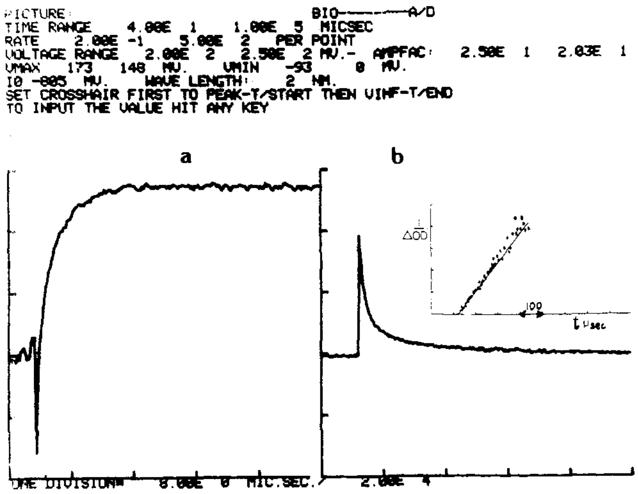

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PICTURE:                              BIO————A/D
TIME RANGE    4.00E  1    1.00E  5  MICSEC
RATE    2.00E -1    5.00E  2   PER POINT
VOLTAGE RANGE   2.00E  2   2.50E  2 MV.-  AMPFAC:   2.50E  1   2.03E  1
VMAX   173   148  MV.    VMIN   -93     0  MV.
I0 -805  MV.    WAVE LENGTH:    2  NM.
SET CROSSHAIR FIRST TO PEAK-T/START THEN VINF-T/END
TO INPUT THE VALUE HIT ANY KEY
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Figure 2. Typical kinetic plot for a N_2O-saturated solution containing 9×10^{-4} M $CuSO_4$, 2×10^{-4} M Cr^{2+}_{aq}, and 0.09 M $(CH_3)_2SO$ at pH 3.9. Insert: Fit of the decomposition reaction to a second-order rate law.

in the acidic solutions $0.7 < pH < 3.0$ any transients not observed above pH 3.0; however, the yield of the transient assigned to $CuCH_3{}^+{}_{aq}$, see below, decreased with decreasing pH. These results suggest that either reaction 8 competed efficiently with reaction 12 or that the radical $(CH_3)_2\dot{S}OH$ is unreactive toward $Cu^+{}_{aq}$ and $Cu^{2+}{}_{aq}$ or forms no observable transient when reacting with them.

Thus in solutions at pH ≥3.0 all the primary free radicals are transformed under the experimentaly conditions into $\cdot CH_3$ radicals during the pulse. Under these conditions one observes the formation of a short-lived transient. The rate of formation of this transient obeys a pseudo-first-order rate law, the rate being proportional to the concentration of $Cu^+{}_{aq}$. We therefore assign the transient to $CuCH_3{}^+{}_{aq}$. The specific rate of reaction 4 calculated from the results is $k_4 = (3.5 \pm 0.4) \times 10^9$ M^{-1} s^{-1} in good agreement with the earlier estimate of Ferraudi of $k_4 \geq 10^9$ M^{-1} s^{-1}.[5]

The spectrum of $CuCH_3{}^+{}_{aq}$ (Figure 1) is in good agreement with the partial spectrum reported by Ferraudi.[5] It is of interest to compare the spectra of the Cu^{II}–R complexes reported in the literature. λ_{max} = 340, 375, 395, 395, 450, and 385 nm for CuH^+,[10] $CuCH_3{}^+$, $CuCH_2CH_2OH^+$,[3] $CuCH_2CH(CH_3)OH^+$,[3] $CuCH_2OH^+$,[3] and $CuCO_2$,[6] respectively. These results are in agreement with expectations for a LMCT absorption band. The observed order of λ_{max} is in agreement, where known, with that of the corresponding $(H_2O)Cr^{III}$–R complexes,[14-16] which were also assigned to LMCT transitions. It is of interest to note that the results suggest that the optical electronegativity of unsubsituted alkyl radicals, $\cdot CH_3$, $\cdot CH_2CH_2OH$, and $\cdot CH_2CH(CH_3)OH$, is smaller than that of hydrogen atoms.

The decomposition of $CuCH_3{}^+{}_{aq}$ at pH ≥2.5 obeys a second-order rate law with $2k = (1.8 \pm 0.2) \times 10^7$ M^{-1} s^{-1}, the rate being independent of the concentrations of $Cu^{2+}{}_{aq}$, $(CH_3)_2SO$, and CH_3CO_2Na; see Figure 2. These results are in disagreement with those of Ferraudi;[5] we have no explanation as to the origin of the discrepancy. In acidic solutions, pH ≤1.5 the decomposition reaction obeys a first-order rate law; e.g., at pH 1.0 $k_{dec} = (2 \pm 0.5) \times 10^2$ s^{-1}. Aliquots (100-mL) of solutions containing 8×10^{-4} M Cu^{2+}, 2×10^{-4} M Cu^+, 2×10^{-4} M $Cr(III)_{aq}$, and 0.09 M $(CH_3)_2SO$ at pH 3.7 and 1.0 were irradiated by 15 pulses, giving a dose of 5.0×10^4 rad. The gaseous products were analyzed by gas chromatography. In the solutions at pH 3.7, ethane was the product whereas at pH 1.0 methane was the product.

The results thus suggest that at pH ≥2.5 the decomposition of $CuCH_3{}^+{}_{aq}$ occurs via

$$2CuCH_3{}^+{}_{aq} \rightarrow 2Cu^+{}_{aq} + C_2H_6 \qquad 2k = 1.8 \times 10^7\ M^{-1}\ s^{-1} \tag{13}$$

The mechanism of this reaction does not involve the homolytic decomposition

$$CuCH_3{}^+{}_{aq} \rightleftharpoons Cu^+ + \cdot CH_3 \tag{14}$$

followed by

$$CuCH_3{}^+{}_{aq} + \cdot CH_3 \rightarrow Cu^+{}_{aq} + C_2H_6 \tag{15}$$

or

$$2(\cdot CH_3) \rightarrow C_2H_6 \tag{16}$$

as the observed rate of reaction 13 is independent of the concentration of $Cu^+{}_{aq}$. The results do not enable a detailed analysis of the mechanism of reaction 13, which might occur directly as written or via a rate-determining methyl-transfer reaction

$$2CuCH_3{}^+ \rightarrow Cu(CH_3)_2{}^+{}_{aq} + Cu^+{}_{aq} \tag{17}$$

followed by a fast reductive-elimination step

$$Cu(CH_3)_2{}^+{}_{aq} \rightarrow Cu^+{}_{aq} + C_2H_6 \tag{18}$$

The dependence of the rate of decomposition of $CuCH_3{}^+{}_{aq}$ on the ionic strength, up to 0.1 M $NaClO_4$, was studied. A plot of log k vs. $\mu^{1/2}/(1 + 1.33\mu^{1/2})$ gave a slope of 0.8 ± 0.1, in reasonable agreement with the expected slope of 1.02 for reactions 13 or 17.

The results in acidic solutions indicate that under these conditions the heterolytic decomposition

$$CuCH_3{}^+{}_{aq} + H_3O^+{}_{aq} \rightarrow Cu^{2+}{}_{aq} + CH_4 \tag{19}$$

is faster than reactions 13 or 17.

It is of interest to note that $CuCH_3{}^+{}_{aq}$ decomposes via a bimolecular or a heterolytic process, depending on pH, but not via a homolytic process as observed for $CuCH_2OH^+{}_{aq}$[3] and $[CuCO_2]_{aq}$.[6] This observation indicates that the metal–carbon bond strength in $CuCH_3{}^+{}_{aq}$ is stronger than in $CuCH_2OH^+{}_{aq}$ and $[CuCO_2]_{aq}$. Alternatively this observation might be due to the slow rate of reaction of methyl radicals with $Cu^{2+}{}_{aq}$,[5] which if reaction 15 is also not fast will result in kinetics that apparently do not involve a homolytic contribution.

Registry No. $CuCH_3{}^+$, 67049-30-3; $CH_3\cdot$, 2229-07-4; Cu^+, 17493-86-6.

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Electronic States of Rhodium(I) Binuclear A-Frame Complexes

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and G. A. Crosby*[1b]

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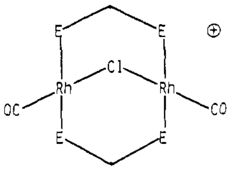
The Rh(I) binuclear A-frame complexes $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$ and $[Rh_2(CO)_2Cl(dam)_2]BPh_4$ with the structure



I

where E = P or As and

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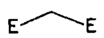
(1) (a) Eastern New Mexico University. (b) Washington State University.



is dppm, bis(diphenylphosphino)methane, or dam, bis(diphenylarsino)methane, are observed to luminesce both at 77 K and at room temperature. The luminescences display temperature dependences that are analogous to the temperature-dependent luminescence behavior observed from Rh(I) and Ir(I) binuclear complexes with face-to-face metal orientations.[2,3] The A-frame luminescences are interpreted as fluorescences and phosphorescences arising from metal-centered excited electronic states.

Experimental Section

The yellow crystalline compound $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$ and the orange crystalline compound $[Rh_2(CO)_2Cl(dam)_2]BPh_4$ were prepared by the method of Mague and Sanger.[4] Both products gave satisfactory elemental analyses. Absorption spectra were measured in CH_2Cl_2 solutions and in KBr matrices on a Varian Cary 219 UV-visible spectrophotometer. Emission spectra were recorded in the polycrystalline state on a custom-built prism spectrophotometer equipped with a dry-ice-cooled red-sensitive (RCA 7102) photomultiplier tube with an internal Corning 3-70 filter. Signals were detected in the dc mode and acquired by computer. Samples were excited with the beam of a 200-W Hg arc lamp that was passed through a $CuSO_4$ filter and Corning 7-60 and 7-37 filters and then focused through an array of quartz lenses. Emission spectra are not corrected.

Results

In CH_2Cl_2, $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$ displays a broad absorption peak at 22 600 cm^{-1} (see Figure 1). In KBr, this compound shows an absorption band at 22 400 cm^{-1} at room temperature and 22 600 cm^{-1} at 77 K.

The analogous rhodium molecule containing the dam bridging unit, $[Rh_2(CO)_2Cl(dam)_2]BPh_4$, in CH_2Cl_2 at room temperature, displays a broad absorbance at 23 000 cm^{-1} (see Figure 2). In KBr, $[Rh_2(CO)_2Cl(dam)_2]BPh_4$ at room temperature exhibits an absorbance band at 22 000 cm^{-1} and, at 77 K, a band at 21 400 cm^{-i}.

The dppm-bridged rhodium(I) A-frame complex, $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$, displays emission at both 77 K and room temperature (see Figure 1). At 77 K, this molecule exhibits an intense low-energy band at 11 000 cm^{-1} with a higher energy shoulder at 12 900 cm^{-1}. At room temperature, both a low-energy band at 10 700 cm^{-1} and a less intense higher energy band at 15 300 cm^{-1} are observed.

The luminescence of the complex $[Rh_2(CO)_2Cl(dam)_2]BPh_4$ at 77 K is characterized by an intense low-energy band at 10 700 cm^{-1} and a higher energy emission at 15 700 cm^{-1} that is observable with an expanded ordinate (see Figure 2). At room temperature this A-frame molecule displays an intense luminescence at 15 800 cm^{-1} with a lower energy shoulder at 10 900 cm^{-1}.

Discussion

Temperature dependences and overlap of absorption and luminescence bands for these A-frame systems suggest the assignment of the higher energy luminescence as a fluorescence and the lower energy band as a phosphorescence. This is most clearly seen for $[Rh_2(CO)_2Cl(dam)_2]BPh_4$ (see Figure 2). The lower energy electronic absorption overlaps with the tail of the higher energy luminescence, indicating that the absorption and the respective luminescence (i.e., fluorescence) have the same excited-state parentage. The lower energy luminescence of $[Rh_2(CO)_2Cl(dam)_2]BPh_4$ is a comparatively weak shoulder at room temperature but predominates at 77 K. If a phosphorescence assignment is made for the lower energy emission band, then the diminished emission intensity as temperature is increased can be easily explained as temperature-dependent phosphorescence quenching. The enhancement of the higher energy emission relative to the lower energy luminescence as temperature increases provides additional support for the assignment of the former as a fluorescence.

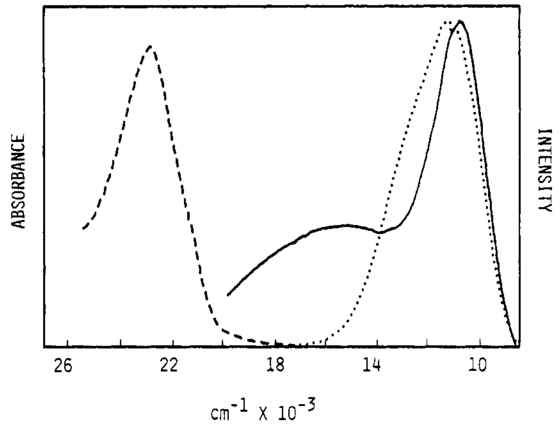


Figure 1. Absorption and luminescence spectra of $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$: absorption in CH_2Cl_2 solution at room temperature (- - -); emission of polycrystalline powder at room temperature (—) and at 77 K (···).

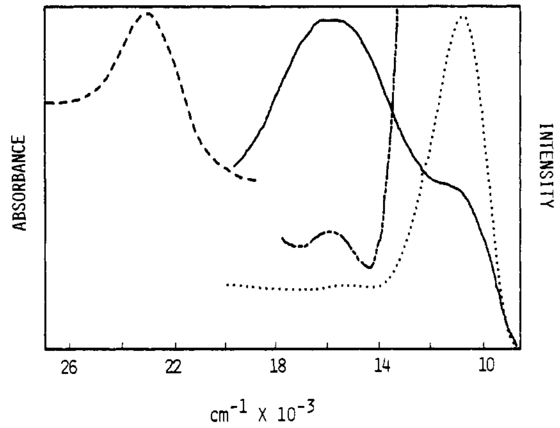


Figure 2. Absorption and luminescence spectra of $[Rh_2(CO)_2Cl(dam)_2]BPh_4$: absorption in CH_2Cl_2 solution at room temperature (- - -); emission of polycrystalline powder at room temperature (—), at 77 K (···), and with an expanded ordinate at 77 K (·-·).

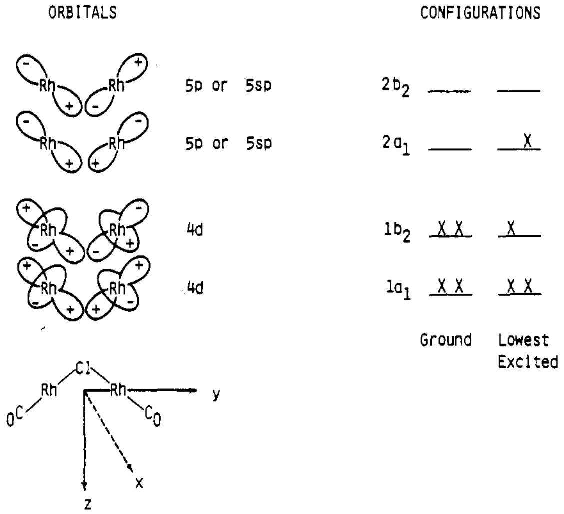


Figure 3. Orbital and configuration diagram for $C_{2v}(y)$ A-frame d^8 binuclear complexes.

The compound $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$ displays a broad low-energy luminescence with a long high-energy tail at 77 K (see Figure 1). It is postulated that this high-energy tail represents an unresolved fluorescence on the shoulder of the stronger phosphorescence. The obvious intermediate-energy shoulder on the low-energy emission (i.e., phosphorescence) of $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$ suggests a mixture of at least two unresolved bands within the phosphorescence envelope.

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The orbitals and terms (C_{2v}, A-frame systems) relevant to the analysis of the low-energy electronic transitions in these systems are shown in Figure 3. In this model, the y axis is chosen as the metal–metal axis. Transition assignments based upon this orbital scheme, similar to the schemes for C_{2h}, D_{2h}, and D_{4h} Rh(I) and Ir(I) binuclear systems employed by Mann et al.,[5] Fordyce and Crosby,[2] and Kenney et al.[3] are as follows: phosphorescence, $^3B_2 \rightarrow {}^1A_1$; fluorescence, $^1B_2 \rightarrow {}^1A_1$; absorption, $^1A_1 \rightarrow {}^1B_2$. We have chosen our axis system to agree with the assignments of Marshall et al. for the room-temperature luminescence from $[Ir(\mu\text{-pz})(COD)]_2$ (pz is pyrazolyl; COD is 1,5-cyclooctadiene).[6]

In the proposed model, the ground-state metal–metal bond order is formally zero; a bond order of 1.0 is predicted for the lowest excited singlet and triplet configurations. These A-frame Rh(I) molecules represent another group of d^8 square-planar bridged systems in which the molecules are predicted to contract when excitation occurs.[2,3,7]

The $^3B_2$ excited term yields A_1, B_1, and A_2 spin–orbit states; the A_2 state cannot couple with the A_1 ground state by an electronic dipole mechanism. From a correlation with the states of more symmetrical systems[2] this forbidden component is predicted to be the lowest component in the triplet manifold; thus, it can be predicted that the phosphorescence lifetimes of these A-frame complexes should mimic the behavior of the more symmetrical D_{2h} rhodium complexes and become exceedingly long (milliseconds) at temperatures below 10 K.[2] Temperature-dependent lifetime studies are planned.

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Registry No. $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$, 67202-35-1; $[Rh_2(CO)_2Cl(dam)_2]BPh_4$, 70561-97-6.

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Hydrostannolysis Reactions of $M_2(NMe_3)_6$ (M = W, Mo)

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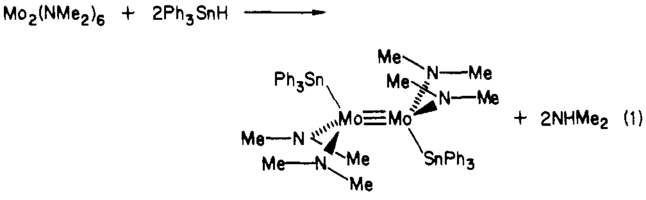
Interest in heterometallic transition-metal complexes containing metal-metal bonds has grown recently. Examples include transition metal–transition metal,[1] transition metal–post transition metal,[2] and transition metal–main group metal[3] bonds. Part of this interest arises from the frequent use of main-group metals as "promoters" of heterogeneous transition-metal catalysts.[4] An interesting homogeneous example is the hydroformylation catalyst formed from mixtures of Pt complexes and $SnCl_2$.[5]

As part of our interest in this area we have examined the reaction of tin hydrides with tungsten and molybdenum alkoxides and amides with the aim of displacing alcohols or amines and forming M–Sn bonds. This type of process is referred to as hydrostannolysis and has been successfully used for the preparation of Sn–Sn[6] and M–Sn (M = Ti, Zr)[7] bonds. In this work we find that hydrostannolysis reactions of the tungsten and molybdenum amides $M_2(NMe_2)_6$ yield complexes containing one and two M–Sn bonds. The singly substituted Sn complexes $M_2(Ph_3Sn)(NMe_2)_5$ (**2**), are rare examples of isolatable complexes of this type with different coordination environments at each metal center.[8]

Results and Discussion

Preparation and Characterization of 1,2-$Mo_2(Ph_3Sn)_2(NMe_2)_4$. Yellow $Mo_2(NMe_2)_6$ reacts rapidly with 2 equiv of Ph_3SnH in chlorobenzene to give an orange solution. Orange crystals of 1,2-$Mo_2(Ph_3Sn)_2(NMe_2)_4$ (**1**) deposit on standing (eq 1).



1

At 30 °C the ^1H NMR spectrum of **1** shows signals for the phenyl rings and two signals for the NMe_2 groups. When the sample is warmed, the NMe_2 signals coalesce ($\Delta G^{\ddagger} = 70.3$ kJ/mol at $T_c = 80$ °C). Such temperature-dependent behavior is typical[9] of rotationally hindered NMe_2 groups where each methyl group can be either proximal or distal to the M–M triple bond (see the structure shown in eq 1). Closely related complexes, 1,2-$M_2(NMe_2)_4(Sn(SnMe_3)_3)_2$, were prepared by treating $M_2Cl_2(NMe_2)_4$ with $LiSn(SnMe_3)_3$ and show similar NMR behavior ($\Delta G^{\ddagger} = 68.8$ and 70.6 kJ/mol for M = Mo and W, respectively.[10] The ^{119}Sn spectrum of **1** shows a single tin resonance at 6.7 ppm ($SnMe_4$ reference).

Preparation and Characterization of $M_2(Ph_3Sn)(NMe_2)_5$. When $W_2(NMe_2)_6$ is treated with excess Ph_3SnH, a slow reaction occurs and the only product obtained is $W_2(Ph_3Sn)(NMe_2)_5$ (**2a**, eq 2). None of the doubly substituted product (the tungsten equivalent of **1**) is formed. The analogous molybdenum complex **2b** can be prepared by the reaction of $Mo_2(NMe_2)_6$ with 1 equiv of Ph_3SnH.

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