afforded pure **15a** as a pale yellow solid, (mp 160–165 °C dec). Anal. Calcd for $[C_9H_{14}Cl_2Pd]_2$: C, 36.09; H, 4.71. Found: C, 35.91; H, 4.83. Heating a sample of the original product mixture or pure **15a** at reflux in CH_3CN (50 mL) for 24 h afforded a mixture of **15a**/**15b**/**16** (8:1:2 ratio, 98%).

Chloropalladation of 17. The product was filtered through a small silica gel column (CH_2Cl_2) and crystallized from CH_2Cl_2/hexanes (−10 °C) to afford a pale yellow solid which was identified by NMR spectroscopy (Tables I and II) as consisting of **18a** and **18b** (2.5:1 ratio, 85%), mp 159 °C. Anal. Calcd for $[C_7H_{10}Cl_2Pd]_2$: C, 30.97; H, 3.71. Found: C, 30.70; H, 3.80. A sample of the mixture (0.04 g, 0.07 mmol) was heated to reflux in CH_3CN (10 mL) for 24 h. The solution was cooled and the solvent removed to afford the initial mixture (0.04 g, 100%).

Chloropalladation of 6. The product was identified by NMR spectroscopy[10a] as **5a** (99% yield). A sample of **5a** (0.31 g, 0.49 mmol) was heated to reflux in CH_3CN (50 mL, 96 h). Removal of the solvent under reduced pressure afforded a mixture identified as consisting of **5a**, **5b**, and **5c** (1.8:1.0:5.1) by ^1H NMR spectroscopy[10a] (0.31 g, 100%). Fractional recrystallization of the mixture afforded a pure sample of **5c** (0.11 g). This sample was heated to reflux in CH_3CN (50 mL) for 96 h. Removal of the solvent under reduced pressure lead to a mixture of **5a**, **5b**, and **5c** (1.8:1.0:5.1; 0.11 g, 100%).

Chloropalladation of 19. The product **20** was identified by NMR spectroscopy (Tables I and II) (99% yield). Crystallization from CH_2Cl_2/hexanes afforded an analytically pure sample, mp 160 °C dec. Anal. Calcd for $[C_9H_{14}Cl_2Pd]_2$: C, 36.09; H, 4.71. Found: C, 36.23; H, 4.95.

Chloropalladation of 21. The product was identified by NMR spectroscopy (Table I) as consisting of **22a**, **22b**, and **22c** (2.2:1.8:1.0, 98%), mp 80–90 °C. Anal. Calcd for $[C_{12}H_{20}Cl_2Pd]_2$: C, 42.19; H, 5.90. Found: C, 42.38; H, 6.13. A sample of the initial mixture (0.13 g, 0.19 mmols) was heated to reflux in CH_3CN (25 mL) for 96 h. Removal of the solvent under reduced pressure afforded a mixture of **22a**, **22b**, and **22c** (2.1:1.2:1.0, 0.13 g, 100%).

Chloropalladation of 23. The product was identified by NMR spectroscopy (Table I) as consisting of a mixture of **24a**, **24b**, and **24c** (2.1:1.9:1.0, 99%), mp 180–185 °C dec. Anal. Calcd for $[C_{14}H_{24}Cl_2Pd]_2$: C, 45.37; H, 6.53. Found: C, 45.25; H, 6.74. Fractional crystallization of the mixture from CH_2Cl_2/hexanes afforded a solid consisting of **24a**, **24b**, and **24c** (1.0:1.0:1.4 by ^1H NMR integration). Recrystallization of the resultant mother liquors from CH_2Cl_2/hexanes afforded a sample of **24a** and **24b** (1.5:1.0 by ^1H NMR integration). Upon heating to reflux in CH_3CN (50 mL) both samples were quantitatively converted into a mixture of **24a**, **24b**, and **24c** (2.1:1.9:1.0).

Chloropalladation of 25. The product was identified by NMR spectroscopy (Table I) as consisting of **26a**, **26b**, and **26c** (3.0:1.3:1.0, 98%). Fractional crystallization of the mixture from CH_2Cl_2/hexanes afforded a pure sample of **26c** (Table II), mp 185–190 °C dec. Anal. Calcd for $[C_{17}H_{30}Cl_2Pd]_2$: C, 49.59; H, 7.34. Found: C, 49.60; H, 7.54. Heating either a sample of the initial mixture or of pure **26c** to reflux in CH_3CN (25 mL) for 48 h quantitatively afforded a mixture of **26a**, **26b**, **26c**, and **26d** (1.5:1.0:3.3:1.0).

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The Nature of the Low-Lying Excited States of Bridged Rhodium(I) and Iridium(I) Binuclear Complexes

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Electronic absorption and luminescence measurements on the four binuclear systems $[Rh(CO)Cl(dppm)]_2$, $[Rh(CO)Cl(dam)]_2$, $[Ir(CO)Cl(dppm)]_2$, and $[Ir(CO)Cl(dam)]_2$ [dppm = bis(diphenylphosphino)methane and dam = bis(diphenylarsino)methane] are reported at room temperature and 77 K. These d^8 rhodium(I) and iridium(I) molecules exhibit temperature-dependent low- and high-energy luminescences that are interpreted as the phosphorescences and the fluorescences arising from the metal-centered $np_z \rightarrow (n-1)d_{z^2}$ transition (n = 6 for Ir and 5 for Rh).

Introduction

Numerous studies[1-10] have focused on the synthesis, structure, and chemistry of bridged binuclear rhodium(I) complexes. Interest in these intensely colored molecules with square-planar-metal coordination geometry stems from their capacity to bind biologically and catalytically important small molecules (e.g., CO, CO_2, H_2O, $HC{\equiv}CR$, H^+) and from their ability to serve as catalysts. More recently,[9,11-13] attention has been directed toward the iridium(I) analogues of these rhodium systems. Spectroscopic studies have concentrated on structural elucidation

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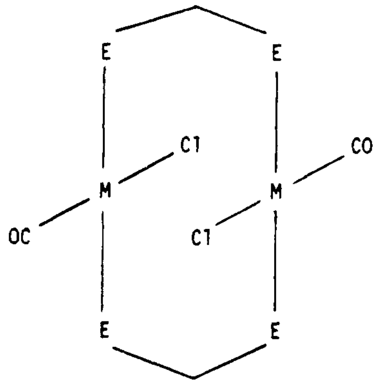
via IR and NMR. Almost all of the electronic spectroscopic data on these systems are derived from solution absorption measurements at room temperature.

This work addresses the temperature-dependent electronic absorption and luminescence behavior of two 4d^8 rhodium(I) molecules, [Rh(CO)Cl(dppm)]$_2$ and [Rh(CO)Cl(dam)]$_2$, and their 5d^8 iridium(I) analogues, [Ir(CO)Cl(dppm)]$_2$ and [Ir(CO)Cl(dam)]$_2$ [dppm = bis(diphenylphosphino)methane and dam = bis(diphenylarsino)methane]. All four systems are assumed to have the trans[14] structure I.[2,7,9,12]



I

M = Rh, Ir

E = P, As

These spectroscopic results comprise the first reported luminescence measurements and electronic assignments on "face-to-face" bridged iridium species and the first on these particular rhodium(I) complexes. They complement the recent report of Marshall et al. on the [Ir(μ-pz)(COD)]$_2$ (pz = pyrazolyl, COD = 1,5-cyclooctadiene) system that has an open structure and lower symmetry.[13]

Experimental Section

Standard Schlenk techniques and dry deoxygenated solvents were employed in all preparations. All subsequent manipulations involving iridium products were carried out by using Schlenk or glovebag techniques. Bis(diphenylphosphino)methane, bis(diphenylarsino)methane, and bis(μ-chloro)bis(1,5-cyclooctadiene)diiridium(I) dimer, [Ir(COD)Cl]$_2$, were obtained from Strem Chemicals, Inc. Tetracarbonylbis(μ-chloro)dirhodium(I), [Rh(CO)$_2$Cl]$_2$, was obtained from Aldrich Chemical Co. Bis(μ-chloro)dicarbonyltetrakis(cyclooctene)diiridium(I), [Ir(CO)Cl(c-octene)$_2$]$_2$, was obtained from Alfa Products. Matheson UHP grade CO was employed. [Rh(CO)Cl(dppm)]$_2$ and [Rh(CO)Cl(dam)]$_2$ were synthesized according to the procedure given by Mague and Mitchener.[1]

Preparation of [Ir(CO)Cl(dppm)]$_2$. The following modification of Sanger's method was used in this synthesis.[4] The reaction mixture [Ir(COD)Cl]$_2$ and dppm in distilled benzene purged by CO bubbling was stirred for several days at room temperature and then was refluxed under a CO atmosphere. The mixture turned dark purple when hot, changed to orange when warm, and turned light yellow when cold. The cool mixture was filtered under Ar atmosphere, washed with benzene and ether, and vacuum dried. The precipitate turned to a peach color while drying. The compound was then heated to 82 °C while still under vacuum. A bright red-violet microcrystalline product resulted. Anal. Calcd: C, 48.79; H, 3.46; P, 9.68. Found: C, 48.01; H, 3.50; P, 9.02.

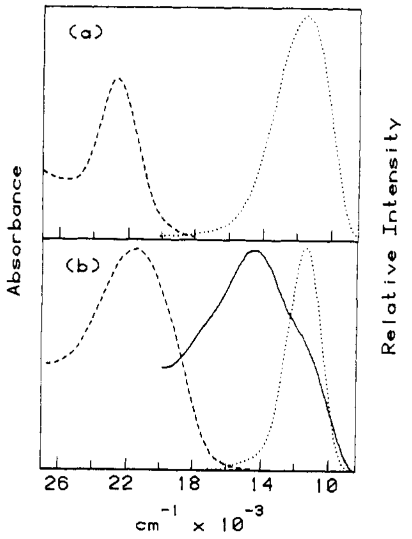


Figure 1. Absorption and emission spectra of bridged rhodium binuclear complexes: (a) [Rh(CO)Cl(dppm)]$_2$; (b) [Rh(CO)Cl(dam)]$_2$. Absorption in CH$_2$Cl$_2$ at room temperature (- - -); emission from polycrystalline powder at room temperature (—) and at 77 K (···). For molecular extinction coefficients, see ref 3, Table II.

Preparation of [Ir(CO)Cl(dam)]$_2$. A sample of 0.22 g (0.466 mmol) of dam in 35 mL of distilled spectroscopic grade acetone was purged by vigorous Ar bubbling for about 10 min. To this clear solution was added 0.20 g (0.210 mmol) of [Ir(CO)Cl(c-octene)$_2$]$_2$, a green-yellow powder, in small amounts. The solution turned purple on addition of the metal complex and a deep purple precipitate formed. The precipitate was filtered under an Ar atmosphere, washed with acetone and diethyl ether, and dried under vacuum. A bright purple-pink air-sensitive precipitate was recovered. Anal. Calcd: C, 42.90; H, 3.05. Found: C, 42.07; H, 3.21.

Spectroscopic Measurements. The CH$_2$Cl$_2$ used in spectroscopic measurements was purified by washing with water and sodium carbonate solution, drying over calcium chloride, and fractionally distilling. Absorption spectra were obtained in CH$_2$Cl$_2$ at room temperature on a Cary 219 spectrophotometer. Solid-state KBr pellet absorption spectra were also recorded. Luminescence spectra were measured on a custom-built prism spectrophotometer employing a cooled red-sensitive photomultiplier tube with dc detection and computer data acquisition. Samples were excited with the beam of a 200-W Hg arc lamp. The exciting light was passed through a CuSO$_4$ solution filter and Corning 7-60 and 7-37 filters and then directed to the sample through an array of quartz lenses.

Luminescence lifetimes were measured with a computer-controlled Biomation 6500 waveform recorder connected to the output of a cooled red-sensitive photomultiplier tube wired for fast response. The sample was excited with the filtered 337-nm line of a Molectron UV 22 pulsed nitrogen laser. The emitted light was focused through a KNO$_2$ solution filter onto the entrance slit of a Spex Minimate monochromator tuned within the emission band envelope. For all luminescence and luminescence lifetime studies, microcrystalline powders of the samples were placed between quartz disks sealed with indium gaskets. Iridium samples were prepared for study under an Ar atmosphere. Spectroscopic studies at 77 K were carried out in quartz optical Dewars.

Results

Shown in Figure 1 are the absorption and emission spectra for [Rh(CO)Cl(dppm)]$_2$ and [Rh(CO)Cl(dam)]$_2$. No room-temperature emission was observed from [Rh(CO)Cl(dppm)]$_2$. Absorption and emission spectra for [Ir(CO)Cl(dppm)]$_2$ and [Ir(CO)Cl(dam)]$_2$ are displayed in Figure 2. Listed in Table I are absorption maxima, emission maxima, and decay times measured at 77 K.

Each of the four complexes displays a well-defined low-energy absorption band (see Figures 1 and 2). Bridging

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[14] The trans (i.e., C_{2h}) geometry of the rhodium dimers has been confirmed by X-ray crystallography; the geometry of the iridium dimers has not been determined conclusively although current evidence suggests a trans assignment.

Table I. Photophysical Properties of Rhodium(I) and Iridium(I) Binuclear Molecules at Room Temperature (RT) and 77 K

complex	absorpn $\bar{\nu}_{max}$, cm^{-1} CH$_2$Cl$_2$	KBr^a	fluorescence $\bar{\nu}_{max}$,^{b} cm^{-1}	phosphorescence $\bar{\nu}_{max}$,^{b} cm^{-1}	τ, μs
[Rh(CO)Cl(dppm)]$_2$					
77 K		22 000		11 400	
RT	22 600	21 900			
[Rh(CO)Cl(dam)]$_2$					
77 K		21 200	14 700 (sh)	11 200	~1
RT	21 500	21 800	14 300 (vb)	11 100 (sh)	
[Ir(CO)Cl(dppm)]$_2$					
77 K		18 900	16 300 (w)	11 700	~2
RT	19 300	19 200	15 000 (sh)	11 800	
[Ir(CO)Cl(dam)]$_2$					
77 K		19 300	16 900	12 900	~3
RT	18 800	19 200	16 600 (sh)	12 800	
assignt	$^1A_g \rightarrow {}^1B_u$ $1b_u \rightarrow 2a_g$		$^1B_u \rightarrow {}^1A_g$ $2a_g \rightarrow 1b_u$	$^3B_u \rightarrow {}^1A_g$ $2a_g \rightarrow 1b_u$	

^{a}Pellet. ^{b}sh = shoulder; vb = very broad; w = wide.

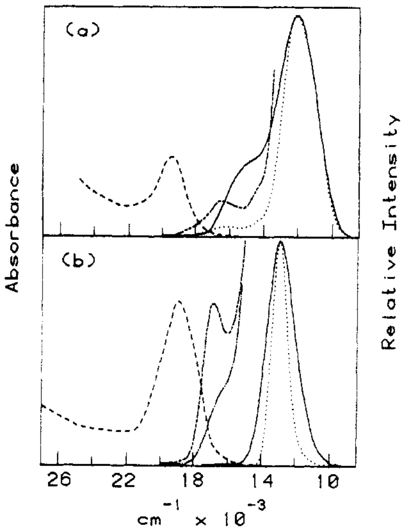

Figure 2. Absorption and emission spectra of bridged iridium binuclear complexes: (a) [Ir(CO)Cl(dppm)]$_2$; (b) [Ir(CO)Cl(dam)]$_2$. Absorption in CH$_2$Cl$_2$ at room temperature (- - -); emission from polycrystalline powder at room temperature (—) and at 77 K (···). Expanded sensitivity of room temperature emission (-·) and of 77 K emission (- - -).

ligand choice does not significantly affect the band maximum for a given metal [i.e., Rh(I), dppm, 22 600 cm^{-1}, dam, 21 500 cm^{-1}; Ir(I), dppm, 19 300 cm^{-1}, dam, 18 800 cm^{-1}]. These room-temperature CH$_2$Cl$_2$ solution absorption maxima are very close to the corresponding room-temperature and 77 K KBr pellet absorption maxima for all four systems (see Table I). The molecules do exhibit absorption bands at higher energy but they are not addressed in this study. Scans on the low-energy side of the principal low-energy absorption band revealed no measurable features for any of the four species.

At 77 K the rhodium complexes displayed low-energy emission bands maximizing at 11 400 cm^{-1} (dppm) and 11 200 cm^{-1} (dam), each with a long tail at higher energy. Neither of the rhodium molecules showed a distinctive band at higher energy when the ordinate was expanded. [Rh(CO)Cl(dppm)]$_2$ was not observed to emit light in the polycrystalline state at room temperature. At room temperature, [Rh(CO)Cl(dam)]$_2$ exhibited a broad high-energy band at 14 300 cm^{-1} with a less intense lower energy shoulder at 11 100 cm^{-1}.

At 77 K the iridium complexes displayed low-energy emission bands at 11 700 cm^{-1} (dppm) and 12 900 cm^{-1} (dam) each with weaker well-resolved bands at higher energy. These higher bands maximized at 16 300 cm^{-1} (dppm) and 16 900 cm^{-1} (dam). For [Ir(CO)Cl(dppm)]$_2$ at 77 K an additional small shoulder appeared at 14 200 cm^{-1}, between the low- and high-energy bands. The luminescence of the iridium species at room temperature was characterized by a low-energy band with a less intense higher energy shoulder. For both iridium molecules the low-energy band was broader at room temperature than at 77 K and the strength of the emission much diminished. Generally, the emission maxima at room temperature were not shifted greatly (400 cm^{-1}) from the emission maxima at 77 K with the exception of the high-energy band of [Ir(CO)Cl(dppm)]$_2$, whose room-temperature maximum was moved about 1300 cm^{-1} to the red from the maximum at 77 K.

The molecules containing the dppm-bridging ligand, [Rh(CO)Cl(dppm)]$_2$ and [Ir(CO)Cl(dppm)]$_2$, displayed much broader low-energy luminescence bands, about 1300 cm^{-1} broader (fwhm), than those of the analogous dam-bridged species, [Rh(CO)Cl(dam)]$_2$ and [Ir(CO)Cl(dam)]$_2$. Within the group, [Ir(CO)Cl(dam)]$_2$ luminesced with the greatest intensity, [Ir(CO)Cl(dppm)]$_2$ and [Rh(CO)Cl(dam)]$_2$ luminesced with an approximately equal intensity although with much less intensity than [Ir(CO)Cl(dam)]$_2$, and [Rh(CO)Cl(dppm)]$_2$ was a very weak emitter. The lower energy emission bands of the rhodium and iridium molecules exhibit lifetimes in the microsecond range at 77 K with some nonexponential behavior (see Table I). The lifetimes of the higher energy emission bands at 77 K fell below the detection limit of our apparatus (20 ns).

Discussion

All available experimental evidence for these systems, i.e., lifetime data, temperature dependence of emission, relative positions of emission, and absorption bands, is consistent with the assignment of the higher energy luminescence as a fluorescence and the lower energy emission as a phosphorescence. The evidence is most conclusive for [Rh(CO)Cl(dam)]$_2$ (Figure 1b) since the principal absorption band overlaps the tail of the higher energy luminescence band, indicating that the absorption and the fluorescence have the same excited state parentage. The lower energy luminescence of [Rh(CO)Cl(dam)]$_2$ is a comparatively weak shoulder at room temperature but dominates at 77 K. If a phosphorescence assignment is made for this band, then the diminished emission intensity at higher temperature is easily rationalized as temperature-dependent phosphorescence quenching. The enhancement of the higher energy luminescence band relative to the lower energy one as temperature increases provides additional evidence for assigning the former to a fluorescence.

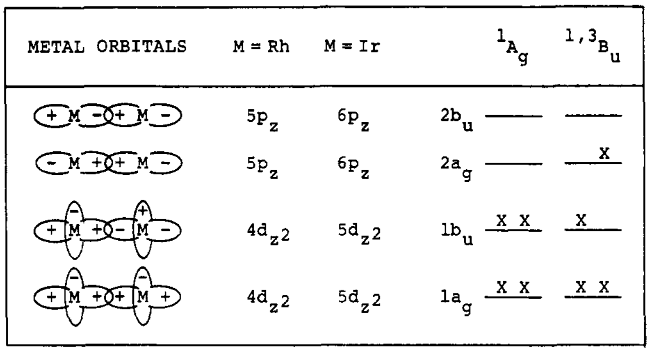

Figure 3. Proposed valence orbitals and states for bridged rhodium(I) and iridium(I) binuclear complexes. States are classified according to C_{2h} (x) where the M–M axis is the z axis (see text).

Finally, these assignments are supported by the short lifetime of the higher energy luminescence (<20 ns) and the longer lifetime (1 μs) of the lower energy luminescence at the reference temperature of 77 K. Although no band was resolved, the long high-energy tail on the 77 K emission spectrum of $[Rh(CO)Cl(dppm)]_2$ (Figure 1a) suggests a weak unresolved fluorescence tail on the phosphorescence maximum analogous to what is seen for $[Rh(CO)Cl(dam)]_2$ at 77 K. Unfortunately, no room-temperature emission spectra could be obtained from this weakly emitting system to confirm the existence of fluorescence.

The two iridium complexes exhibit somewhat different temperature-dependent luminescence behavior from that of their rhodium analogues. The low-energy emission band predominates both at room temperature and at 77 K. For $[Ir(CO)Cl(dam)]_2$, the higher energy luminescence is very weak at both 77 K and room temperature. If it is postulated that the intersystem crossing rate is enhanced by the larger spin–orbit-coupling constant introduced by the substitution of rhodium for iridium, then a phosphorescence/fluorescence assignment is reasonable for the lower/higher energy luminescence band. The dominance of phosphorescence is completely analogous to the behavior of the $[Pt_2H_8P_8O_{20}]^{4-}$ ion.[15] The position of the weak higher energy luminescence and its overlap with the corresponding absorption band are also consistent with a fluorescence assignment to the former. Spin–orbit coupling may also account for the presence of the intermediate energy shoulder present in the 77 K luminescence spectrum of $[Ir(CO)Cl(dppm)]_2$. A higher sample temperature could favor a transition to the ground-state singlet from a higher energy component of the lowest spin–orbit coupled triplet term or perhaps from a higher triplet.

The orbitals, configurations, and states relevant to the analysis of the low-energy electronic transitions in these systems are shown in Figure 3. To facilitate comparisons between these d^8 binuclear systems and d^8 binuclear complexes with D_{4h}[16] and D_{2h}[17] symmetry, a right-handed coordinate system is chosen for these C_{2h} binuclears that preserves the z axis as the metal–metal axis. Within this convention, the x axis becomes the principle C_{2h} symmetry axis. The normal C_{2h} character table, defined with respect to a z principal symmetry axis, is easily converted to the desired C_{2h} (x) character table by the coordinate permutation $x \rightarrow y$, $y \rightarrow z$, and $z \rightarrow x$.

The ground-state metal–metal bond order of these C_{2h} binuclear species is formally zero; a bond order of 1.0 is predicted for the lowest excited singlet and triplet terms. The well-resolved low-energy absorption observed in all of these systems is assigned to $^1A_g \rightarrow {}^1B_u$ (C_{2h}). The fluorescence and phosphorescence transition assignments are $^1B_u \rightarrow {}^1A_g$ and $^3B_u \rightarrow {}^1A_g$, respectively.

Within this electronic model for these C_{2h} binuclear systems the three spin–orbit coupled states arising from the triplet manifold (B_u, $2A_u$) are all dipole allowed. Thus, no significant increase in the phosphorescence lifetime of any of these systems is expected as the temperature is lowered. This predicted behavior contrasts with the observed temperature-dependent behavior of the phosphorescence lifetime of D_{4h} and D_{2h} binuclears.[15,17] In the latter systems, the dramatic increase in the phosphorescence lifetime as the temperature decreased was attributed to the preferential population of a low-lying dipole forbidden component of the spin–orbit coupled triplet manifold. No symmetry-forbidden triplet component is predicted for these C_{2h} systems.

Several previous workers[4,6,10,18] have assigned the low-energy absorptions of rhodium(I) dam- and dppm-bridged molecules to metal-to-ligand charge-transfer transitions primarily because of their high intensities; however, they seem to be better characterized by the metal-centered assignments adopted by Fordyce and Crosby that also accommodate intensely allowed transitions in the visible region of the spectrum.[17] In both the Ir(I) and Rh(I) species under study, the position of the low-energy absorption maximum is not greatly affected by replacement of dppm with dam, by change of environment from solid state to solution, or by change of temperature. This experimental evidence is consistent with metal-centered orbital assignments. The evident similarities within the two rhodium luminescence spectra and the two iridium luminescence spectra also suggest metal-centered transitions. Differences between the electronic spectra of the rhodium and iridium systems could become manifest at temperatures well below 77 K. We predict that the phosphorescence lifetimes of both rhodium species will remain in the microsecond range even to very low temperatures, unlike the more symmetric species (D_{2h}) studied earlier;[17] whereas we expect substantial increases in the phosphorescence decay times of the iridium species well above 10 K if the cis configuration (C_{2v}) is present. If the complexes possess a trans configuration (C_{2h}), as we have implicitly assumed above and as preliminary data seem to indicate,[12] then no dramatic lengthening of the lifetime, as $T \rightarrow 0$ K, is expected. Temperature-dependent studies on these and other analogous molecules are planned.

Finally, we comment specifically on the role of spin–orbit coupling in these systems. Because of the incorporation of heavy-metal ions in the structures one would, in analogy with numerous other complexes of rhodium, iridium, and ruthenium, expect no fluorescence at all and enormous triplet splittings (>10^3 cm^{-1}). That fluorescence occurs and the spin–orbit splittings of the lowest triplet levels are small (<50 cm^{-1}) is a consequence of the near cylindrical symmetry of the metal-centered molecular orbitals with respect to the binuclear axis.[17] To first order the lowest excited singlet and triplet states involve no nodes about the metal–metal axis; thus no orbital magnetism is generated about this axis and, to first order, the spin–orbit coupling vanishes. The spectroscopic consequence of this circumstance is that these heavy-metal binuclear species behave more like organic systems than their mononuclear

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analogues.

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Registry No. $[Ir(CO)Cl(dppm)]_2$, 99511-21-4; $[Ir(COD)Cl]_2$, 12112-67-3; $[Ir(CO)Cl(dam)]_2$, 99511-22-5; $[Ir(CO)Cl(cot)_2]_2$, 51812-37-4; $[Ph(CO)Cl(dam)]_2$, 99511-23-6; $[Ph(CO)Cl(dppm)]_2$, 99511-24-7.

Palladium-Catalyzed Additions of Amines to Conjugated Dienes: Alteration of Behavior of (Triphenylphosphine)palladium Catalysts with Amine Hydroiodide Salts

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When amine hydroiodide salts are present, (triphenylphosphine)palladium catalyst systems are capable of effecting the addition of primary and secondary amines to certain conjugated dienes. The generality and mechanistic aspects of these reactions were investigated.

Introduction

We have found that amine hydroiodide salts are capable of altering the behavior of (triphenylphosphine)palladium catalyst systems in reactions of amines with conjugated dienes. Such reactions produce 1:1 adducts which, in the case of 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene, consist primarily of products resulting from a 1,4-addition of the N–H moiety across the diene system. These addition products are obtained in fair to good yields with only traces of 1,2-addition products and octadienyl amines (1:2 adducts) being formed. Literature reports of similar systems using (triphenylphosphine)palladium catalysts without the amine hydroiodide salt indicate that octadienylamines are the major products.[1,2] Octadienylamines are also the major products in reactions employing phosphonite[3,4] and 1,5-cyclooctadienyl ligands.[5]

Other reports indicate that when a diphosphine ligand, e.g., 1,2-bis(diphenylphosphino)ethane, is substituted for triphenylphosphine (no amine hydroiodide salt), 1:1 adducts are obtained,[6,7] but in some cases the products consist of considerable quantities of 1,2-addition products. Another group has had some success in obtaining 1:1 adducts using a palladium acetoacetate–tributylphosphine–triethyl aluminum catalyst system, but reports that octadienylamines are the major products in reactions using 1,3-butadiene or isoprene.[8]

In this paper we report the results of our studies concerned with the generality and mechanistic aspects of these reactions incorporating the amine hydroiodide salts and offer an explanation for the poor or nonexistent yields of 1,2-addition products.

Results and Discussion

The results of some of our experiments involving reactions of equimolar amounts of amines and dienes using a catalyst precursor system of palladium acetate, triphenylphosphine, and triethylammonium iodide in quantities of 1, 2, and 10 mol %, respectively, are listed in Table I. No 1:1 adducts were obtained if any one of these substances were excluded. The minimum quantity of amine salt needed for optimum conditions (rate and yield) seems to differ for each reaction although we found no noticeable improvement when more than 10 mol % was used. The reaction of diethylamine with isoprene seems to proceed as well with 3 mol % amine salt as with 10 mol % salt, but the rates are slower when quantities less than 3 mol % are used. Similar results were obtained by using other amine hydroiodide salts. Successful results are also possible using reduced catalyst quantities as evidenced by the reaction of isoprene with diethylamine using 0.2 mol % palladium acetate, 0.4 mol % triphenylphosphine, and 1.0 mol % triethylammonium iodide which resulted in 52% isolated yield of a mixture of *N*-(2-methyl-2-buten-

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