(1)–Rh(2)–Cl(2) and H(1)–Rh(2)–H(2) angles. The positions of the hydride ligands are significant for a number of reasons.

The hydrides are primarily localized on Rh(2). The Rh(2)–H distances (1.55 (7), 1.48 (7) Å) are typical for terminal hydride ligands.[9,10] The coordination geometry at Rh(2) is regular six-coordinate with bond angles of 88–95° between cis ligands. Consequently, single site oxidative addition of dihydrogen appears to have occurred. Notice that the hydrides are bound to a rhodium center lacking a carbonyl ligand. Since Rh(PPh₃)₃Cl forms a stable adduct with dihydrogen while Rh(PPh₃)₂(CO)Cl does not,[11] it appears that carbon monoxide ligands deactivate Rh(I) toward reaction with dihydrogen. The high trans effect of the hydride ligands has lengthened the Rh(2)–Cl distances relative to the Rh(1)–Cl and Rh(3)–Cl distances while the oxidation of Rh(2) has shortened the Rh(2)–P bonds relative to the Rh(1)–P and Rh(3)–P bonds.

There is some evidence for a semibridging interaction between the hydrides and the terminal rhodium atoms. The phosphorus-decoupled ^{1}H NMR spectrum shows a doublet of doublets with two Rh–H couplings. The larger (24.7 Hz) is assigned to the Rh(2)–H coupling while the smaller (10.9 Hz) is assigned to the Rh(1)–H(1) and Rh(3)–H(2) coupling. The observation of coupling to Rh(1) and Rh(3) should not be surprising. The hydride ligands lie directly above the planar Rh(CO)ClP₂ end groups, and the filled d_{z^2} and empty p_z orbitals of Rh(1) and Rh(3) are directed toward these hydrides. Nevertheless, the interactions must be weaker than those that are present in normal bridging hydrides. The Rh(2)···Rh(1) and Rh(2)···Rh(3) distances are considerably longer than the Rh–Rh distances in other complexes with more or less symmetrically bridging hydrides including the following (Å). [Rh₂(μ-dpm)₂(μ-H)(μ-CO)(CO)₂]⁺: Rh–Rh, 2.731 (2); Rh–H, 1.97 (11), 1.75 (11).[2] [Rh₂(μ-dpm)₂(μ-H)(μ-CO)Cl₃: Rh–Rh, 2.7464 (7); Rh–H, 1.76 (6), 1.65 (6).[4] Rh₃-(μ-H)₃[P(OMe)₃]₆: Rh–Rh, 2.803 (7), 2.780 (6), 2.856 (8); Rh–H, 1.76 (3) average.[12] Rh₂(μ-H)₂(H)₂[P(NMe₂)₃]₄: Rh–Rh, 2.734 (1); Rh–H$_{br}$, 1.68 (3), 1.77 (3).[9] Rh²(μ-H)₂[P(O-i-Pr)₃]₄: Rh–Rh, 2.65 (1); Rh–H, 1.805 (14), 1.812 (13).[13] Also, the Rh(1)···H(1) (2.02 (7) Å) and Rh(3)···H(3) (2.02 (7) Å) distances are longer and the Rh(2)–H distances are shorter than those in normal hydride bridges.[14]

Site-selective (that is, addition at a single metal center) dihydrogen addition to polynuclear rhodium complexes appears to be emerging as a significant charcteristic of these species. Other examples include the addition to (Ph₃P)₂Rh(μ-Cl)₂Rh(PPh₃)₂ to form (Ph₃P)₂Rh(μ-Cl)₂Rh(H)₂(PPh₃)₂[15] and to ((Me₂N)₃P)₂Rh(μ-H)₂Rh(P(NMe₂)₃)₂ to form ((Me₂N)₃P)₂Rh(μ-H)₂Rh(H)₂(P(NMe₂)₃)₂.[9] Examples of multicentered dihydrogen addition are at present limited to two-centered addition to sulfur-bridged, diiridium complexes.[16,17] In contrast, multicentered dihalogen addition to polynuclear complexes appears to be a much more widespread phenomenon.[1,18]

The observation of site-selective dihydrogen addition is particularly noteworthy because it suggests that polynuclear catalysts can be designed with rhodium centers specifically for activating dihydrogen and with other metal centers for binding and activating a second substrate.

The reaction chemistry of [Rh₃(μ-dpmp)₂(H)₂(CO)₂(μ-Cl)₂]⁺ and related hydrides is under investigation. [Rh₃(μ-dpmp)₂-(H)₂(CO)₂Cl₂][BPh₄] is a catalyst for hydrogenation of terminal olefins. It hydrogenates 1-phenyl-2-propyne catalytically to *cis*-1-phenyl-2-propene. With carbon monoxide it reacts by apparent dihydrogen loss to form [Rh₃(μ-dpmp)₂(CO)₃(μ-Cl)-Cl][BPh₄] in 90% yield.

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Photoemission from Tungsten Alkylidyne Complexes in Fluid Solution

Sir:

Over the past 2 decades there has been much interest in organometallic species that luminesce at room temperature in fluid solution upon excitation with visible irradiation. Such species have low-lying excited states, which may allow utilization of optical energy in the preparation of useful chemical products.[1] Despite this interest there exists a scarcity of such species. In most cases where the desired luminescence is observed, it has been associated with a charge-transfer transition involving metal $d\pi$ electrons and the π^* orbital of a ligated aromatic diimine.[2] To the best of our knowledge emission in fluid solution from a species containing a metal–carbon multiple bond has not been noted in the literature. We report here on a new class of luminescent organometallic complexes, containing a metal–alkylidyne linkage and having the general stoichiometry [XW(CO)₂L₂(CR)] (where X = halide, L = donor ligand, and R = phenyl),[3] which yield emission in fluid solution upon visible excitation. We find the luminescent properties of these complexes to be very dependent on both the nature of the R group and the L ligand. This dependence leads us to the conclusion as discussed below that the luminescent state is associated with the alkylidyne ligand.

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Figure 1. Absorption (—) and corrected emission (- - -) spectra of [BrW(CO)₂(TMEDA)(CPh)] in CH₂Cl₂ at 298 K.

The absorption and emission spectra of [BrW(CO)₂(TME-DA)(CPh)] (TMEDA = tetramethylethylenediamine) are shown in Figure 1 and are typical of this class of complexes. Note that under the conditions employed the emission spectrum is quite broad and structureless, indicative of a large degree of vibrational coupling, similar to that observed for the solution emission of [Ru(bpy)₃]²⁺ (bpy = 2,2′-bipyridine).[6] We associate the luminescence with the lowest energy absorption band at 22 030 cm⁻¹ (454 nm), based on the observation that excitation in the region from 22 220–20 000 cm⁻¹ causes the emission. Further, the coincidence of the emission onset with the low-energy tail of the 22 030 cm⁻¹ absorption suggests that the excited state initially generated by this absorption is the emissive state.

We tentatively have assigned the lowest energy transition to a d metal to π* alkylidyne charge-transfer transition. In the case where R is a phenyl group, the excited state consists of a molecular orbital composed of the conjugated interaction of the π* alkylidyne orbital with the π* system of the phenyl group. This assignment is by analogy with that of [*trans*-ClCr(CO)₄(CPh)] for which molecular orbital calculations have been carried out.[7] These calculations indicate the LUMO contains 42% CPh π* character interacting with the metal dπ orbitals. A similar assignment has been suggested by Vogler for [Os(CPh)(CO)₂(PPh₃)₂]; although this complex has a different geometry from that of the current system, the lowest lying excited state appears to be similar.[8] Our assignment is supported by the experimental data provided in Table I. As can be seen from the first three entries, varying the halide ligand trans to the alkylidyne has only a minor effect on the absorption and emission spectroscopy, suggesting that the halide-associated p orbitals are not significantly involved in the initial state.[9] On the other hand, variation of the alkylidyne R group has a tremendous impact on the observed spectra, as expected if the excited state is π* alkylidyne in nature. If the phenyl group is replaced with a *tert*-butyl group, the complex is found not to emit in fluid solution. Significant changes in the absorption spectrum are also observed. Of primary interest is the shift in the lowest observed absorption band toward the blue by ~5100 cm⁻¹, consistent with the removal of conjugation from the LUMO orbital. Absence of fluid-solution emission under these conditions further suggests that conjugation between the alkylidyne linkage and the phenyl π* system is the physical source of the appreciable rate constant for radiative decay.

The nature of the donor ligand (L) also strongly influences the observed luminescent properties. For example, replacing TMEDA by bipyridine totally quenches the fluid-solution emission. As shown in Table I, this substitution also causes a significant red shift (2600 cm⁻¹) in the lowest absorbance peak of the complex.

Table I. Spectroscopic Properties of [XW(CO)₂(L₂)(C–R)] Complexes[a]

R	X	L₂	emission[b] λ_max, cm⁻¹	absorption[c] λ_max, cm⁻¹ ε, M⁻¹ cm⁻¹[f]
Ph	Cl⁻	TMEDA	15 630	22 320 (393)
Ph	Br⁻	TMEDA	15 870	22 220 (400)
Ph	I⁻	TMEDA	15 870	22 030 (560)[e]
tert-butyl	Cl⁻	TMEDA		27 470 (617)
Ph	Cl⁻	bpy		19 760[d]
Ph	Cl⁻	(py)₂	16 000	21 690 (1064)
Ph	Cl⁻	diphos	15 650	23 000 (368)

[a] Spectra have been obtained in toluene at 298 K. No solvent dependence is observed among this solvent, CHCl₃, and CH₂Cl₂. Emission spectra were obtained with a Perkin-Elmer MPF-66 spectrometer, while absorption spectra were produced with a HP-8450 spectrometer. [b] The certainty of these peaks is ±150 cm⁻¹ due to their broad nature. [c] ±50 cm⁻¹. [d] As discussed in the text, this absorption is MLCT dπ → π* bpy in nature, not totally alkylidyne based. [e] The increase in ε here as compared with that in the first two entries is associated with overlap from higher energy absorptions. [f] Based on a Beer's law fit to solutions in the concentration range from 10⁻⁶ to 10⁻³ M.

By comparison with the absorption spectrum[10] of [W(CO)₄bpy], this lowest energy band is believed to contain a large component of dπ metal to bpy π* charge-transfer character. Internal quenching of the emission via the bpy π* orbital is consistent with the behavior of [W(CO)₄bpy] in fluid solution.[11] This interpretation is confirmed by replacing the bipyridine ligand with a bis(pyridine) ligand system, thus raising the energy of the L π* orbitals. Absorption spectroscopy now indicates the lowest lying state to be similar to that of the TMEDA complex with a metal d-orbital to pyridine π* transition lying approximately 7800 cm⁻¹ to the blue of the lowest observed absorption. In this case coupling between L π* system and the alkylidyne excited state is not expected. Thus, one predicts and observes emission in fluid solution for this complex (Table I). Similarly, replacement of TMEDA with diphos (Ph₂P(CH₂)₂PPh₂) yields a luminescent complex, establishing that the nitrogen's σ-donor properties are not associated with production of the luminescent state.

As can be seen in Figure 1, besides the visible absorption band there are two other prominent peaks associated with the [BrW-(CO)₂(TMEDA)(CPh)] absorption spectrum. Excitation spectroscopy indicates that irradiation into either of these absorptions produces emission from the π* alkylidyne level, indicating efficient nonradiative coupling between these higher energy states and the LUMO. No other emission is observed from these higher energy states in room-temperature, fluid solution. Consistent with this result is the finding that the radiative quantum yield for this system of 5.3 × 10⁻⁴ is wavelength-independent (from 28 000 to 20 000 cm⁻¹) for all wavelengths tested.[13] Similarly, the excited-state lifetime for the room-temperature complex, 180 ns, is invariant over the same spectral region.[14]

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We associate the highest energy transition (39 530 cm^{-1}, $\epsilon \sim$ 23 500 L mol^{-1} cm^{-1}) with a d metal to π^* CO charge-transfer absorption on the basis of its invariance with substitution at the X, L, or R positions and the similarity between the energy of this transition and that identified as d metal $\rightarrow \pi^*$ CO in [W(CO)$_6$].[12] This assignment is also consistent with the reported molecular orbital calculation carried out for the [XCr(CO)$_4$(CPh)] analogue.[7] The absorption at 30 580 cm^{-1} (ϵ = 13 000 L mol^{-1} cm^{-1}) is assigned to the conjugated alkylidyne–phenyl $\pi \rightarrow \pi^*$ transition on the basis of the spectra of free benzene and its derivatives.[15]

Substitution of a *tert*-butyl group for the phenyl group of the complex causes this peak to shift up in energy (λ_{max} = 33 330 cm^{-1}) and decrease by an order of magnitude in intensity (ϵ = 1400 L mol^{-1} cm^{-1}), consistent with the destruction of the alkylidyne conjugation and removal of the corresponding bathochromic effect. Whether or not this assignment accounts for all of the absorbance in this portion of the spectrum is still under investigation.

Finally we note, concomitant with the observed luminescence, there appears to be a bimolecular photochemical reaction channel, consistent with the relatively long excited-state lifetime. The nature of this photochemistry is currently under investigation along with a more detailed analysis of the nature of the luminescent excited state.

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(15) (a) Free benzene[15b] exhibits a $\pi \rightarrow \pi^*$ transition at 37 200 cm^{-1} with a molar extinction coefficient of 11 L mol^{-1} cm^{-1} while free acetylene[15c] absorbs at 42 200 cm^{-1} to the extent of 7 L mol^{-1}cm^{-1}. Conjugation of these two systems in diphenylacetylene[15b] shifts the $\pi \rightarrow \pi^*$ transition to 33 900 cm^{-1} raising the molar extinction coefficient to 29 000 L mol^{-1} cm^{-1}. (b) "DMS Atlas of Organic Compounds"; Butterworths: London, 1966; Vol. I and II. (c) Nakayama, T.; Watanabe, K. *J. Chem. Phys.* **1964**, *40*, 558–561.

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Quantitative Generation of Singlet Dioxygen via the Reaction of Tris(bipyridine)ruthenium(III) with Superoxide Ion in Aqueous Solution

Sir:

Although there is a great deal of interest in the possible generation of singlet dioxygen by the one-electron oxidation of superoxide ion,[1] the available evidence suggests that this is a rare occurrence both in aqueous solution[2] and in nonaqueous solvents.[1] In the few cases where there appears to be unequivocal proof of the production of singlet dioxygen by the reaction of O$_2^-$ with one-electron oxidants, the yields are very small ($\sim$4% in the reaction between ferrocenium ion and superoxide ion in acetonitrile[3] and $\sim$11% in dimethylformamide[4]) and/or are unspecified.[4,5] The reaction between Ru(bpy)$_3^{3+}$ (bpy = 2,2'-bipyridine) and O$_2^-$ and the possible generation of singlet dioxygen as a

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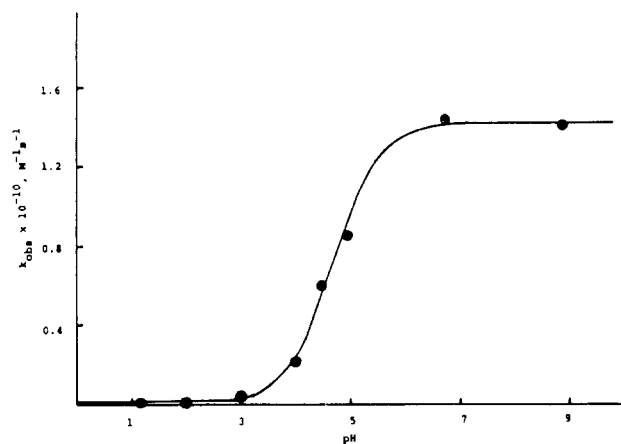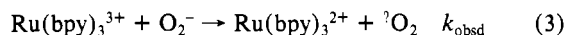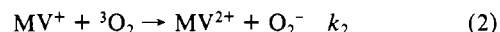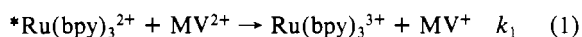

Figure 1. Observed second-order rate constant for the Ru(bpy)$_3^{3+}$–O$_2^-$ reaction vs. pH: (circles) observed values; (solid line) values calculated from eq 7 with the parameters given in the text.

reaction product has been postulated by several authors,[6-12] but kinetic studies of the reaction or experimental evidence for the formation of singlet dioxygen has not been published. In one case,[12] an estimate of the rate constant for electron transfer in the postulated cage Ru(bpy)$_3^{3+}$|O$_2^-$ has been advanced.

We report herein a useful photochemical method for the aqueous generation of superoxide ion, the kinetics of its oxidation by Ru(bpy)$_3^{3+}$ as a function of pH, and the quantitative production of singlet dioxygen in the title reaction. The method is based on the reported[13] formation of hydrogen peroxide in a photoelectrochemical cell consisting of Ru(bpy)$_3^{2+}$, N,N'-dimethyl-4,4'-bipyridinium (hereinafter referred to as methylviologen, MV^{2+}), and dioxygen, the known[14] reaction of the radical MV$^+$ with dioxygen, and the popular[15] sensitizer Ru(bpy)$_3^{2+}$.

When aqueous solutions (pH 2–9, ionic strength 0.10 M maintained with LiCl, 23 °C) of Ru(bpy)$_3^{2+}$ ($\sim$5 × 10^{-5} M), MV^{2+} ($\sim$0.01 M), and dioxygen ((0.70–10) × 10^{-4} M) are subject to flash photolysis (300-ns pulse from a Phase-R DL1100 dye laser, Coumarin 460), following excitation three reactions proceed in sequence (eq 1–3). Under our usual experimental conditions,

$$*\text{Ru(bpy)}_3^{2+} + \text{MV}^{2+} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{MV}^+ \quad k_1 \quad (1)$$

$$\text{MV}^+ + {}^3\text{O}_2 \rightarrow \text{MV}^{2+} + \text{O}_2^- \quad k_2 \quad (2)$$

$$\text{Ru(bpy)}_3^{3+} + \text{O}_2^- \rightarrow \text{Ru(bpy)}_3^{2+} + {}^?\text{O}_2 \quad k_{obsd} \quad (3)$$

the first reaction is too rapid to be detected (k_1 = 1.0 × 10^9 M^{-1} s^{-1},[15,16] with [MV^{2+}] = 0.010 M, the lifetimes of *Ru(bpy)$_3^{2+}$ are $\sim$90 and $\sim$86 ns in D$_2$O and H$_2$O, respectively) and results in the "instantaneous" bleaching of the Ru(bpy)$_3^{2+}$ absorption at 452 nm and the appearance of the 605- and 395-nm absorption

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