just the π correlation energy is obtained by SDTQ CI calculations in a portion of the full π space, a single–triplet energy difference of 10 kcal/mol is obtained. This is roughly two-thirds of the singlet–triplet energy separation calculated for trimethylenemethane,[17,30] the best studied non-Kekulé hydrocarbon.

The computed energy difference between the $^3B_2$ ground state of **2** and the ^1A_g ground state of **3** does depend on the method of correlation energy recovery. This is not really surprising since the open-shell $^3B_2$ RHF (and $^1A_1$ TCSCF) wave function should have less correlation energy than the closed-shell ^1A_g wave function. Consequently, the calculated $^3B_2$–^1A_g energy difference will depend critically on the relative amount of the ^1A_g correlation energy that is recovered.

The estimated SDQ energies place ^1A_g below $^3B_2$ by about 7 kcal/mol. However, as discussed in the previous section, this number is probably not reliable, due to the relatively small amount of the SD correlation energy recovered variationally and the resulting uncertainties in both ΔE_{SD} and in ΔE_Q. As shown in Table I, the quadruples corrections estimated by eq 5 are substantial (>50 kcal/mol), because of the large number of σ and π valence electrons being correlated in **2** and **3**. As a result, the particularly large uncertaintes in ΔE_Q could result in a substantial error in the energy difference computed between ^1A_g and $^3B_2$.

We believe that the variational SDTQ π CI energies provide a better estimate of the energy difference between the ground states of **2** and **3**.[29] In fact, the 11-orbital π CI energy difference of 24 kcal/mol probably represents a lower bound to the actual energy difference between ^1A_g and $^3B_2$. As shown in Table II, perturbation theory suggests that CI calculations that included the σ orbitals would provide a small amount of additional differential stabilization for ^1A_g.

Even a $^3B_2$–^1A_g energy difference substantially less than 24 kcal/mol would probably be consistent with Hehre's lower limit of 26 kcal/mol for the energy difference between **2** and **3**.[11] It seems likely that the rate constant for deprotonation of the singlet *m*-methylbenzyl cation to the $^3B_2$ ground state of **2** would be very small, due to the unfavorable entropy of activation term expected for intersystem crossing. Therefore, even if deprotonation of the cation to $^3B_2$ were thermodynamically favorable, the ground state of the cation might be kinetically inaccessible under Hehre's ICR conditions.

Deprotonation of *m*-methylbenzyl cation to the $^1A_1$ state of **2** should not have an unfavorable entropy of activation, since no spin multiplicity change is required during this reaction.[31] Therefore, it seems plausible that it is the difference in energy between this excited state of **2** and the ground state of **3** upon which a lower limit of 26 kcal/mol can be placed from the data of Hehre et al. We calculate that $^1A_1$ lies 10 kcal/mol above $^3B_2$. Therefore, the difference between the $^3B_2$ ground state of **2** and the ^1A_g ground state of **3** could be as low as 16 kcal/mol and still be consistent with the experimental data of Hehre et al. Nevertheless, our theoretical results indicate that the energy difference between the ground states is at least 50% higher than this lower bound.

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(31) It remains to be investigated whether deprotonation of the *m*-methylbenzyl cation to form the $^1A_1$ state of **2** might require a higher activation enthalphy than deprotonation of the ortho or para cation, beyond that expected solely on the basis of the difference in thermodynamic stabilities of the products. More generally, it may be asked whether there are unusual features that are present transition state connecting a closed-shell carbocation or carbanion with a diradical and that destabilize the transition state.

Luminescent Iridium(I), Rhodium(I), and Platinum(II) Dithiolate Complexes

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Abstract: A new series of Ir(I) complexes [Ir(L)(L′)(mnt)]$^-$ (L = L′ = CO, P(OPh)$_3$; L + L′ = 1,2-bis(diphenylphosphino)ethane; L = CO, L′ = PPh$_3$, CN$^-$; mnt = maleonitriledithiolate) have been prepared which luminesce in the solid state at room temperature and in frozen glass media. Emission is also observed from the corresponding Rh(I) and Pt(II) complexes including the new compounds [PtL$_2$(mnt)] (L = P(OEt)$_3$, P(OPh)$_3$; L$_2$ = 1,5-cyclooctadiene, bis(diphenylphosphino)methane). At 77 K the solid-state emissions are highly structured and the highest energy emission maxima fall between 13.7 and 18.1 kcm^{-1}. Excitation spectra are also highly structured, mirroring the emission spectra. The Stokes shifts for these complexes are relatively small (typically ~400 cm^{-1}), indicating an excited-state geometry similar to that of the ground state. Structure in the emission and excitation spectra is attributed to vibrations within the metal–mnt moiety, with the dominant progression (~1400 cm^{-1} in emission spectra and ~1250 cm^{-1} in excitation spectra) corresponding to the mnt C=C vibration. Emission lifetimes range from 8 to 400 μs. From the evidence presented, the emission–absorption system for all of the complexes studied is assigned as a common singlet–triplet d–π^*(mnt) metal-to-ligand charge transfer.

The discovery of metal complexes having long-lived excited states is important to the development of new metal complex photochemistry.[1] Excited states in these systems may be of ligand field, charge transfer, or intraligand origin, and the nature of them is often probed through detailed spectroscopic and lifetime measurements. The observation of high-resolution vibrational structure in electronic emission and absorption spectra is particularly useful and provides information about changes in metal–ligand bonding between ground and excited states. This in-

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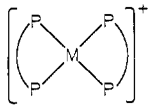
formation can aid in the assignment of electronic transitions and is vital to a fundamental understanding of photochemical reactions.

Perhaps the most intensively studied class of luminescent transition-metal complexes are the d^6 diimine chelates of the group 8 elements, and in particular, $Ru(bpy)_3^{2+}$.[2,3] These complexes possess excited states which are sufficiently long lived in solution to undergo bimolecular reactions. The emission spectra of the Ru(II) and Os(II) bipyridyl and *o*-phenanthroline chelates exhibit a single vibrational progression of ~1300 cm^{-1}, and this progression has been cited as evidence to support the assignment of a metal-to-ligand charge transfer excited state in these complexes.[4] Much of the recent interest in these d^6 aromatic diimine complexes and in particular $Ru(bpy)_3^{2+}$ stems from the development of schemes for water splitting based on electron-transfer quenching of the excited states of these complexes.[3b–h]

Among square-planar d^8 complexes, $PtCl_4^{2-}$ exhibits highly structured emission and absorption spectra.[5] The lowest energy electronic transition, assigned as a ligand field d–d type results in a significant Pt–Cl bond elongation in the excited state (0.2 Å calculated from vibronic intensities in emission and absorption spectra[6]). This bond lengthening is consistent with the photolability of complexes of this type.[7]

At the time we undertook our present study, luminescence from monomeric Ir(I) and Rh(I) complexes had been reported for only four compounds, A, containing bis(tertiary phosphine) ligands.[8,9]



M = Rh, Ir; $\overset{\frown}{P\,P}$ = 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2 bis(diphenylphosphino)ethylene

Emission spectra of these complexes were unstructured and emission lifetimes ranged from 8 to 28 μs (rigid glass at 77 K). The emission was assigned to originate from a predominantly metal-to-ligand charge-transfer excited state primarily on the basis of absorption band intensity and energy ordering Ir(I) < Rh(I) ≪ Pt(II), MCD spectra, and analogy to the well-studied $Pt(CN)_4^{2-}$.[10]

Very recently, Crosby and Fordyce[11] have reported luminescence from Ir(I) and Rh(I) complexes containing *N*-heterocyclic, diene, and bis(tertiary phosphine) and bis(tertiary arsine) ligands. Emission spectra were unstructured except for complexes of the type $[Ir(L_2)(COD)]^+$, where L_2 is a chelating ligand. For L_2 = bis(1,2-diphenylphosphino)ethylene, the Ir(I) COD complex exhibited a 650-cm^{-1} progression which was apparently vibrational in nature but unassigned.[11b] For L_2 = bpy, the Ir(I) complex showed a 1300-cm^{-1} progression[11a] similar to that seen for the d^6 bpy systems such as $Ru(bpy)_3^{2+}$.[3a,4] Emission lifetimes varied from 1 to 76 μs for these systems in rigid glass media at 77 K, and the emitting states for these complexes were assigned as having metal-to-ligand charge-transfer character on the basis of spectral data including the vibrational progressions and lifetime measurements.

In this paper we describe the synthesis and spectroscopic investigation of a new series of Ir(I) mnt complexes which, along with their Rh(I) and Pt(II) analogues, exhibit unusually structured emission and excitation spectra. Our results for the d^8 mnt complexes reported here are discussed in comparison with other square-planar d^8 systems. A preliminary account of this work has been given.[12]

Experimental Section

Materials. The following compounds were used as received: iridium trichloride hydrate, rhodium trichloride hydrate, and potassium tetrachloroplatinate (Johnson Matthey), triphenylphosphine (Strem), 1,2-bis(diphenylphosphino)ethane (dppe) (Ventron), triphenyl phosphite, 1,5-cyclooctadiene (COD), and tetra-*n*-butylammonium (TBA) bromide (Aldrich), triethyl phosphite (Eastman), and potassium cyanide (Mallinckrodt). Sodium maleonitriledithiolate (mnt), bis(triphenylphosphine)iminium (PPN) chloride, and (PPN)CN were prepared according to literature methods.[13] Reagent grade solvents were used for syntheses. For spectroscopic measurements acetonitrile (Aldrich spectrophotometric grade) was distilled from calcium hydride and EPA mixed solvent was prepared from five parts ethyl ether (Baker Photrex), five parts isopentane (Aldrich spectrophotometric grade), and two parts ethanol (Baker Photrex).

Preparation of Complexes. The complex $TBA[Ir(CO)_2Br_2]$ was prepared from iridium trichloride hydrate by the method of Cleare and Griffith[14] and recrystallized from acetone–2-propanol. The complexes $[Rh(CO)_2(mnt)]^-$, $[Rh(CO)(PPh_3)(mnt)]^-$, and $[Rh(P(OPh)_3)_2(mnt)]^-$,[15] and $Pt(PPh_3)_2(mnt)$,[16] $(TBA)_2[Pt(mnt)_2]$,[17] and $Pt(COD)Cl_2$[18] were prepared according to established procedures. The tendency of the rhodium bis(triphenyl phosphite) compound to form an oil in the initial precipitation step can be reduced by employing a minimum excess of $P(OPh)_3$ in the reaction. The complex $Pt(dppm)Cl_2$ (dppm = bis(diphenylphosphino)methane) was provided by Dr. Edward Nanni.

All syntheses were performed under a nitrogen atmosphere, using conventional vacuum-line and inert-atmosphere techniques. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

$TBA[Ir(CO)_2(mnt)]$. $TBA[Ir(CO)_2Br_2]$ (1.00 g, 1.54 mmol) and $Na_2(mnt)$ (0.40 g, 2.1 mmol) were dissolved in 50 mL of 3:2 ethanol–acetone, and the solution refluxed for 46 h. The resultant red-brown solution was concentrated under vacuum to ~10 mL, and 14 mL of water was added slowly to give a light tan crystalline preciptate which was collected by filtration and washed with water, 2-propanol, and ether to give 0.81 g (84%) of $TBA[Ir(CO)_2(mnt)]$: IR 2213 (m, C≡N), 2048 (s, CO), 1975 (s, CO) cm^{-1}. Anal. Calcd for $IrC_{22}H_{36}N_3O_2S_2$: C, 41.89; H, 5.75; N, 6.66; S, 10.16. Found: C, 41.93; H, 5.80; N, 6.66; S, 10.23.

$PPN[Ir(CO)_2(mnt)]$. This complex was best prepared by metathesis from the TBA^+ salt. $TBA[Ir(CO)_2(mnt)]$ (0.199 g, 0.32 mmol) and PPNCl (0.347 g, 0.60 mmol) were dissolved in 10 mL of acetone. Addition of water gave a light tan crystalline precipitate which was collected by filtration and washed with water, ethanol, and ether to give 0.262 g (90%) of $PPN[Ir(CO)_2(mnt)]$: IR 2206 (m, C≡N), 2037 (s, CO), 1968(s, CO) cm^{-1}. No IR peaks due to TBA^+ were evident.

$K[Ir(CO)_2(mnt)]$. This complex was only prepared once and a good synthetic procedure has not been established. A solution of 0.50 g (1.4 mmol) of iridium trichloride hydrate in 10 mL of 1:1 concentrated hy-

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(2) Abbreviations: bpy, 2,2′-bipyridine; mnt, maleonitriledithiolate; dppe, 1,2-bis(diphenylphosphino)ethane; dppm, bis(diphenylphosphino)methane; COD, 1,5-cyclooctadiene; TBA, tetra-*n*-butylammonium; PPN, $[(Ph_3P)_2N]^+$; Ph, phenyl; Et, ethyl; Me, methyl; MLCT, metal-to-ligand charge transfer; LMCT, ligand-to-metal charge transfer; IL, intraligand.

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drobromic acid (48%)/formic acid (88%) was refluxed for 8 h, giving a light orange solution. Formic acid (5 mL) was added and continued reflux for 1 h gave a light yellow solution. An aqueous solution of 0.70 g (5.9 mmol) of KBr was added and the solvent removed under vacuum to give a brown solid which was dried under vacuum. Addition of acetone gave an orange solution and a white precipitate (presumably KBr). The orange solution was transferred to another flask via cannula. A solution of 0.9 g (5 mmol) of Na_2(mnt) in ethanol was added, and the mixture refluxed for 23 h. The resultant deep red solution was filtered and the solvent removed under vacuum. Addition of acetonitrile to the residue gave a red solution and a light-colored precipitate (presumably KBr and Na_2(mnt)). The solution was filtered and the solvent removed under vacuum to give a red oil. After some unsuccessful manipulations, a small amount of partly crystalline tan-brown solid was precipitated from an acetone solution by adding CH_2Cl_2. The solvent was removed via cannula and the product identified as K[Ir(CO)$_2$(mnt)] by its luminescence and IR spectrum: 2210 (s, CN), 2046 (vs, CO), 1961 (vs, CO), 1476 (s), 1165 (m), 1151 (s), 1112 (m), 1074 (sh), 1047 (w), 1013 (w), 865 (m), 604 (w), 546 (m), 513 (s) cm^{-1}. Upon exposure to air the solid rapidly turned darker brown.

PPN[Ir(CO)(PPh$_3$)(mnt)]. PPN[Ir(CO)$_2$(mnt)] (0.201 g, 0.216 mmol) and PPh_3 (0.0755 g, 0.288 mmol) were placed in a flask, and 10 mL of acetone was added. Vigorous gas evolution ensued. The solution was stirred for 10 min and concentrated to ~2 mL under vacuum. Upon addition of 16 mL of 2-propanol a powdery yellow precipitate formed and was collected by filtration, washed with 2-propanol and ether to give 0.217 g (86%) of PPN[Ir(CO)(PPh$_3$)(mnt)]: IR 2198 (m, $C\equiv N$), 1943 (s, CO) cm^{-1}.

TBA[Ir(CO)(PPh$_3$)(mnt)] was prepared by a strictly analogous procedure: IR 2194 (m, $C\equiv N$), 1948 (s, CO) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.68 and 7.41 (m, C_6H_5), 3.41, 1.80, 1.41, 0.96 (m, $NCH_2CH_2CH_2CH_3$). Anal. Calcd for $IrC_{39}H_{51}N_3OPS_2$: C, 54.14; H, 5.94; N, 4.86; P, 3.58; S, 7.41. Found: C, 53.96; H, 5.97; N, 4.86; P, 3.57; S, 7.26.

PPN[Ir(P(OPh)$_3$)$_2$(mnt)]. A solution of 0.503 g (0.543 mmol) of PPN[Ir(CO)$_2$(mnt)], 0.37 mL (1.4 mmol) of P(OPh)$_3$, and 15 mL of acetone was stirred at ~60 °C for 1 h. The volume of solution was reduced to ~10 mL under vacuum and 14 mL of 2-propanol was added. Upon concentration of the solution under vacuum to ~5 mL, an orange powdery precipitate formed. An additional 10 mL of 2-propanol was added and the precipitate collected by filtration, washed with 2-propanol and ether to give 0.75 g (93%) of PPN[Ir(P(OPh)$_3$)$_2$(mnt)]: IR 2197 cm^{-1} ($C\equiv N$).

TBA[Ir(P(OPh)$_3$)$_2$(mnt)] was prepared by a strictly analogous procedure, using a minimum excess of P(OPh)$_3$. The product tended to form an oil due to the presence of excess P(OPh)$_3$ but could be isolated by repeated rapid precipitations from acetone–2-propanol solution. IR 2196 cm^{-1} ($C\equiv N$); ^{1}H NMR ($CDCl_3$) δ 6.9–7.3 (m, C_6H_5), 3.18, 1.56, 1.40, 0.96 (m, $NCH_2CH_2CH_2CH_3$). Anal. Calcd for $IrC_{56}H_{66}N_3O_6P_2S_2$: C, 56.27; H, 5.56; N, 3.52; P, 5.18; S, 5.36. Found; C, 55.91; H, 5.71; N, 3.56; P, 5.09; S, 5.38.

TBA[Ir(dppe)(mnt)]. TBA[Ir(CO)$_2$(mnt)] (0.162 g, 0.256 mmol) and dppe (0.121 g, 0.302 mmol) were placed in a flask, and 3 mL of acetone was added. Vigorous gas evolution ensued. The red-brown solution was stirred at ~35 °C for 1 h. 2-Propanol (8.5 mL) was added and the solution concentrated slightly under vacuum, resulting in the formation of a rust-orange crystalline precipitate. The mixture was set aside at −20 °C for 3 h. The precipitate was collected by filtration and washed with 2-propanol and ether to give 0.199 g (80%) of TBA[Ir(dppe)(mnt)]: IR 2191 cm^{-1} ($C\equiv N$); ^{1}H NMR (acetone-d_6) δ 7.86 (m, 8 H, from homonuclear decoupling $^3J_{P-H}$ = 10.3 Hz, o-C_6H_5), 7.27 (m, 12 H, m-, p-C_6H_5), 2.26 (m with two intense inner peaks separated by 16.9 Hz, 4 H, CH_2P), 3.35, 1.75, 1.39, and 0.94 (m, 8 H, 8 H, 8 H, 12 H, $NCH_2CH_2CH_2CH_3$).

PPN[Ir(dppe)(mnt)]. The reaction of PPN[Ir(CO)$_2$(mnt)] and dppe was followed by ^{31}P NMR spectroscopy. PPN[Ir(CO)$_2$(mnt)] (0.10 g, 0.11 mmol) and dppe (0.050 g, 0.13 mmol) were placed in a 10-mm NMR tube, and ~2.5 mL of acetone-d_6 was distilled in under vacuum. The tube was sealed under vacuum and allowed to warm to room temperature during which vigorous gas evolution occurred and the solution turned deep red. The reaction to form PPN[Ir(dppe)(mnt)] was complete within 20 min by ^{31}P NMR spectroscopy: δ 47.2 (s, b, coordinated dppe), 22.4 (s, PPN$^+$), −11.7 (s, free dppe).[19]

(PPN)$_2$[Ir(CO)(CN)(mnt)]. To a solution of 0.092 g (0.099 mmol) of PPN[Ir(CO)$_2$(mnt)] in 6 mL of acetonitrile was added dropwise a solution of 0.073 g (0.129 mmol) of (PPN)CN in 7 mL of acetonitrile. A crystalline amber-brown precipitate started to form after ~3 mL of the cyanide solution was added. The solution was concentrated to ~6 mL under vacuum and 7 mL of 2-propanol was added. The solution was again concentrated under vacuum to ~6 mL and set aside at −20 °C for 1 h. The precipitate was collected by filtration and washed twice with 2-propanol and twice with ether to give 0.135 g (93%) of (PPN)$_2$[Ir(CO)(CN)(mnt)]: IR 2190 (m, mnt $C\equiv N$), 2090 (m, CN), 1916 (s, CO) cm^{-1}. Anal. Calcd for $IrC_{78}H_{60}N_5OP_4S_2$: C, 64.01; H, 4.13; N, 4.79; S, 4.38. Found: C, 63.79; H, 4.20; N, 4.82; S, 4.37.

Pt(dppm)(mnt). A mixture of 0.256 g (0.394 mmol) of Pt(dppm)Cl_2 and 0.088 g (0.47 mmol) of Na_2(mnt) in 5 mL of acetone was stirred at ~40 °C for 2.5 h during which a peach-colored precipitate formed. The precipitate was collected by filtration and washed with acetone, water, 2-propanol, and ether to give 0.198 g of Pt(dppm)(mnt). The combined filtrate and washings were filtered to give an additional 0.035 g (total yield 82%) of product. The IR spectrum contained peaks due to coordinated dppm (assigned by comparison to a spectrum of Pt(dppm)Cl_2) and peaks assignable to mnt: 2202 (s, $C\equiv N$), 1473 (s, $C=C$), and 1153 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.74 and 7.47 (m, 20 H, C_6H_5), 4.73 (t with Pt satellites, 2 H, $^2J_{P-H}$ = 10.9 Hz, $^3J_{Pt-H}$ = 46.7 Hz, CH_2); mass spectrum (70 eV), parent ion at m/e 719. Anal. Calcd for $PtC_{29}H_{22}N_2P_2S_2$: C, 48.40; H, 3.08; N, 3.89; P, 8.61; S, 8.91. Found: C, 47.76; H, 3.08; N, 3.80; P, 8.42; S, 9.07.

Pt(COD)(mnt). A mixture of 0.080 g (0.21 mmol) of Pt(COD)Cl_2 and 0.049 g (0.26 mmol) of Na_2(mnt) in 5 mL of ethanol was stirred at 40 °C for 24 h during which a yellow precipitate formed. Water (8 mL) was added and the solution cooled to 0 °C. The precipitate was collected by filtration and washed with water, 2-propanol, and ether to give 0.081 g (86%) of Pt(COD)(mnt). The IR spectrum contained peaks due to coordinated COD (assigned by comparison to a spectrum of Pt(COD)Cl_2) and additional peaks assignable to mnt: 2212 (s, $C\equiv N$), 1503 (s, $C=C$), and 1160 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.63 (s with Pt satellites, 4 H, $^2J_{Pt-H}$ = 54.3 Hz, vinyl H), 2.62 (m, 8 H, methylene H); mass spectrum (70 eV), parent ion at m/e 443.

Pt(P(OEt)$_3$)$_2$(mnt). To a mixture of 0.096 g (0.22 mmol) of Pt(COD)(mnt) in 7 mL of acetone was added 0.12 mL (0.70 mmol) of P(OEt)$_3$, yielding a clear light-orange solution. After stirring 10 min the solution was concentrated under vacuum to ~1 mL. Addition of 9 mL of heptane gave a peach-colored crystalline precipitate which was collected by filtration and washed 3 times with heptane and once with pentane to give 0.133 g (92%) of Pt(P(OEt)$_3$)$_2$(mnt). The IR spectrum contained peaks due to coordinated P(OEt)$_3$ (assigned by comparison to a spectrum of P(OEt)$_3$) and additional peaks assignable to mnt: 2205 (s, $C\equiv N$), 1489 (s, $C=C$), and 1153 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.15 (m, 2 H, CH_2), 1.35 (t, 3 H, J = 7.1 Hz, CH_3) (Homonuclear decoupling experiments establish that the resonance at δ 4.15 is a broad pseudotriplet (3.9-Hz peak separations) further split into a quartet pattern by the resonance at δ 1.35 (J = 7.1 Hz).); mass spectrum (70 eV), parent ion at m/e 667. Anal. Calcd for $PtC_{16}H_{30}N_2O_6P_2S_2$: C, 28.79; H, 4.53; N, 4.20; P, 9.28; S, 9.61. Found: C, 28.63; H, 4.30; N, 4.16; P, 9.27; S, 9.64.

Pt(P(OPh)$_3$)$_2$(mnt). A mixture of 0.033 g (0.074 mmol) of Pt(COD)(mnt) and 58 μL (0.22 mmol) of P(OPh)$_3$ in 5 mL of ethanol was stirred at 35 °C for 10 h during which a light yellow precipitate formed. The precipitate was collected by filtration and washed with ethanol and ether to give 0.052 g (73%) of Pt(P(OPh)$_3$)$_2$(mnt): IR 2212 cm^{-1} ($C\equiv N$); ^{1}H NMR ($CDCl_3$) δ 7.25 (m, m-C_6H_5), 7.18 (m, p-C_6H_5), 7.03 (d, J = 8.0 Hz, o-C_6H_5); mass spectrum (70 eV), parent ion at m/e 955 (±2). Anal. Calcd for $PtC_{40}H_{30}N_2O_6P_2S_2$: C, 50.26; H, 3.16; N, 2.93; P, 6.48; S, 6.71. Found: C, 49.84; H, 3.23; N, 2.89; P, 6.65; S, 6.94.

Physical Measurements. IR spectra were obtained from KBr pellets on a Perkin-Elmer 467 spectrophotometer. ^{1}H NMR spectra (400.134 MHz) were recorded on a Bruker WH-400 spectrometer. A JEOL JNM-PS-100 spectrometer was used to obtain ^{31}P (40.482 MHz) NMR spectra. Chemical shifts are reported in ppm downfield from external references (Me_4Si for ^{1}H and 85% H_3PO_4 for ^{31}P, calculated by using δ_P −4.1 for PPh_3) and calculated in some cases from internal solvent peaks ($CHCl_3$ δ_H 7.24, acetone-d_5 δ_H 2.04). UV–visible spectra were recorded on Perkin-Elmer 330 and Cary 14 spectrophotometers. Spectra at 77 K were obtained from samples in 1-cm square quartz cells, using a liquid-nitrogen-filled quartz Dewar with flat windows. Mass spectra were recorded on a Dupont 21-490 B mass spectrometer.

Samples for emission experiments were sealed in 2-mm o.d. Pyrex tubes. Emission and excitation spectra (uncorrected) were recorded on a Perkin-Elmer MPF-44A fluorescence spectrophotometer (R 446 F photomultiplier tube) equipped with Perkin-Elmer phosphorescence accessory 063-0504. To determine emission lifetimes, samples were excited with a Garching N_2 laser (Model SP-1/II) which produced 337-nm pulses having a full width at half-maximum of ca. 0.5 ns. A small fraction of the exciting light was split off and directed onto a photodiode

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[19] The large downfield coordination shift of the dppe resonance (58.9 ppm) is indicative of a monomeric chelate complex with a five-membered ring. See: Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435–1439.

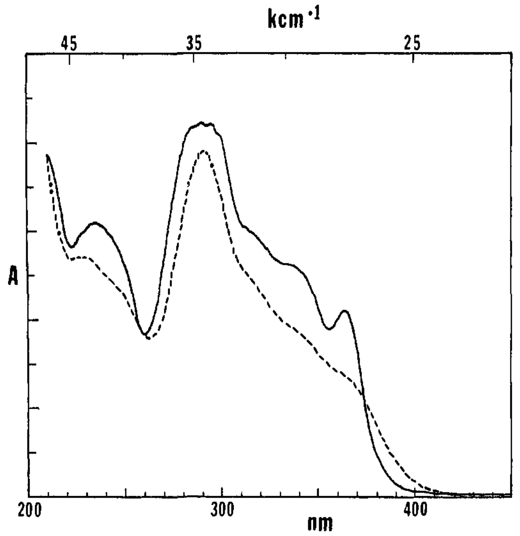
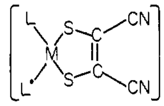


Figure 1. Electronic absorption spectra of TBA[Ir(CO)$_2$(mnt)] in EPA solution at room temperature (--) and 77 K (–).

used for triggering the electronics. Front surface luminescence from the sample was focused onto a Hamamatsu R443 photomultiplier tube (PMT) which was fitted with a UV cutoff filter and monochromator. The PMT output signals were sampled and averaged with a Tektronix digital processing oscilloscope. Time resolved spectra were recorded with a frequency-doubled Holobeam ruby laser and a Princeton Applied Research gated OMA I multichannel analyzer.

Results

Syntheses. The complexes studied are of general formulae I–III.



Ia–e, M = Ir; $n = 1$
IIa,b,d, M = Rh; $n = 1$
IIIb,f–h, M = Pt; $n = 0$

a, L = L' = CO
b, L = L' = P(OPh)$_3$
c, L + L' = dppe
d, L = CO, L' = PPh$_3$
e, L = CO, L' = CN$^-$
f, L + L' = COD
g, L = L' = P(OEt)$_3$
h, L + L' = dppm

The iridium complexes Ia–e were synthesized as their NBu$_4^+$ (TBA$^+$) salts via the reaction of TBA[Ir(CO)$_2$Br$_2$] and Na$_2$(mnt) in acetone–ethanol, yielding Ia, and subsequent substitution of CO by L, leading to [Ir(CO)L(mnt)]$^-$ (Id,e) or [IrL$_2$(mnt)]$^-$ (Ib,c). The PPN$^+$ ((Ph$_3$P)$_2$N$^+$) salts of Ia–e were obtained by analogous procedures or by metathesis. The substitution reactions are essentially quantitative as judged by IR spectroscopy in the CO stretching region and in selected instances by isolated product yields.

The complexes Pt(COD)(mnt) (IIIf) and Pt(dppm)(mnt) (IIIh) are readily prepared from the dichlorides Pt(COD)Cl$_2$ and Pt(dppm)Cl$_2$. Substitution of the COD ligand in Pt(COD)(mnt) by P(OEt)$_3$ and P(OPh)$_3$ gives Pt(P(OEt)$_3$)$_2$(mnt) (IIIg) and Pt(P(OPh)$_3$)$_2$(mnt) (IIIb), respectively. The platinum compounds were characterized by IR, NMR, and electronic spectroscopy, mass spectrometry, and elemental analysis. All of the new iridium and platinum compounds are air stable as solids except for Ic, which decomposes over a period of several hours when exposed to air. The Rh(I) complexes IIa, IIb, and IId, and the Pt(II) derivatives Pt(PPh$_3$)$_2$(mnt) and (TBA)$_2$[Pt(mnt)$_2$] were synthesized following previously published procedures.[15-17]

Electronic Absorption Spectra. The room-temperature and 77 K absorption spectra of TBA[Ir(CO)$_2$(mnt)] in EPA (5:5:2 ethyl ether–isopentane–ethyl alcohol) are shown in Figure 1. In concentrated acetonitrile solution weak bands can be observed at longer wavelengths. When the temperature is lowered to 77 K, the first intense absorption band resolves into a well-defined maximum at 364 nm. A similar result is found for TBA[Rh(CO)$_2$(mnt)] which exhibits a low-energy maximum at 368 nm in EPA at 77 K. Table I presents room-temperature electronic absorption spectral data ($\lambda_{max} < 35\,000$ cm^{-1}) for the luminescent compounds. In general, the Ir and Pt complexes have weak ($\epsilon \sim 10$ M^{-1} cm^{-1}) absorption bands at 5000–10000 cm^{-1} lower in energy than the first intense absorption maxima. Similar weak absorption bands could not be observed for the Rh compounds. The first intense absorption bands occur at about the same energy for corresponding Rh and Ir compounds, while similar absorptions for Pt complexes are found to be considerably blue-shifted. We have been unable to obtain 77 K absorption spectra showing the weak low-energy absorption bands of these compounds due in part to their small extinction coefficients coupled with insufficient solubility of these compounds at lower temperatures.

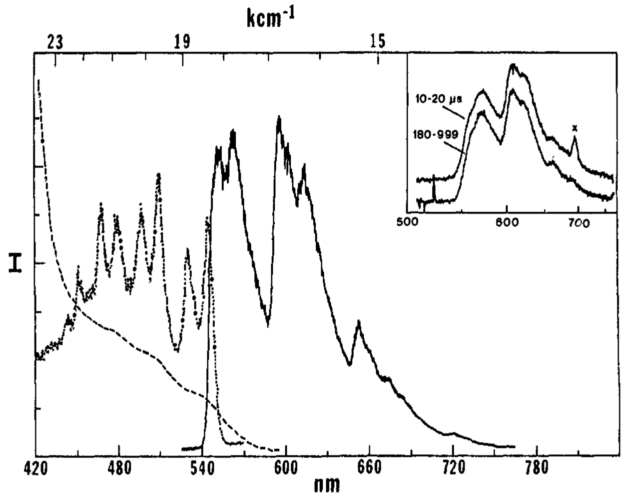


Figure 2. Emission (–, solid state, 77 K), excitation (···, solid state, 77 K), and absorption (--, CH$_3$CN solution, 298 K) spectra of TBA[Ir(CO)$_2$(mnt)]. The inset shows emission spectra of the PPN salt (solid state, 77 K) at different time intervals following pulsed-laser excitation. The peak marked "X" in the short time spectrum is due to residual intensity of the laser pulse at double the exciting wavelength.

The first intense absorption band of TBA[Rh(P(OPh)$_3$)$_2$(mnt)], which is resolved from higher energy maxima, shows some solvent dependence (solvent (λ_{max}, nm): benzene (401), THF (392), CH$_2$Cl$_2$ (394), acetone (393), methanol (396), acetonitrile (392), Me$_2$SO (398)) although no trend with solvent polarity is evident.

Electronic Emission and Excitation Spectra. All of the iridium complexes along with TBA[Rh(P(OPh)$_3$)$_2$(mnt)] and all of the platinum compounds except for (TBA)$_2$[Pt(mnt)$_2$] luminesce detectably at room temperature in the solid state. Luminescence is not observed in fluid solution but is seen in EPA glasses at 77 K. We have also observed luminescence from compound Ib in sulfolane glass at 253 K. At low temperatures the solid-state emissions become highly structured and the emission intensity increases. An emission spectrum of Ib obtained at 12 K is nearly identical with the 77 K spectrum. Emissions from EPA glasses were less resolved than the solid-state emissions.

Figures 2 and 3 show representative emission and low-energy excitation and absorption spectra for compounds Ia and Id. In addition, the figure insets show time-resolved emission spectra which indicate that the emissions decay uniformly. Most of the carbonyl substituted compounds have emission spectra similar to Figure 3 although their structure is generally less resolved. Table II presents the 77 K highest energy emission and lowest energy excitation maxima, along with emission lifetimes and 298 K IR spectral data. A complete listing of emission and low-energy excitation maxima appears in Table III (supplementary material).

Emission and excitation spectra of Pt(P(OEt)$_3$)$_2$(mnt) (IIIg) along with energy spacings between peak maxima are presented in Figure 4. The emission spectrum exhibits a ground state

Table I. Electronic Absorption Spectral Data[a]

compd	$\times 10^3$ cm^{-1} (ϵ_{max}), 298 K	compd	$\times 10^3$ cm^{-1} (ϵ_{max}), 298 K
TBA[Ir(CO)$_2$(mnt)]	18.48 sh (3.2)	[Pt(COD)(mnt)]	18.52 sh (3)
	19.88 sh (5.5)		25.84 sh (590)
	20.92 sh (6.7)		28.90 (5560)
	27.62 sh (5580)		30.30 (6240)
	29.41 sh (7510)	[Pt(P(OEt)$_3$)$_2$(mnt)]	18.18 sh (3.2)
	31.45 sh (9500)		19.49 sh (5.2)
	34.36 (19 400)		20.83 sh (6.8)
TBA[Ir(CO)(PPh$_3$)(mnt)]	17.24 sh (10.3)		28.33 (5260)
	18.69 sh (20.6)		29.59 sh (4800)
	25.64 sh (4650)		34.48 sh (7400)
	30.49 (11 900)	[Pt(P(OPh)$_3$)$_2$(mnt)]	18.45 sh (2)
	33.22 (12 100)		19.69 sh (3)
TBA[Ir(P(OPh)$_3$)$_2$(mnt)]	17.51 sh (10.0)		29.07 (5870)[b]
	18.87 sh (14.5)		30.49 sh (3950)
	25.64 sh (4430)		33.33 sh (5160)
	31.35 (12 500)	[Pt(dppm)(mnt)]	28.41 (5950)[b]
	34.36 (13 600)		34.97 sh (13 900)
TBA[Ir(dppe)(mnt)][c]	16.72 sh (31)	[Pt(PPh$_3$)$_2$(mnt)]	17.86 sh (2)[d]
	17.86 sh (45)		19.08 sh (3)[d]
	22.73 sh (5500)		24.39 sh (515)
	26.46 (12 000)		27.32 (6200)
(PPN)$_2$[Ir(CO)(CN)(mnt)]	22.27 (2830)		28.57 sh (3740)
	26.25 (4500)		34.97 sh (14 900)
	29.59 (9200)	(TBA)$_2$[Pt(mnt)$_2$][e]	14.41 sh (49)
	33.67 sh (8500)		15.65 sh (56)
TBA[Rh(CO)$_2$(mnt)]	27.55 sh (5650)		18.50 sh (1220)
	33.78 (14 700)		21.10 (3470)
AsPh$_4$[Rh(CO)(PPh$_3$)(mnt)]	25.64 sh (4460)		29.70 (15 600)
	31.65 (13 300)		32.30 (13 400)
TBA[Rh(P(OPh)$_3$)$_2$(mnt)]	25.51 (4430)		
	29.41 sh (8400)		
	32.15 (16 500)		

[a] Acetonitrile solutions. [b] Broad tail into visible region. [c] Acetone solvent. [d] Dichloromethane solvent. [e] Data taken from Shupack et al.: Shupack, S. I.; Billig, E.; Clark, R. J. H.; Williams, R.; Gray, H. B. *J. Am. Chem. Soc.* 1964, *86*, 4594–4602.

Table II. Electronic Emission and Excitation, and IR Spectral Data

compd	first em max, $\times 10^3$ cm^{-1}, 77 K	first excitn max, $\times 10^3$ cm^{-1}, 77 K	lifetime,[a] μs, 77 K	IR[b] ν_{CO}, cm^{-1}
TBA[Ir(CO)$_2$(mnt)]	18.06	18.36	78	2048, 1975
TBA[Ir(CO)$_2$(mnt)] (EPA[c])	17.78	*d*	105	
PPN[Ir(CO)$_2$(mnt)]	17.89 sh	18.26	93	2037, 1968
TBA[Ir(CO)(PPh$_3$)(mnt)]	16.52	16.91	30 (13)	1948
TBA[Ir(CO)(PPh$_3$)(mnt)] (EPA)	15.15	*d*		
PPN[Ir(CO)(PPh$_3$)(mnt)]	16.43	16.84	25 (4)	1943
(PPN)$_2$[Ir(CO)(CN)(mnt)]	15.11	16.94	8	1916
TBA[Ir(P(OPh)$_3$)$_2$(mnt)]	16.85	17.18	40 (19)	
TBA[Ir(P(OPh)$_3$)$_2$(mnt)] (EPA)	15.45	*d*	89	
PPN[Ir(P(OPh)$_3$)$_2$(mnt)]	16.39 sh	17.06	21 (8)	
TBA[Ir(dppe)(mnt)]	14.71	16.69		
TBA[Rh(CO)$_2$(mnt)]	16.42	17.57	238	2059, 1993
PPN[Rh(CO)$_2$(mnt)]	17.45 sh	17.84	389	2052, 1986
TBA[Rh(CO)(PPh$_3$)(mnt)]	16.14	16.66	99	1962
PPN[Rh(CO)(PPh$_3$)(mnt)]	16.20	16.57	303	1954
AsPh$_4$[Rh(CO)(PPh$_3$)(mnt)]	15.95	16.34	132	1957
TBA[Rh(P(OPh)$_3$)$_2$(mnt)]	16.59	16.84	281 (85)	
PPN[Rh(P(OPh)$_3$)$_2$(mnt)]	15.55	16.68	155	
[Pt(COD)(mnt)]	17.86	18.18		
[Pt(P(OEt)$_3$)$_2$(mnt)]	17.66	17.84		
[Pt(P(OEt)$_3$)$_2$(mnt)] (EPA)	17.81	*d*		
[Pt(P(OPh)$_3$)$_2$(mnt)]	16.53 sh	18.45		
[Pt(dppm)(mnt)]	16.39	17.54		
[Pt(PPh$_3$)$_2$(mnt)]	15.34	17.09	24	
(TBA)$_2$[Pt(mnt)$_2$]	13.76	16.83		

[a] Values in parentheses were determined at 298 K, estimated error limit ±10%. [b] KBr pressed pellets. [c] Ether-isopentane-ethanol (5:5:2). [d] A low-energy excitation maximum could not be observed due to the diluteness of the sample.

vibrational progression of 1430 cm^{-1} and two or more lower energy progressions. The larger spacing corresponds most closely to the localized C=C stretch of the mnt ligand which occurs at 1489 cm^{-1} in the IR spectrum. Excited state vibrational progressions are observed in the excitation spectrum with spacings of 1245 and 480 cm^{-1}. Most of the Ir and Rh compounds have excitation spectra similar to Figure 4 with nearly identical vibrational spacings and have emission spectra in which the major vibrational progression is typically 1400 cm^{-1}. In IR spectra of the Rh and Ir compounds, counterion absorptions obscure bands due to the metal–mnt group below 1500 cm^{-1}. Therefore, K[Ir(CO)$_2$(mnt)] was prepared and found to exhibit a C=C stretch at 1476 cm^{-1}. The next lower vibration occurs at 1165 cm^{-1}. For Pt(P(OEt)$_3$)$_2$(mnt) the observed Stokes shift between the highest energy emission and lowest energy excitation is only 180 cm^{-1}. While the observed Stokes shifts depend in part on spectral

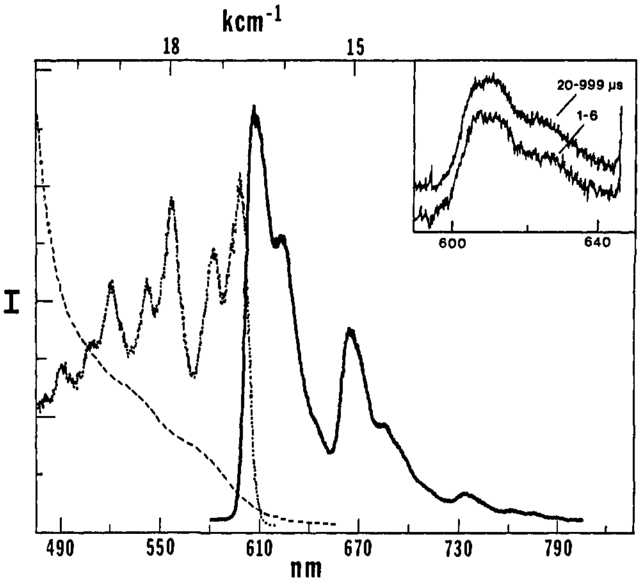


Figure 3. Emission (–, solid state, 77 K), excitation (···, solid state, 77 K), and absorption (--, CH_3CN solution, 298 K) spectra of PPN[Ir(CO)(PPh_3)(mnt)]. The inset shows emission spectra at different time intervals following pulsed-laser excitation.

resolution, they are found to be less than 400 cm^{-1} in many cases.

Additional information for the determination of the emitting state in these complexes was obtained by examining samples of TBA[Ir$(CO)_2Br_2$] and Na_2(mnt) for possible emission. Neither was found to emit observably at 77 K.

Emission Lifetimes. The emissions exhibit single exponential decay upon low-intensity pulsed laser excitation. Many samples exhibited nonexponential decay behavior when excited with the N_2 laser at full power, (5 μJ, 0.5 ns). The emissions could be analyzed as either mixed first- and second-order or two first-order decays. When the laser intensity was reduced by a factor of 10, all samples showed good first-order decay behavior. This suggests that at high intensities annihilation processes (bimolecular deactivation of two excited species) can compete with unimolecular decay for many of these complexes. Lifetimes for the Rh complexes are several times longer than those for the corresponding Ir compounds (Table II). Lowering the temperature from 298 to 77 K typically leads to a 3-fold increase in lifetime.

Discussion

The most distinctive physical property of the complexes reported here is their luminescence in the solid state and in rigid glasses. For the iridium complexes I, the platinum complexes III, and the TBA salt of the rhodium system IIb, the solid-state luminescence is readily seen at room temperature, while for the other rhodium complexes, luminescence is observed upon cooling.

Assignment of the Emitting State. Particularly notable in the 77 K emission and excitation spectra of the complexes reported here is the rich vibrational structure which is observed (see, for example, Figures 2–4). The similarity of these spectra, including the vibrational structure for the different mnt compounds, indicates that these complexes possess a common emitting state. For all of these complexes, the emission and excitation spectra mirror each other, indicating that they correspond to the same electronic transition in emission and excitation. Moreover, the same electronic transition is observed in the solution absorption spectra of the Ir and Pt complexes as the weakly allowed, lowest energy absorption maxima (see Tables I and II).[20] The analogous low-energy transitions are not observed in absorption spectra of the Rh compounds, although they are seen in the 77 K excitation spectra. The observation of luminescence from dilute rigid glass solutions indicates that the emission is of molecular origin and not a result of dimeric structure, aggregation or stacking as seen for other planar d^8 complexes.[21]

The structure in the emission and excitation spectra of the mnt complexes is attributable to vibrations associated with the metal–mnt moiety, which is the single common structural unit possessed by these complexes. We assign the most pronounced vibrational progression to $\nu_{C=C}$ of the mnt ligand. On the basis of this result, a d–d assignment for the emitting state is highly unlikely. Therefore, in developing an assignment for the emitting state in these complexes we consider as the logical possibilities (1) a mnt intraligand (IL) π–π^* state, (2) a metal-to-ligand charge transfer (MLCT) state involving mnt, and (3) a ligand-to-metal charge transfer (LMCT) state involving mnt.

An analysis of the data in Tables I and II shows that as the net electron-donor ability of the ligand set L and L′ increases, the highest energy emission and lowest energy excitation and absorption maxima all decrease in energy. This is most clearly indicated for derivatives Ia, Id, and Ic, which have their first emission maxima at 18.06, 16.52, and 14.71 × 10^3 cm^{-1}, their first excitation maxima at 18.36, 16.91, and 16.69 × 10^3 cm^{-1}, and their absorption maxima at 18.48, 17.24, and 16.72 × 10^3 cm^{-1}. Similar trends are evident for the Rh and Pt compounds. The net electron-donor ability of the ligands L and L′ is reflected by ν_{CO} in the IR spectra for the CO-containing compounds.

Another general trend is the metal dependence of Rh ~ Ir < Pt for the energy of the absorption–emission system. For example, the complexes TBA[Rh$(P(OPh)_3)_2$(mnt)], TBA[Ir$(P(OPh)_3)_2$(mnt)], and Pt$(P(OPh)_3)_2$(mnt) have lowest energy excitation maxima at 16.84, 17.18, and 18.45 × 10^3 cm^{-1}, respectively, and emission onsets (where emission intensity is 10% of maximum) at 16.91, 17.22, and 17.61 × 10^3 cm^{-1}, respectively. These effects of metal and ligand L on the absorption–emission energy argue convincingly for a MLCT assignment involving π^*(mnt) for the absorption–emission system.[22]

Other facts and observations lend additional weight to the d→π^*(mnt) assignment. The small Stokes shifts (<400 cm^{-1} in many cases) indicate that the emitting state is essentially undistorted from the planar ground-state geometry. This result along with the vibrational structure associated with the mnt ligand allows us to rule out a d–d assignment for the absorption–emission transition since we expect d–d or ligand field states of planar d^8 complexes to be quite distorted from the ground-state geometry.[23] Moreover, the complex $[Ir(CO)_2Br_2]^-$, which should have d–d and d–π^*(CO) states similar to those of $[Ir(CO)_2(mnt)]^-$, shows no detectable emission at 77 K, providing additional corroboration for our conclusion. The free ligand Na_2(mnt) also does not emit observably at 77 K whereas IL π–π^* emissions are usually observed for free as well as complexed ligand. This result rules against the IL π–π^* possibility for the emitting state in these complexes.

The MLCT assignment which we propose here for the lowest energy electronic transition is in accord with that reported pre-

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[20] An exception to this behavior is observed for $[Pt(mnt)_2]^{2-}$ which exhibits a lowest energy absorption band at 14.41 × 10^3 cm^{-1} and a lowest energy excitation maximum at 16.83 × 10^3 cm^{-1}. This difference is not unexpected since the absorption band has been assigned to a d–d transition.[25a,b]

[21] Emission from concentrated acetonitrile solutions of $[Rh(tol)_4]PF_6$ (tol = *p*-methylphenyl isocyanide) has been attributed to a metal-localized transition in the dimer $[Rh_2(tol)_8]^{2+}$. See: Miskowski, V. M.; Nobinger, G. L.; Kliger, D. S.; Hammond, G. S.; Lewis, N. S.; Mann, K. R.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 485–488. Similar emissions have recently been reported for other d^8 face-to-face dimers. Fordyce, W. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 985–988. Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *Ibid.* **1981**, *103*, 7061–7064. Che, C.-M.; Butler, L. G.; Gray, H. B. *Ibid.* **1981**, *103*, 7796–7797 and references therein.

[22] The trend of absorption–emission energy with ligand is rationalized in the following way. The energy of the metal d orbitals is influenced by the π-acceptor and σ-donor ability of L and L′ in a way such that the greater the overall electron-donor ability of the ligands, the more electron rich the metal is, and hence, the higher in energy the essentially nonbonding and weakly antibonding metal d orbitals are. If the energy of the π^*(mnt) orbital is assumed to remain essentially fixed for all L, then it follows that emission from a d→π^*(mnt) state should decrease in energy as ligand-donor ability increases.

[23] The Stokes shift for $PtCl_4^{2-}$, which exhibits d–d emission, is ~4500 cm^{-1} (Tuszynski, W.; Gleimann, G. *Z. Naturforch. A* **1979**, *34*, 211–219). Since a ligand field transition will promote an electron from a d orbital predominantly pointing away from the ligands to an orbital directed toward the ligands ($d_{x^2-y^2}$), a significant excited-state distortion would be expected.

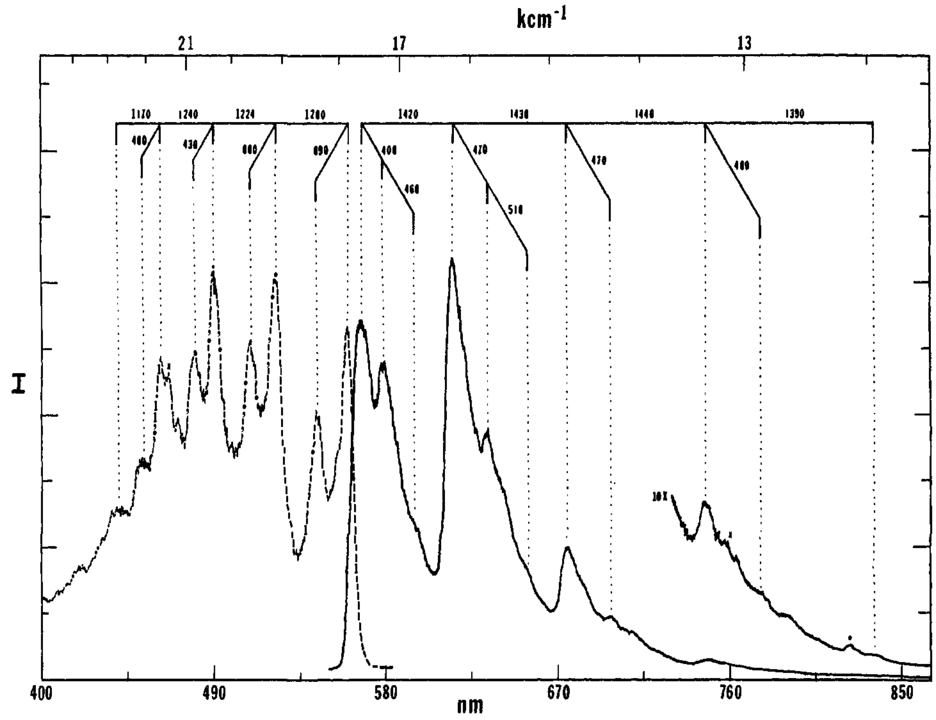

Figure 4. Emission and excitation spectra of $Pt(P(OEt)_3)_2(mnt)$ in the solid state at 77 K. The spurious peaks marked "X" are due to variations in source intensity or detector response.

viously for planar Ir(I) and Rh(I) compounds containing π-acceptor ligands.[24] In the present series of compounds the π acceptor corresponds to a π^* function of the mnt ligand which is known to have a delocalized π orbital system.[25]

Vibrational Structure. The regular spacings between peaks in emission and excitation spectra (see Figures 2–4) indicate that the structure can be interpreted in terms of vibrational progressions in the ground and excited states. Since the resolved vibrational spacings (~1250 and 480 cm^{-1} in excitation spectra and ~1400 cm^{-1} in emission spectra) are essentially independent of the ligands L and L′, the vibrations responsible, as well as the electronic transition itself, must be metal–mnt localized. Vibrations due to the metal–mnt group are known from the IR spectrum of $K[Ir(CO)_2(mnt)]$ and from the reported IR and Raman vibrational analyses of the complexes $[M(mnt)_2]^{2-}$, M = Ni, Pd, and Pt.[25b,c] Spectra of the four complexes are extremely similar in the region 500–2500 cm^{-1} so the assignments of Schlapfer and Nakamoto[25c] for $[Ni(mnt)_2]^{2-}$ should be appropriate for the emitting compounds. The localized mnt C=C stretch occurs at ~1480 cm^{-1} and the nearest-neighboring vibration appears at ~1160 cm^{-1} (assigned to coupled C–C and C–S modes). Therefore, we assign the ~1400-cm^{-1} progression in the emission spectra to the mnt C=C stretch. The progression of ~1250 cm^{-1} in the excitation spectra logically corresponds to the mnt C=C stretch in the π^*(mnt) excited state which is C=C antibonding. Although the mnt C=C bond order is reduced in the excited state, the small observed Stokes shifts indicate that the emitting state is essentially undistorted from the planar ground-state geometry.

Some precedent exists for vibrational structure in electronic transitions of mnt compounds. The complexes $[M(mnt)_2]^{2-}$, M = Ni, Pd, and Pt, exhibit structured MLCT absorption bands which have been assigned to vibronic transitions involving $\nu(C{\equiv}N)$ fundamentals in the excited-state complex.[25b] Progressions in mnt C=C were observed in the range 1400–1440 cm^{-1}. Our excited-state mnt C=C progressions (from excitation spectra) are lower in energy and are observed at ~1250 cm^{-1}. Part of this difference can be attributed to the fact that the π^*(mnt) excited state in the bis(mnt) complexes $[M(mnt)_2]^{2-}$ is delocalized over two mnt ligands and that bonding changes in the dithiolate chelate ring upon one-electron excitation will be consequently smaller.

Spin Character and Further Comments on the Emitting State. Although spin selection rules may be considerably relaxed due to spin–orbit coupling in these second and third row transition-metal compounds,[26] evidence exists for substantial spin-forbidden character in the emission–absorption system. Emission lifetimes are quite long, ranging from 8 to 400 μs at 77 K. The lifetimes are several times longer for Rh than Ir as expected for a spin-forbidden transition on the basis of their relative spin–orbit coupling constants.[27] Also, the lowest energy absorption bands for the Ir and Pt complexes have extremely small extinction coefficients (ϵ ~2–30) for an electronically allowed MLCT transition. These results indicate considerable spin-forbidden character for the emission–absorption system which we thus assign as ^{3}(d–π^*(mnt)).[28]

Some interesting spectroscopic comparisons can be made between the mnt compounds and other planar d^8 metal complexes which exhibit spin-forbidden charge-transfer emission. First, the extinction coefficients we observe for the lowest energy absorption bands in room temperature spectra are small (ϵ ~2–30) compared to values reported for $[Ir(dppe)_2]Cl$ (ϵ 800)[8] and $[Ir(ethylenediamine)(COD)]ClO_4$ (ϵ 200).[11a] Another distinct feature of the mnt compounds is the large separation between corresponding singlet and triplet absorption bands. For the Ir and Rh mnt complexes, the first intense absorption band (ϵ ~5000) is logically singlet MLCT. The singlet–triplet splitting for Ir mnt compounds is then 6000–9000 cm^{-1}. Considerably smaller singlet–triplet splittings have been reported for $[Ir(dppe)_2]Cl$ (3500 cm^{-1})[8] and $[Ir(ethylenediamine)(COD)]ClO_4$ (3200 cm^{-1}).[11a] At present we are unable to explain satisfactorily the large singlet–triplet splittings and the low extinction coefficients for the triplet MLCT

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[28] This notation, ^{3}(d–π^*(mnt)), denotes the triplet state arising out of the d–π^*(mnt) excited configuration. Because of the low symmetry of the complexes, group theoretical notation is not informative here.

absorptions which we observe for the mnt compounds.[29]

Multiple-state emissions from spin–orbit split excited states have been found for most of the previously reported luminescent Ir(I) and Rh(I) complexes.[11,30] The key experimental evidence cited for multiple-state emission was often the temperature dependence of emission lifetimes below 77 K. For many of the compounds no significant spectral changes were observed. We note that the 12 and 77 K emission spectra of complex Ib are essentially superimposable. All of our data can be interpreted in terms of a single emitting electronic state; however, the possibility of multiple-state emission still exists in a situation where either only one state is responsible for the bulk of the observed emission or the emitting excited states (which must be in thermal equilibrium) have nearly identical emission spectra. Further studies of the temperature dependence of emission lifetimes seems to be in order for these systems.

Finally, environmental rigidity appears to be required to observe luminescence from the Rh, Ir, and Pt mnt compounds. This is a general result for planar d^8 complexes and a solvent relaxation study has been reported.[31] We have also noticed a counterion effect on emission intensity. At room temperature, the TBA$^+$ salts of the Ir complexes display brighter luminescence than the PPN$^+$ salts. An extreme example of this effect is found in complex IIb, which as the TBA$^+$ salt exhibits bright luminescence at room temperature whereas no luminescence could be detected for the PPN$^+$ salt. The origin of this curious effect is unknown, but it may relate to the structural rigidity of the lattices in the TBA$^+$ and PPN$^+$ salts. This observation is under continuing study.

Conclusion

We have discovered a new series of luminescent d^8 complexes which have highly structured emission and excitation spectra. With the mnt compounds reported here, we have greatly extended the number and variety of d^8 complexes exhibiting emission, and have developed a class of compounds ideally suited to detailed spectroscopic study. The luminescing excited state is essentially undistorted from the planar ground-state geometry and is assigned to be ^{3}(d–π^*(mnt)). The vibrational structure is attributed to progressions in the mnt C=C vibration and other vibrations associated with the metal–mnt moiety. While the mnt complexes do not luminesce in fluid solution, studies to develop the photochemistry of these systems are continuing.

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Registry No. IaTBA, 84623-79-0; IaPPN, 84623-80-3; IaK, 84623-81-4; IbPPN, 84642-22-8; IbTBA, 84623-91-6; IcTBA, 84623-85-8; IcPPN, 84642-23-9; IdPPN, 84623-83-6; IdTBA, 84623-89-2; Ie(PPN)$_2$, 84642-25-1; IIaTBA, 30845-95-5; IIaPPN, 84642-26-2; IIbTBA, 29985-53-3; IIbPPN, 84642-28-4; IIdAsPh$_4$, 63159-12-6; IIdTBA, 29985-52-2; IIdPPN, 84642-27-3; IIIb, 84623-88-1; IIIf, 80316-84-3; IIIg, 84623-87-0; IIIh, 84623-86-9; [Pt(PPh$_3$)$_2$(mnt)], 62637-80-3; (TBA)$_2$[Pt(Mnt)$_2$], 42401-87-6; TBA[Ir(CO)$_2$Br$_2$], 73190-78-0; Pt(dppm)Cl$_2$, 52595-94-5; Pt(COD)Cl$_2$, 12080-32-9.

Supplementary Material Available: Complete listing of electronic emission and low-energy excitation maxima (2 pages). Ordering information is given on any current masthead page.

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[29] One possibility is that the highest occupied molecular orbital (formally assigned as a metal d orbital) has considerable ligand π character. This would lead to lower extinction coefficients (due to the reduced effect of spin–orbit coupling) and larger singlet–triplet splittings (due to increased electron correlation).

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Vibrational Spectroscopy of the Electrode–Solution Interphase. 2. Use of Fourier Transform Spectroscopy for Recording Infrared Spectra of Radical Ion Intermediates

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Abstract: High-quality infrared spectra of the radical ions of benzophenone, anthracene, and tetracyanoethylene were recorded during electrolysis of the substrates at a platinum electrode by using a specular reflection apparatus and a Fourier transform infrared spectrometer. Evidence of adsorption of benzophenone was indicated, whereas simple ion spectra were observed for anthracene and tetracycloethylene. Versatility of the technique is discussed.

The investigation of heterogeneous and homogeneous electrode processes by infrared coupled spectroelectrochemical techniques has been reported. Thus work on the electrosorption of methanol on platinum electrodes[1] and adsorbed hydrogen on platinum[2,3] and studies of the platinum–acetonitrile interface,[4] adsorption of acrylonitrile,[5] and changes in the water structure at metal electrodes[3,6] have been completed.

The use of Fourier transform infrared spectrometers has proven to be a convenient rapid method for obtaining infrared spectral differences between two polarization potentials at an electrode interface.[4] We report here the ease with which the vibrational spectra of free-radical ions may be observed by using this technique. Traditionally, it has been rather difficult to obtain free-

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