized compounds should be unquenched. The behavior of compounds 5 and 6 is consistent with this conclusion. The methyl-Ir(III) compounds are substantially more difficult to oxidize than Ir(I); the model compound Ir(CH<sub>3</sub>)Cl(CO)(4-methylbenzoate)(P(tol)<sub>3</sub>)<sub>2</sub>, analogous to compound 5, shows no oxidation current to 2 V vs SCE. Thus these methyl-Ir(III) compounds should not, and experimentally do not, quench rhodamine fluorescence. Ferrocene, which is very easily oxidized (ca. 0.4 V relative to SCE), should-and does, re compound 4-quench rhodamine fluorescence.7 Note that electron transfer in the opposite direction, where the Ir(I) center of compound 1b is reduced to Ir(0) with formation of the rhodamine radical cation, is endergonic in Table II by more than 1 V and should not contribute to excited-state quenching.

One comparison that should be noted explicitly is the relationship between the Ir(I) compound **1b** and Ir(III) compound **5**. Apart from the structural changes (e.g., *trans*-CO-rhodamine in the square-planar compound, *cis*-CO-rhodamine in the octahedral compound) the Ir(III) compound **5** is formally derived from the Ir(I) compound by the addition of methyl chloride, although a less direct approach was required for the actual synthesis. In the conventional organometallic description, the addition of methyl chloride is a two-electron oxidation ("oxidative addition") and the oxidized, Ir(III), center is difficult to oxidize further. A less conventional but extremely useful rationalization is that the Ir(I) center contains a nonbonding lone pair of electrons in its  $d_{z^2}$  orbital (see **11a**) and addition of methyl chloride ties up this lone pair



in a primarily Ir-C  $\sigma$ -bonding orbital (11b). Viewed in this manner the Ir(I) compound 1b is analogous to the (aminomethyl)naphthalene compound 12a (in which fluorescence is quenched by electron transfer from the nitrogen lone pair) and the methyl-Ir(III) compound is analogous to the N-protonated compound 12b (in which fluorescence is restored).<sup>12</sup>

The hydrido compounds 7 and 8 extend this picture. If the methyl-Ir(III) compound 5 represents an "oxidative addition" of

<sup>(11) (</sup>a) Seeber, R.; Mazzocchin, G. H.; Minniti, D.; Romeo, R.; Uguagliati, P.; Belluco, U. J. Organomet. Chem. 1978, 157, 69-74. (b) Ahrland, S.; Chatt, J. J. Chem. Soc. 1957, 1379-1386. Hartley, F. R. The Chemistry of Platinum and Palladium; Wiley: New York, 1973; pp 456-459.

<sup>(12)</sup> Mes, G. F.; van Ramesdonk, H. J.; Verhoeven, J. W. J. Am. Chem. Soc. 1984, 106, 1335-1340.

CH<sub>3</sub>Cl to the Ir(I) compound 1b-SO<sub>3</sub>CF<sub>3</sub>, the dihydrido compounds 7 and 8 represent the addition of  $H_2$  to an Ir(I) center, which also is normally viewed as a formal oxidation of the metal center. But recent studies of polyhydrido compounds by Crabtree and Quirk<sup>13</sup> have shown that H<sub>2</sub> addition may actually increase the electron density at certain metal centers, a phenomenom they have called "reductive addition". The quenching observed for the rhodamine chromophore in compound 7, then, could be the result of unexpectedly facile oxidation of the supposedly "Ir(III)" center. In view of other work on molecular dihydrogen complexes, we suspect the classical dihydrido "H-Ir(III)-H" electronic structure of compound 7 actually bears a component of the nonclassical dihydrogen " $(H_2)$ -Ir(I)" electronic structure,<sup>14</sup> which is responsible for the facile oxidation. Cyclic voltammetry on the model compound IrH2(P(tol)3)2(p-methylbenzoate) in CH2Cl2 solution did not show a clean oxidation wave, but did show slight current flow beginning at about +0.3 volts relative to ferrocene, perhaps indicating the onset of slow electron transfer at the electrode surface.

However, quenching could also result from some intrinsic property of the hydrido ligands (perhaps vibronic coupling or easily oxidized "hydride ions"). To check this, we prepared compound 8, which is intensely luminescent; this proves that rhodamine is not invariably quenched by Ir hydrides. The underlying difference between the metal centers of 7 and 8, which causes quenching in 7 but prevents it in 8, must reflect the presence of the CO ligand in 8. We postulate that the CO ligand has two relevant effects: CO lowers the electron density (and ease of oxidation) by backbonding with the Ir d orbitals, and it may somehow enforce the classical "H-Ir(III)-H" electronic structure on the dihydridoiridium entity, suppressing any contribution from the rhodamine-quenching nonclassical "(H<sub>2</sub>)-Ir(I)" electronic structure. We hoped measurements of NMR T1 relaxation times for the hydrido hydrogen atoms would provide additional evidence for at least some participation in compound 7 by the putative nonclassical " $(H_2)$ -Ir(I)" electronic structure,<sup>14</sup> which should have unusually short (ca. 0.1 s) T1 relaxation times. However, the actual values (0.37 s in compound 7, 0.42 and 0.46 s for the inequivalent hydrido ligands in compound 8) only marginally support this hypothetical nonclassical structure.

A third effect of the CO ligand must be mentioned: It causes the  $\eta^2$  structure of compound 7 to open up to  $\eta^1$  binding of the rhodamine's carboxylate group. But  $\eta^2$  vs  $\eta^1$  rhodamine binding by itself does not cause profound quenching of luminescence intensities in compounds 5 and 6 and therefore should not be responsible for the differences between compounds 7 and 8.

The ferrocenylphosphine compound 4 reveals nearly complete quenching of the rhodamine fluorescence. While ferrocene is well-known to quench excited states,<sup>15a</sup> the exact mechanism of quenching is thought to be triplet energy transfer in the systems studied. But it is quite clear from the above discussion that an electron-transfer mechanism is also thermodynamically accessible (approx. 0.8 V exergonic). Compound 4 was initially prepared for another reason: We had been surprised by intense luminescence exhibited by the PtMe(diphos)rhodamine compound 3, which (see above) seemed anomalous when compared to compound 2. We wondered if it were "real", that is, if all emission emanated from bound intact compound 3 and not from free rhodamine, liberated by a photochemical reaction, sample hydrolysis, or decomposition, and/or thermodynamic equilibration with dissociated ligand (eq 4). Indeed, ligand loss under high dilution conditions is frequently proposed for the operation of homogeneous catalysis by transition-metal compounds, especially compounds of the precious metals. To check this, we prepared compound 4, which



chemically and structurally resembles the emissive diphos compound 3 but which bears the ferrocene entity.<sup>15b</sup> We expected the ferrocene entity to quench bound rhodamine, and residual fluorescence then would suggest free rhodamine. From the data for the ferrocenylphosphine compound (Table I) we estimate that the maximum amount of free rhodamine cannot exceed 13%; this by assuming bound rhodamine is entirely quenched and free rhodamine exhibits its natural intrinsic luminescence. The latter assumption is supported experimentally by addition of ClSiMe<sub>3</sub>; the solution now contains the freed (trimethylsilyl)rhodamine (10) and exhibits luminescence identical with the reference standard. Thus we conclude that most-at least 87% and probably more-of the rhodamine in compound 4 (and compound 3 by analogy) is bound. The intense luminescence of compound 3, therefore, is "real" and indicates a slow excited-state electron-transfer rate. This supports the conclusion drawn above that electron transfer in 3 is slightly endergonic.

Part of our "burden of proof", if we propose electron transfer as the dominant quenching mechanism, is to show evidence against other commonly encountered quenching mechanisms, especially intersystem crossing and energy transfer.

Even though all these compounds are diamagnetic and have singlet ground states, the mere presence of heavy-metal atoms forces us to consider intersystem crossing (ISC) as a possible quenching mechanism. But the collection of compounds itself is the best evidence against rapid intersystem crossing: Some of the compounds display fluorescence intensity as great as that of the reference compound 10, which has no atom heavier than sulfur. It is reasonable, but admittedly not rigorous, to assume that rates of intersystem crossing should be roughly the same for all these structurally similar compounds 1-3 and 5-8. (The ferrocene entity of compound 4 may accelerate ISC.) Thus if ISC is slow in some of these compounds, which it must be in the highly fluorescent compounds 3, 5, 6, and 8, it should be comparably slow in the other compounds and should not be responsible for their markedly diminished fluorescence. We suspect that the benzoate ligating group "insulates" the rhodamine from the spin-orbit coupling effects of the heavy-metal atom in addition to holding the metal atom an appreciable distance from the centroid of the chromophore.<sup>4h</sup> In another article we will discuss our studies of acridine complexes, where intersystem crossing does become a major mechanism for excited-state quenching.

Energy transfer from rhodamine to other low-lying excited states of the metal complexes must also be considered as a possible quenching mechanism. We can dismiss any participation by arylphosphine-centered excited states, because compounds **3**, **5**, **6**, and **8** exhibit luminescence comparable to the rhodamine standard **10**; clearly the arylphosphine-centered excited states do not cause quenching in these intensely luminescent compounds and should not cause quenching in the other compounds. Quenching by metal-centered excited states is more difficult to dismiss, especially in compounds **1**, which have an inherently colored metal center indicative of low-lying excited states. But  $Ir(P(tol)_3)_2(CO)Cl$  has a lowest energy absorption at approximately 440 nm (22 700/cm).<sup>16</sup> While  $Ir(P(tol)_3)_2(CO)Cl$  is not

<sup>(13)</sup> Crabtree, R. H.; Quirk, J. M. J. Organomet. Chem. 1980, 199, 99-106.

<sup>(14)</sup> Crabtree, R. H.; Lavin, M.; Bonneviot, L. J. Am. Chem. Soc. 1986, 108, 4032-4037.

<sup>(15) (</sup>a) Wrighton, M. S.; Pdungsap, L.; Morse, D. L. J. Phys. Chem.
1975, 79, 66-71. Vikesland, J. P.; Wilkinson, F. Trans. Faraday Soc. 1977, 1082-1093.
(b) We assume "normal" coordination of bis(diphenyl-phosphino)ferrocene, without direct Pt-Fe bonding in the ground state. See: Sato, M.; Sekino, M.; Akabori, S. J. Organomet. Chem. 1988, 344, C31-C34 and references therein.

<sup>(16)</sup> Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Vaska, L. Inorg. Chem. 1976, 15, 1485-1488.

emissive under normal conditions, we estimate a hypothetical emission maximum at 481 nm (20800/cm) by assuming a Stokes shift of 1900/cm. (This is the value of the Stokes shift observed for the intensely emissive compound Ir(diphos)<sub>2</sub>Cl.<sup>17</sup>) This excited state is still about 2600/cm higher in energy than the rhodamine excited state (estimated 550 nm, 18 200/cm). Using the formula  $k(E) = k(E=0) \exp(-E/kT)$  and 2600/cm for E, we estimate energy transfer to be a factor of  $2 \times 10^{-5}$  slower than it would be if the metal center provided an excited state at the same energy as the rhodamine singlet. This latter rate we estimate by noting that the excited state will be largely triplet in character and rates of singlet  $\rightarrow$  triplet energy transfer are typically in the range  $10^{+7}$ -10<sup>+9</sup>/s even when energetically favored, so the rate of energy transfer for compounds 1a,b is probably only of the order  $10^{+2}/10^{+5}$ /s. Recalling that the excited-state lifetime of rhodamine in compound 10 is  $4.5 \times 10^{-9}$  s, we see this rate of energy transfer would be much too slow to cause significant quenching, and we are left with energetically favorable electron transfer as the dominant quenching mechanism for compounds 1. Quenching by energy transfer is even more unlikely in compounds 2 and 7, which have colorless metal centers with no low-lying excited states.

What happens after the excited state of the rhodamine accepts an electron from the metal center? For now we propose that the electron transfer states of all the compounds rapidly recombine to the ground state. We have attempted to observe the putative transient electron-transfer state of compound 1b using laser flash photolysis, but we have been unable to detect any transient species, presumably because its lifetime is much less than the laser pulse width (ca. 1 ns in our apparatus). The short lifetime(s) of the transient species prevents us from directly distinguishing between electron transfer and other quenching mechanisms, but short transient lifetime/rapid recombination is consistent with the photostabilities of these compounds: In concentrated CD<sub>2</sub>Cl<sub>2</sub> solution (0.01-0.1 M) the compounds are stable (no discernible changes in NMR spectra) even after several hours of irradiation by the intense 546-nm line of a 1000-W Hg/Xe lamp. In the future we hope to manipulate these transient electron-transfer states to achieve interesting chemical transformations.

A final observation concerning the electron-transfer quenching mechanism: In transition-metal compounds bearing organic ligands with extensive  $\pi$  systems, e.g., bipyridine, there is significant oscillator strength associated with direct metal  $\rightarrow$  ligand charge transfer, and radiative decay of the charge transfer state is often easily observable. But with the present compounds, there is no detectable absorption that leads directly to the charge/ electron transfer state. (There may be feeble bands in the absorption spectrum appropriate for this transition, but if present they are obscured by the intense rhodamine absorption.) This charge/electron transfer state, then, is accessible only as the time evolution of an initially rhodamine-localized excitation. In this respect the present compounds resemble recent model compounds for photosynthetic centers, where an initially porphyrin-localized excitation rapidly evolves into an electron-transfer state involving other groups attached by insulating tethers.18

It is instructive to compare the behavior of the rhodamine compounds with that of the anthracene-cobalt cage compound 13 recently reported by Mau et al.<sup>4g</sup> In the cobalt complex,



fluorescence of the attached anthracene chromophore is nearly completely quenched when the cobalt center is in the 3+ oxidation



Figure 1. Perspective drawing of  $[Rh(CO)(P(tol)_3)_2(rhodamine)]^+$ (compound 1a). Atoms are drawn at the 25% probability level, and hydrogen atoms and *p*-tolyl groups are omitted for clarity. Selected bond distances (angstroms) and angles (degrees): Rh(1)-P(1), 2.331 (5); Rh(1)-P(2), 2.330 (5); Rh(1)-C(1) 1.790 (21); Rh(1)-O(2), 2.073 (11); C(1)-O(1), 1.169 (20); P(1)-Rh(1)-P(2), 177.1 (2); C(1)-Rh(1)-O(2), 174.8 (6); C(1)-Rh(1)-P(1), 90.5 (5); C(1)-Rh(1)-P(2), 90.1 (6); O-(2)-Rh(1)-P(1), 88.0 (3); O(2)-Rh(1)-P(2), 91.1 (3). Additional data are available as Supplementary Material.

state. While both energy transfer and electron transfer from the excited anthracene chromophore to the Co(III) center are possible quenching mechanisms, the authors believe that energy transfer dominates. When the cobalt center is reduced to Co(II), the anthracene chromophore recovers a small amount of fluorescence intensity, ascribed to less efficient energy transfer from anthracene to Co(II). This is the exact opposite of the behavior observed for the rhodamine compounds, where the oxidized metal centers permit rhodamine fluorescence and the reduced metal centers quench fluorescence, primarily by metal-to-chromophore electron transfer.

Structure of Compound 1a. As a means of verifying the binding of the rhodamine chromophore to the metal center, the crystal structure of compound 1a was determined by X-ray diffraction. A perspective drawing of the cation is presented in Figure 1, with selected bond distances and angles in the caption. Additional details are described in the Experimental Section, and complete crystallographic data are available as Supplementary Material (see paragraph at the end of the article). The molecular structure of compound 1 can be described as three mutually orthogonal planes: (1) the coordination plane, containing the rhodium atom and the ligating C(1), P(1), P(2), and O(2) atoms; (2) the benzoate group, containing the carboxylate atoms C(98), O(2), and O(3) and the ring carbon atoms C(92)-C(97); (3) the rhodamine chromophore itself, consisting of the xanthene nucleus (atoms C(70)-C(75), C(80)-C(85), O(4)) and the nitrogen atoms N(1) N(2) of the diethylamino substituents. The angles between these planes are as follows 1-2, 84.2°; 2-3, 96.7°; 1-3, 80.0°. Interatomic distances and angles within the rhodamine portion of the structure (see Supplementary Material) are normal, considering the large standard deviations, an unfortunate consequence of disorder in the anion position and in cocrystallized ether of solvation, and the relatively low data:parameters ratio.

While carboxylates are very common ligands throughout the transition-metal series, crystallographically characterized examples of a nonbridging  $\eta^1$  carboxylate bound to a square-planar d<sup>8</sup> cobalt-group metal center are very rare.<sup>19</sup> Also, while rhodamine compounds and derivatives are well-known, there is only one

<sup>(17)</sup> Geoffroy, G. L.; Wrighton, M. S.; Hammond, G. S.; Gray, H. B. J. Am. Chem. Soc. 1974, 96, 3105-3108.

<sup>(18)</sup> For leading references see: Warman, J. M. Nature (London) 1987, 327, 462-464.

<sup>(19)</sup> Hossain, S. F.; Nicholas, K. M.; Teas, C. L.; Davis, R. E. J. Chem. Soc., Chem. Commun. 1981, 268-269.



**Figure 2.** Stereoviews of the crystal packing of compound **1a**. Solvent molecule, SbF<sub>6</sub> counterions, *p*-tolyl groups, and hydrogen atoms are omitted for clarity. The intermolecular interaction between rhodamine units occurs across the (equivalent) inversion centers  $(0, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . The closest intermolecular Rh-Rh separation is across (equivalent) inversion centers  $(1/2, \frac{1}{2}, 0)$  and  $(0, \frac{1}{2}, \frac{1}{2})$ . The view in part a is down the crystal *b* axis, and the view in part b is down the crystal *a* axis.

previous report of a crystal structure of any rhodamine derivative.<sup>20</sup>

The crystal lattice is best described as consisting of chains of  $Rh(CO)(P(tol)_3)_2(rhodamine)$  cations, with solvent molecules and  $SbF_6$  anions between the chains. The chains are formed by "head-head, tail-tail" intermolecular interactions, as shown schematically in Figure 2. Each intermolecular interaction occurs across an inversion center. The face-face separation of the rhodamine chromophores (3.70 Å interplanar separation) is slightly larger than "typical" interplanar separations (3.3–3.6 Å) seen for rhodamine 123<sup>20</sup> and related dye compounds, for example, Potenza et al.'s rhodinol derivative.<sup>21</sup> The face-face "dimer" is reminescent of the "special pair" of chromophores in the photo-

synthetic reaction center, which encourages the analogy drawn earlier between the behavior of compounds 1 and models for photosynthetic centers.<sup>22</sup> The Rh-Rh separation is 7.39 Å, compared with 9.19 Å reported for one isomorph of RhCl- $(CO)(PPh_3)_2$ .<sup>23</sup> This distance is too large to allow significant ground-state interaction between rhodium centers.

### Summary and Conclusions

The compounds described in this article constitute a series of systematically related transition-metal compounds, each bearing the rhodamine B chromophore. From the absorption and emission spectra of these compounds we have extracted trends that are suggestive of an excited-state electron-transfer mechanism for quenching the rhodamine chromophore. In compounds where the transition-metal center has been chemically modified to increase its oxidation potential, excited-state electron transfer is suppressed.

An apparent tendency for most of these compounds to dissociate and/or decompose under high-dilution conditions has made it impossible to obtain meaningful values for excited-state lifetimes, so rate constants for the electron-transfer quenching processes unfortunately cannot be obtained directly. Even within this severe limitation, our observations enable a number of conclusions to be drawn that had not been apparent previously. First and foremost, the presence of a transition-metal center does not automatically mean excited states of the neighboring organic chromophore will be quenched. As long as the metal atom is kept away from the centroid of the chromophore (ca. 4.8 Å in the bidentate compound 6) even an atom as heavy as iridium does not increase the rate of intersystem crossing enough to cause significant fluorescence quenching. And if the metal atom is so chosen, or chemically substituted, as to keep sufficiently large oxidation and reduction potentials, electron-transfer rates also will be too slow to affect the organic chromophore's excited-state lifetime. Thus rhodamine attached to the easily oxidized Rh(I), Ir(I) centers in compounds 1a,b is quenched, while rhodamine attached to the already oxidized Ir(III) centers in compounds 5, 6, and 8 is fluorescent.

We are now in a position to use qualitative estimates of relative rates of quenching to probe several aspects of coordination chemistry. In this article we have used relative emission intensities to show that rhodamine tends to remain bound to, and be quenched by, the ferrocenylphosphine-platinum center in compound 4, even in solutions as dilute as  $10^{-6}$  M. And rhodamine quenching in compound 7 demands significant electronic differences between it and the fluorescent compound 8, which may result from incipient nonclassical behavior for the dihydrido ligands in 7.

### **Experimental Section**

All reactions were carried out at room temperature in a N2-filled drybox using dried, degassed solvents. Visible, IR, and NMR spectra were measured with Perkin-Elmer 330, 283B, and GE QE-300 instruments, respectively. Emission spectra were measured with a SPEX Fluorolog instrument equipped with dual excitation and emission monochromaters. Absorption and emission data are listed in Table I. IR spectral data are reported for M-CO and/or M-H stretching frequencies, as appropriate, in units of cm<sup>-1</sup> for samples as Nujol mulls. NMR data for the rhodamine compounds are summarized in Table III; chemical shifts are reported in ppm downfield from external Me<sub>4</sub>Si with coupling constants in hertz. Rhodamine B base was obtained from Aldrich Chemical Co. and was purified prior to use by recrystallization from diethyl ether. Note that rhodamine may be toxic and carcinogenic! The herein-reported rhodamine-metal complexes tend to release rhodamine, especially when exposed to moisture and/or halide ions, and therefore must be assumed to have toxicities comparable to rhodamine itself.

Carbonylbis(tri-p-tolylphosphine)(rhodamine)iridium Hexa $fluoroantimonate (1b). [Ir(P(tol)_3)_2(CO)(acetone)][SbF_6] was$ 

<sup>(20)</sup> Abrams, M. J.; Picker, D. H.; Facker, P. H.; Lock, C. J. L.; Howard-Lock, H. E.; Faggiani, R.; Teicher, B. A.; Richmond, R. C. Inorg. Chem. 1986, 25, 3980-3983.

<sup>(21)</sup> Potenza, J. A.; Toby, B. H.; Bird, G. R.; Lalancette, R. A. Acta Crystallogr., Sect. C 1983, C39, 1291-1294.

<sup>(22)</sup> Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. J. Mol. Biol. 1984, 180, 398.

<sup>(23)</sup> Del Pra, A.; Zanotti, G.; Segala, P. Cryst. Struct. Commun. 1979, 8, 959-964. See also: Rheingold, A. L.; Geib, S. J. Acta Crystallogr., Sect. C 1987, C43, 784-786.

**TABLE III: NMR Data of Rhodamine Compounds** 

			rhodamine <sup>b</sup>				
compda	H	H <sub>b</sub> H <sub>c</sub>	Н <sub>d</sub>	H	Hr	phosphine	other
[Rh(CO)(Ptol <sub>3</sub> ) <sub>2</sub> (rhodamine)]SbF <sub>6</sub> (1a)	6.79 (s)	6.44°	6.81 (m), 7.53 (m)	3.584	1.31 (t, 7)	2.32 (s), 7.08 (d, 8), 7.44 (d, 8, of t, 5.5)	
[Ir(CO)(Ptol <sub>3</sub> )(rhodamine)]SbF <sub>6</sub> (1b)	6.76 (d, 2.5)	6.40 (d, 8), 6.46 (dd, 8, 2.5)	6.80 (d, 7), 7.40 (m)	3.60 (m) <sup>d</sup>	1.32 (t, 7.5)	2.33 (s), 7.08 (d, 8.5), 7.45 (d, 8.5, of t, 6)	
[Pt(CH <sub>3</sub> )(Ptol <sub>3</sub> ) <sub>2</sub> (rhodamine)]SbF <sub>6</sub> (2) <sup>e</sup>	6.78 (d, 2)	6.46°	6.90 (m), 7.07 (m), 7.75 (m)	3.57 (m) <sup>d</sup>	1.31 (t, 7.5)	2.32 (s), 7.08 (d, 8), 7.48 (d, 8, of t, 5)	Pt-CH <sub>3</sub> , -0.10 (t, 8; J <sub>H+Pt</sub> = 79 Hz)
[Pt(CH <sub>3</sub> )(Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> )- (rhodamine)]SO <sub>3</sub> CF <sub>3</sub> (3)	6.73 (d, 2.5)	7.12 (d, 9.5), 6.58 (dd, 9.5, 2.5)	7.74 (m), 8.10 (m)	3.52 (qd, 7.5, 3)	1.26 (t, 7.5)	2.15 (m), 7.30 (m), 7.44 (m)	Pt-CH <sub>3</sub> , +0.17 (dd) 8, 3; J <sub>H-Pt</sub> = 52 Hz)
[Pt(CH <sub>3</sub> )(Ph <sub>2</sub> PC <sub>3</sub> H <sub>4</sub> FeC <sub>3</sub> H <sub>4</sub> PPh <sub>2</sub> )- (rhodamine)]SO <sub>3</sub> CF <sub>3</sub> (4)	6.79 (d, 2.5)	7.00 (d, 9), 6.68 (dd, 9, 2.5)	ſ	3.56 (q, 7.5)	1.25 (t, 7.5)	3.96 (br), 4.40 (br), 4.30 (br), 4.37 (br), <i>f</i>	Pt-CH <sub>3</sub> , $-0.11$ (dd) 8, 3.5; $J_{H-Pt} =$ 50 Hz)
[Ir(CH <sub>3</sub> )Cl(CO)(P(tol) <sub>3</sub> ) <sub>2</sub> - (rhodamine)]SO <sub>3</sub> CF <sub>3</sub> (5)	(s) (s)	6.62 <sup>c</sup>	6.95 (dd, 7.5, 1.5), 7.60 (m), 8.17 (dd, 7.5, 1.5)	3.62 (q, 7.5)	1.32 (t, 7.5)	2.28 (s), 7.03 (d, 8), 7.53 (t, 8, of t, 6)	Ir-CH <sub>3</sub> , +0.74 (t, 5)
[Ir(CH <sub>3</sub> )(CO)(P(tol) <sub>3</sub> ) <sub>2</sub> )- (rhodamine)](SO <sub>3</sub> CF <sub>3</sub> ), (6)	7.10 (d, 2.5)	6.18 (d, 9), 6.50 (dd, 9, 2.5)	6.90 (d, 7), 7.50 (m), 7.60 (m)	3.45 (br) <sup>d</sup> 3.75 (br)	1.25 (br) <sup>d</sup>	2.39 (s), 7.25 (d, 7.5), 7.02 (d, 7.5, of t, 5)	Ir-CH <sub>3</sub> , +1.17 (t, 5.5)
[IrH <sub>2</sub> (P(tol) <sub>3</sub> ) <sub>2</sub> (rhodamine)]SbF <sub>6</sub> (7)	6.82 (d, 2.5)	6.53 (d, 10), 6.38 (dd, 10, 2.5)	6.86 (m), 7.47 (m), 7.72 (m)	3.55 (br, m) <sup>d</sup>	1.26 (br, t) <sup>d</sup>	2.35 (s), 7.02 (d, 7.5), 7.31 (m)	Ir-H, -30.00 (t, 17)
[IrH <sub>2</sub> (CO)(P(tol) <sub>3</sub> ) <sub>2</sub> (rhodamine)]SbF <sub>6</sub> (8)	6.83 (d, 2.5)	6.65 (d. 8.5), 6.47 (dd, 8.5, 2.5)	6.87 (d, 6), 7.45 (m)	3.56 (m) <sup>d</sup>	1.27 (t, 7.5)	2.34 (s), 7.07 (d, 8), 7.34 (d, 8, of t, 6)	Ir-H, -7.19 (t, 19, of d, 5) Ir-H, -21.08 (t, 14, of d, 5)
rhodamine B base, leuco form (9)	6.47 (d, 3)	6.56 (d, 9), 6.38 (dd, 9, 3)	7.20 (dd, 7, 1), 7.62 (t of d, 7.5, 1), 7.68 (t of d, 8, 1), 7.98 (dd, 8, 1)	3.38 (q. 7.5)	1.20 (t, 7.5)		
[(SiMe <sub>3</sub> )rhodamine]SO <sub>3</sub> CF <sub>3</sub> (10)	6.82 (d, 2.5)	7.12 (d, 9.5), 6.85 (dd, 2.5, 9.5)	7.31 (dd, 7.1), 7.77 (m), 8.28 (dd, 7.5, 1.5)	3.61 (q, 7)	1.31 (t, 7)		SiMe <sub>3</sub> , –0.01
<sup>a</sup> All chemical shifts in ppm downfield from	ı external SiMe	4. Coupling constant	s in H <sub>r</sub> . Samples in CL H <sub>a</sub> (CH <sub>2</sub> ) <sub>e</sub> -	) <sub>2</sub> Cl <sub>2</sub> at room te —(CH <sub>3</sub> ) <sub>f</sub>	mperature. <sup>b</sup> A	tom labeling scheme:	
		NEt2	z-z-	1 <sub>2</sub> )е—(СН <sub>3</sub> ) <sub>f</sub>			
			<sup>,¶</sup> ≻ <sup>,µ</sup>				

 $^{c}$  H<sub>b</sub>, H<sub>c</sub> are coincident. <sup>d</sup> Poorly resolved owing to <sup>14</sup>N-H coupling and/or diastereotopic splitting. <sup>d</sup> Additional resonances observed for cis isomer; see Experimental Section. <sup>J</sup>Resonance for H<sub>a</sub> overlapping with Ph-P resonances, 7.20 m, 7.4 (br m), 7.57 (m), 7.68 (m).

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prepared from  $IrCl(P(tol)_3)_2(CO)$  by methods analogous to those of Clark and Reimer<sup>24</sup> and Burk and Crabtree.<sup>25</sup> A suspension of the acetone complex (0.47 g) in 20 mL of ether was treated with 0.20 g of rhodamine B base, and the resulting red suspension was stirred for 5 h. The mixture was filtered, yielding 0.57 g of red solid (90%), IR 1965 cm<sup>-1</sup>. The material was recrystallized from dichloromethane solution by vapor diffusion of diethyl ether. *Carbonylbis(tri-p-tolylphosphine)(rhodamine)rhodium Hexafluoroantimonate* (1a) was prepared in an analogous manner; IR 1962 cm<sup>-1</sup>.

Methylbis(tri-p-tolylphosphine)(rhodamine)platinum Hexafluoroantimonate (2). The acetone complex  $[Pt(CH_3)(P-(tol)_3)_2(acetone)][SbF_6]$  was prepared from  $Pt(CH_3)I(P(tol)_3)_2$ by a modification of the literature procedure.<sup>26</sup> This acetone complex (0.16 g) was suspended in 2 mL of tetrahydrofuran, and 0.065 g of rhodamine B base was added. After 10 min, 10 mL of ether was added, and the red suspension was filtered after stirring overnight, providing 0.19 g (88%) of rhodamine complex 2. The NMR spectrum of a freshly prepared solution revealed, in addition to signals listed in Table X (supplementary material) assigned to the trans isomer, discernible signals at 2.27 (s, P(tol)\_3), 1.29 (t, NCH<sub>2</sub>CH<sub>3</sub>), and -0.14 (dd, 7, 3; Pt-CH<sub>3</sub>) indicating a minor component that we assign as the cis isomer. On standing overnight in CD<sub>2</sub>Cl<sub>2</sub> solution the amount of this component increased from ca. 10% to an equilibrium amount of ca. 30%.

Methyl(1,2-bis(diphenylphosphino)ethane)(rhodamine)platinum Trifluoromethanesulfonate (3). PtMe<sub>2</sub>(1,2-bis(diphenylphosphino)ethane)<sup>27</sup> (0.62 g) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was treated with 0.15 g of trifluoromethanesulfonic acid. After stirring for 15 min, the solution was evaporated; pentane was added to the residue, and the white suspension was filtered after stirring 15 min, providing 0.63 g (84%) of PtMe(SO<sub>3</sub>CF<sub>3</sub>)(1,2-bis(diphenylphosphino)ethane); NMR (CD<sub>2</sub>Cl<sub>2</sub>) 0.63 (dd, 7.5, 1.5; J<sub>H-Pt</sub> = 65 Hz), 2.15 (m) 2.40 (m), 7.50 (m), 7.80 (m). A solution of 0.23 g of this material and 0.135 g of rhodamine B base in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and benzene (5 mL) was allowed to stand overnight and then evaporated to half volume. Ether (5 mL) and hexane (5 mL) were added, depositing compound 3 as an oily red material that slowly became microcrystalline, yield 0.25 g (69%).

Methyl(1,1'-bis(diphenylphosphino)ferrocene)(rhodamine)platinum Trifluoromethanesulfonate (4). PtMe<sub>2</sub>(1,1'-bis(diphenylphosphino)(ferrocene) was prepared from  $PtMe_2(C_8H_{12})$ and the phosphine ligand in tetrahydrofuran solution and isolated by concentration and precipitation with ether; NMR  $(CD_2Cl_2)$ 0.27 (m, pseudo d, 2;  $J_{H-Pt} = 70$  Hz), 4.13 (pseudo d, 2;  $J_{H-Pt} = 35$  Hz), 4.24 (pseudo d, 2;  $J_{H-Pt} = 35$  Hz), 7.40 (m), 7.72 (m). A mixture of 0.27 g of this material in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> was treated with 0.051 g of trifluoromethanesulfonic acid and stirred 5 min; then ether (5 mL) and hexane (10 mL) were added slowly, precipitating PtMe(SO<sub>3</sub>CF<sub>3</sub>)(1,1'-bis(diphenylphosphino)ferrocene (0.26 g, 82%) as a sticky yellow solid. To prepare the rhodamine compound, 0.23 g of PtMe(SO<sub>3</sub>CF<sub>3</sub>)(1,1'-bis(diphenylphosphino)ferrocene) and 0.11 g of rhodamine B base were combined in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred for 10 min; the solution was concentrated, 20 mL of ether was added, and the mixture was filtered, collecting 0.23 g red solid compound 4 (66%).

Methylchlorocarbonylbis(tri-p-tolylphosphine)(rhodamine)iridium Trifluoromethanesulfonate (5). The methyl compound  $Ir(CH_3)(Cl)(CO)(P(tol)_3)_2(SO_3CF_3)$  was prepared by reaction of  $IrCl(CO)(P(tol)_3)_2$  with  $CH_3SO_3CF_3$ , following Strope and Shriver;<sup>28</sup> IR 2062 cm<sup>-1</sup>. An ether solution (20 mL) of this methyl compound (0.10 g) was treated with an ether solution (5 mL) of rhodamine B base (0.05 g) and stirred. A red precipitate formed immediately and was collected after ca. 30 min, yield 0.10 g (70%); IR 2047 cm<sup>-1</sup>. The compound was recrystallized from  $CH_2Cl_2$ /ether by cooling to -20 °C.

Methylcarbonylbis(tri-p-tolylphosphine)(rhodamine)iridium Bis(trifluoromethanesulfonate) (6). The methyl compound Ir-(CH<sub>3</sub>)(Cl)(CO)(P(tol)<sub>3</sub>)<sub>2</sub>(SO<sub>3</sub>CF<sub>3</sub>) was prepared as for **5** above, and 0.85 g was combined with 0.22 g of AgSO<sub>3</sub>CF<sub>3</sub> in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 2.5 h, the mixture was filtered and evaporated, leaving 0.70 g of off-white solid, IR 2050 (s), 2070 (w) cm<sup>-1</sup> (74% yield of Ir(CH<sub>3</sub>)(CO)(P(tol)<sub>3</sub>)<sub>2</sub>(SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub>). Rhodamine B base (0.045 g) was added to 0.115 g of this bis-(trifluoromethanesulfonate) compound in 10 mL of ether, and the suspension was stirred overnight. Filtration provided 0.14 g (88%) of compound **6**; IR 2040 cm<sup>-1</sup>. The material was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> solution by vapor diffusion of ether. Anal. Calcd for Ir(CH<sub>3</sub>)(CO)(Ptol<sub>3</sub>)<sub>2</sub>(rhodamine)(SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub>), C<sub>74</sub>H<sub>75</sub>N<sub>2</sub>O<sub>10</sub>F<sub>6</sub>P<sub>2</sub>S<sub>2</sub>Ir<sub>1</sub>: C, 56.09; H, 4.77; N, 1.77%. Found: C, 55.80, 55.85; H, 4.90, 5.10; N, 1.67, 1.72.

Dihydridobis(tri-p-tolylphosphine)(rhodamine)iridium Hexafluoroantimonate (7). The dihydridobis(solvento) compound  $[IrH_2(Ptol_3)_2(acetone)_2]SbF_6$  was prepared following the method of Crabtree et al.<sup>29</sup> A mixture of 0.15 g of this dihydridobis-(solvento) compound and 0.06 g of rhodamine B base in ether was stirred for 3 days and then filtered to yield 0.17 g of red solid compound 7; IR 2230, 2268 cm<sup>-1</sup>. The material was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> by vapor diffusion of ether, but recovery was poor.

Dihydridocarbonylbis(tri-p-tolylphosphine)(rhodamine)iridium Hexafluoroantimonate (8). Hydrogen was bubbled through a CH<sub>2</sub>Cl<sub>2</sub> solution of compound **1b** (0.15 g) for 10 min, and the solution was stirred an additional 2 h under a hydrogen atmosphere. The solution was evaporated, and the residue redissolved in minimum CH<sub>2</sub>Cl<sub>2</sub> and recrystallized by adding ether and cooling to -30 °C. After several days the flask had a band of iridescent red-green crystals and a filmy red deposit. The crystalline portion was carefully separated, yield 0.045 g (30%); IR 2211, 2093, 1994 cm<sup>-1</sup>.

(Trimethylsilyl)rhodamine Trifluoromethanesulfonate (10). Trimethylsilyltrifluoromethanesulfonate (0.11 g) was added to an ether solution of rhodamine B base (0.22 g), and the mixture stirred for 30 min. Filtration provided 0.26 g (79%) of compound 10 as a red powder.

Determination of Relative Emission Yields. A series of five solutions of the reference compound 10 in  $CH_2Cl_2$  was prepared, with optical densities at the absorption maximum (557 nm) varying from 0.044 to 0.447, and emission spectra were measured. An excellent linear correlation was confirmed between the emission intensity at the emission maximum (577 nm) and the integrated intensity of the emitted energy between 560 and 760 nm (maximum deviation from linearity, 1.2%; average deviation, 0.5%). For all subsequent calculations, intensity at emission maximum was used to determine relative emission yield.

This same series of compounds confirmed a correlation between the absorbance of the solutions (same as optical density in 1.00-cm cells) and emission yield, governed by

$$KA(x) \exp(-2.303(0.5)A(x)) \exp(-2.303(0.5)A(m))$$
 (5)

where A(x) is absorbance of the solution at the exciting wavelength (557 nm) and A(m) is the absorbance at the emitting wavelength (577 nm). For these solutions, A(m) = 0.222A(x), so the equation reduces to

$$emission = KA(x) \exp(-1.41A(x))$$
(6)

with K the only parameter to be fit. With this second equation, emission from the standard samples of compound 10 was fit satisfactorily, with maximum deviation 9%, average deviation 5%.

To obtain the relative emission yields of compounds 1-8, a solution of each compound in freshly dried  $(P_2O_5)$ , vacuum-transferred  $CH_2Cl_2$  was prepared, with optical density in the range

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(26) Chisholm, M. H.; Clark, H. C. Acc. Chem. Res. 1973, 6, 209.

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Bennett, M. A.; Tomkins, I. B. J. Chem. Soc., Dalton Trans. 1976, 439-446. (28) Strope, D.; Shriver, D. F. Inorg. Chem. 1974, 13, 2652-2666. For a recent review of trifluoromethanesulfonate compounds see: Lawrence, G. A. Chem. Rev. 1986, 86, 17-33.

<sup>(29)</sup> Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. J. Am. Chem. Soc. 1982, 104, 107-113.

0.10–0.30 at the absorption maximum (see Table I). After measuring the optical density, the emission spectrum was measured, with excitation at the maximum absorption wavelength. After the emission had been measured, the absorption spectrum was remeasured to confirm minimal sample decomposition (less than 10% change in optical density for all solutions, typical changes 2–5%). Equation 6 was employed to obtain the expected emission for unquenched rhodamine chromophore. Then a small amount, ca. 10  $\mu$ L, of a CH<sub>2</sub>Cl<sub>2</sub> solution of ClSiMe<sub>3</sub> (ca. 1 M) was added to each solution; this released the rhodamine entity as its SiMe<sub>3</sub> ester (the reference compound 10). Absorbance and emission were again measured, and the emission was fit by the above equation. The final value, the relative emission yield of the rhodamine compound, was figured according to

rel emis yield = [(OEC)/(CEC)]/[(OES)/(CES)] (7)

where OEC is observed emission from the compound, CEC is calculated emission from the compound (using eq 6), OES is observed emission after silvlation, and CES is calculated emission after silylation (again using eq 6). With this procedure, much of the error arising from the approximations in eq 6 will cancel, as will most fluctuations in instrument response as well as the effect of differing extinction coefficients between bound and silvlated rhodamine. But we have no way to correct for errors resulting from sample decomposition, whether by inadvertantly introduced impurities or by intrinsic reactions (see Results and Discussion section). Thus the relative emission yields listed in Table I are best viewed as representing approximate upper limits for each compound. Repeat determinations are consistent with estimated relative errors of ca.  $\pm 10\%$ , except for compound 2, which has widely varying emission intensities (see Results and Discussion). Absolute quantum yields have not been measured, but values of ca. 50% have been reported for rhodamine B in alcohol solvents.<sup>6</sup>

X-ray Data Collection and Structure Refinement for Compound 1a. Crystals of compound 1a were obtained by ether diffusion into a CH<sub>2</sub>Cl<sub>2</sub> solution. At -100 °C the space group is P2/n (no. 232) and a = 29.850 (4), b = 11.666 (2), c = 21.589(3) Å,  $\beta = 92.609$  (1)°, V = 7510.1 Å<sup>3</sup>, Z = 4. Other crystallographic data are listed in Table X (Supplementary Material). A total of 13 166 unique reflections were measured,<sup>30</sup> of which

(30) See, for example: Mayer, J. M.; Thorn, D. L.; Tulip, T. H. J. Am. Chem. Soc. 1985, 107, 7454-7462.

4811 with intensity greater than  $3\sigma$  were used in the final refinement.

The structure was solved by using direct methods. The crystal lattice was found to include molecules of dichloromethane and diethyl ether. The SbF<sub>6</sub> anion occupies two different lattice sites, with half occupancy at each, but appears to be ordered at each site. Residual electron density in the vicinity of the oxygen atom of the diethyl ether solvent molecule suggests some unresolvable disorder. Owing to the large number of atoms (96 non-hydrogen atoms) in the asymmetric unit, C, N, and O atoms of the rhodamine portion were refined isotropically. Refinement converged to R = 0.070 and  $R_w = 0.085$ . Complete crystallographic data and structural details are available as Supplementary Material.

Acknowledgment. This work would have been impossible without the advice and assistance willingly offered by our colleagues. We expressly thank J. C. Calabrese for the crystal structure illustrations, P. L. Watson for the electrochemical measurements, D. C. Roe for determining the T1 relaxation times, Y. Wang for laser flash photolysis studies, and L. J. Ayers for expert technical assistance. We are especially grateful to J. Caspar and D. F. Eaton for lifetime measurements, for their continued interest and advice, and for innumerable helpful comments.

Supplementary Material Available: Tables of final positional and equivalent isotropic thermal parameters, derived interatomic distances and angles, anisotropic thermal parameters, hydrogen atom positions, crystal and refinement data (7 pages); and a listing of  $F_{obs}$  vs  $F_{calod}$  for the reflections used in the refinement (13 pages). Ordering information is given on any current masthead page.