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Electronic Absorption and Magnetic Circular Dichroism Spectra of Some Planar Platinum(II), Palladium(II), and Nickel(II) Complexes with Phosphorus-Donor Ligands

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Solution absorption and 7 T magnetic circular dichroism (MCD) spectra are reported for $[M(DEPE)_2]X_2$ (M = Pt(II), Pd(II), or Ni(II); DEPE = 1,2-bis(diethylphosphino)ethane; X = PF_6^- or ClO_4^-), $[Pt(P(OEt)_3)_4](ClO_4)_2$, $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$ (R = Me or Et), and *trans*-$[M(PR_3)_2(CN)_2]$ (M = Pt(II) or Pd(II), R = *n*-Bu; M = Ni(II), R = Et). Each complex exhibits several intense bands in the UV, which are assigned to metal-to-ligand charge transfer (MLCT). Detailed band assignments are given in terms of a model that includes spin-orbit coupling in excited MLCT states, and the interpretation of the observed MCD terms is discussed. Finally the metal $(n + 1)p_z$ and ligand contributions to the lowest energy empty orbitals are discussed.

Introduction

The intense electronic spectra in the vis-UV region exhibited by many square-planar complexes of nd^8 metal ions that contain π-acceptor ligands have been assigned as metal-to-ligand charge transfer (MLCT).[1-10] The electronic transitions responsible for these intense spectra are visualized as excitations from the highest filled orbitals of the complex, which are predominantly metal-localized nd orbitals, to a low-energy ligand-based orbital of π symmetry (a_{2u} in D_{4h}). The ligand orbital for unsaturated acceptor ligands such as CO, CN^-, CNR, and olefins is constructed from empty ligand π^* MO's, while for saturated donor ligands such as PR_3, $P(OR)_3$, AsR_3, etc. the ligand orbital involves an empty nd orbital of suitable symmetry on the donor atoms. However, in all π-acceptor complexes the metal $(n + 1)p_z$ orbital (z axis taken normal to the molecular plane) has the same symmetry as the ligand-based π orbital and therefore the π orbital is assumed to contain some admixture of the metal $(n + 1)p_z$; i.e. $\psi_\pi = \phi_{\mathrm{Lig}} + \lambda[(n + 1)p_z]$, where λ = mixing coefficient. A recent investigation[6] of absorption and emission spectra of several Rh(I) and Ir(I) complexes containing P- or As-donor ligands suggests that the metal $(n + 1)p_z$ character in excited "MLCT" configurations may be considerable.

In order to further the understanding of the MLCT process, to better characterize the role of the $(n + 1)p_z$ metal orbital in excited configurations, and to provide a general spectroscopic basis for electronic structure, we have undertaken a systematic examination of the spectra of a variety of π-acceptor ligands in complexes of nd^8 metal ions.[7-10] We report here the spectra of several P donor complexes of Pt(II), Pd(II), and Ni(II). Although there have been a number of studies involving P-donor complexes of Rh(I) and Ir(I),[1,2,5,8,9] there have been comparatively few dealing with the M(II) metal ions. For example, an investigation of *cis*- and *trans*-$[Pt(PEt_3)_2(X)(Y)]$, X, Y = H^-, halide, Me^-, or Et^-, was reported recently,[10] which showed clearly a rich pattern of MLCT spectra at energies above 3.0 μm^{-1}. The MLCT spectra blue shift into the UV as the metal oxidation state is raised and the occupied metal orbitals become more stable. Therefore, compared to the visible and near-UV transitions in Rh(I) and Ir(I) complexes, the transitions of the M(II) complexes are often obscured in the UV by strongly absorbing aryl groups, which are common for many P-donor ligands. This is perhaps one of the reasons for few previous studies of M(II) complexes of P-donor ligands. Thus P ligands that are transparent in the UV are necessary for the study of MLCT in the M(II) metal ions. We report here some solution absorption and magnetic circular dichroism (MCD) spectra for $[M(DEPE)_2]X_2$ (M = Pt(II), Pd(II), or Ni(II); DEPE = 1,2-bis(diethylphosphino)ethane; X = PF_6^- or ClO_4^-), $[Pt(P(OEt)_3)_4](ClO_4)_2$, $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$ (R = Me or Et), and *trans*-$[M(PR_3)_2(CN)_2]$ (M = Pt(II) or Pd(II), R = *n*-Bu; M = Ni(II), R = Et). All of the P ligands are transparent in the UV, and in the case of the cyanophosphine complexes the CN^- ligand is also free of strong absorption in the UV.

Experimental Section

Preparation of Compounds. The compounds $[M(DEPE)_2]X_2$ (M = Pt(II) and Pd(II); X = PF_6^- and ClO_4^-) were prepared by treating an aqueous solution of K_2MCl_4 with DEPE (STREM Chemicals, Inc.) under a nitrogen atmosphere. A pink precipitate of $[M(DEPE)_2][MCl_4]$ was formed, which could be dissolved by adding excess ligand. The ClO_4^- or PF_6^- salts were precipitated by adding a saturated aqueous solution of NH_4ClO_4 or NH_4PF_6 to the aqueous solution of the complex. The $[Ni(DEPE)_2]X_2$ salts were prepared by treating an aqueous solution of $NiCl_2 \cdot 6H_2O$ with a stoichiometric amount of the ligand under nitrogen. After some insoluble material was separated, the solution was treated with a saturated aqueous solution of NH_4ClO_4 or NH_4PF_6. The *trans*-$[M(P(n\text{-}Bu)_3)_2(CN)_2]$ (M = Pt(II) and Pd(II)) complexes were prepared by treating methanol solutions of *trans*-$[M(P(n\text{-}Bu)_3)_2Cl_2]$[11,12] with stoichiometric amounts of KCN. In each case KCl was removed by filtration and the remaining solution evaporated under a stream of dry nitrogen. The solids were further purified by extraction into anhydrous ether followed by filtration of the ether solutions. After evaporation of the ether solutions to dryness the solids were recrystallized from hot ethanol. The *trans*-$[Ni(PEt_3)_2(CN)_2]$ complex was prepared from *trans*-$[Ni(PEt_3)_2Cl_2]$ by a published procedure.[13] The cyanophosphine complexes each gave a single sharp ν_{CN}: *trans*-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$, 2120 cm^{-1}; *trans*-$[Pd(P(n\text{-}Bu)_3)_2(CN)_2]$, 2133 cm^{-1}; *trans*-$[Ni(PEt_3)_2(CN)_2]$, 2103 cm^{-1}. The preparation and characterization of the Pt(II) phosphite complexes, $[Pt(P(OEt)_3)_4](ClO_4)_2$ and $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$ (R = Me and Et) are described elsewhere.[14]

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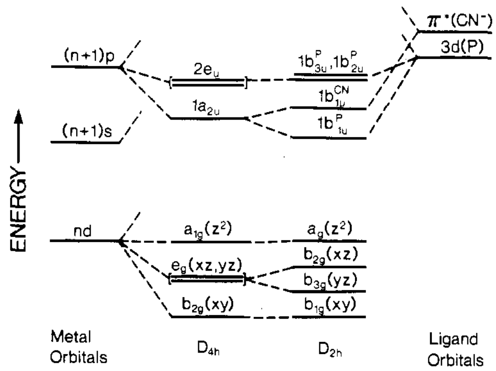

Figure 1. Simplified MO level scheme showing spectroscopically important levels only.

All of the complexes gave satisfactory elemental analyses.

Spectral Measurements. Electronic absorption spectra were obtained with a Cary 1501 spectrophotometer. Simultaneous MCD and absorption spectra measured along the same light path were obtained with a computer-controlled spectrometer built at Northern Illinois University.[15] All MCD spectra were obtained at 7 T with use of a superconducting magnet system (Oxford Instruments SM2-7, fitted with a room-temperature bore). Spectral grade solvents were used throughout.

Molecular Orbitals and Excited States

The complexes studied here are all presumed to be planar, though X-ray structural proof is available only for the $[Pt(P(OH)(OR)_2)_2(P(O)(OR)_2)_2]$ complexes.[14] The single sharp C–N stretching band observed in the IR, together with the method of synthesis from trans starting complexes, is consistent with a trans geometry for the $[M(PR_3)_2(CN)_2]$ complexes. The core symmetry about the metal ion for the $M(DEPE)_2^{2+}$ ions and the Pt(II) phosphite complexes, each of which contain four P donors, is taken to be D_{4h}, while the symmetry of *trans*-$[M(PR_3)_2(CN)_2]$ is D_{2h}. Figure 1 shows the spectroscopically important MO levels for both types of complex (the z axis is taken normal to the molecular plane in both cases, and the CN^- ligands lie along the x axis in the D_{2h} complexes). In keeping with studies of other planar π-acceptor-containing complexes[1-10] the highest energy occupied MO (HOMO) is assumed to be the metal nd_{z^2} orbital (a_{1g} in D_{4h} or a_g in D_{2h}). The complexes thus have diamagnetic, totally symmetric ground states designated $^1A_{1g}$ in D_{4h} or ^1A_g in D_{2h}. The lowest energy unoccupied MO (LUMO) is $1a_{2u}$ in D_{4h} and consists of a linear combination of 3d orbitals of the P ligands and the metal $(n + 1)p_z$ orbital. The LUMO's for the cyanophosphine complexes consist of $1b_{1u}{}^P$ and $1b_{1u}{}^{CN}$, the former consisting of 3d orbitals of the P ligands and the latter consisting of π* orbitals of CN^-, with both having some admixture of metal $(n + 1)p_z$.

The lowest energy excited MLCT configurations and their associated excited states are collected in Table I. Since metal spin–orbit coupling varies as Pt(II), $\zeta_{5d} \simeq 0.35\ \mu m^{-1}$, Pd(II), $\zeta_{4d} \simeq 0.15\ \mu m^{-1}$, and Ni(II), $\zeta_{3d} \simeq 0.07\ \mu m^{-1}$,[16] spin–orbit interaction is expected to be important in the excited states of Pt(II) and, to a lesser extent, Pd(II). Table I therefore includes not only the excited singlet and triplet zero-order states but also the symmetries of the spin–orbit states (characterized by lack of spin multiplicity superscripts). For D_{4h} symmetry only transitions to $E_u(x, y$ polarized) and $A_{2u}(z$ polarized) states are allowed for electric dipole transitions. For D_{2h} symmetry the allowed states are $B_{1u}(z$ polarized), $B_{2u}(y$ polarized), and $B_{3u}(x$ polarized). However, strong spin–orbit interaction will permit formally triplet states to gain considerable singlet character, so transitions to these states can have substantial intensity.

Table I. Excited MLCT Configurations and States

config[a]	no spin–orbit coupling	spin–orbit states[b]
	D_{4h} Symmetry	
$(a_{1g})(1a_{2u})$	$^1A_{2u}$	$1A_{2u}$
	$^3A_{2u}$	$1E_u(1A_{1u})$
$(e_g)^3(1a_{2u})$	^1E_u	$2E_u$
	^3E_u	$3E_u,2A_{2u}(2A_{1u},1B_{1u},1B_{2u})$
$(b_{2g})(1a_{2u})$	$^1B_{1u}$	$(2B_{1u})$
	$^3B_{1u}$	$4E_u(2B_{2u})$
	D_{2h} Symmetry	
$(a_g)(1b_{1u}{}^P)$	$^1B_{1u}{}^P$	$1B_{1u}{}^P$
	$^3B_{1u}{}^P$	$1B_{2u}{}^P,1B_{3u}{}^P(1A_u{}^P)$
$(a_g)(1b_{1u}{}^{CN})$	$^1B_{1u}{}^{CN}$	$1B_{1u}{}^{CN}$
	$^3B_{1u}{}^{CN}$	$1B_{2u}{}^{CN},1B_{3u}{}^{CN}(1A_u{}^{CN})$
$(b_{2g})(1b_{1u}{}^P)$	$^1B_{3u}{}^P$	$2B_{3u}{}^P$
	$^3B_{3u}{}^P$	$2B_{2u}{}^P,2B_{1u}{}^P(2A_u{}^P)$
$(b_{3g})(1b_{1u}{}^P)$	$^1B_{2u}{}^P$	$3B_{2u}{}^P$
	$^3B_{2u}{}^P$	$3B_{1u}{}^P,3B_{3u}{}^P(3A_u{}^P)$
$(b_{2g})(1b_{1u}{}^{CN})$	$^1B_{3u}{}^{CN}$	$2B_{3u}{}^{CN}$
	$^3B_{3u}{}^{CN}$	$2B_{2u}{}^{CN},2B_{1u}{}^{CN}(2A_u{}^{CN})$
$(b_{3g})(1b_{1u}{}^{CN})$	$^1B_{2u}{}^{CN}$	$3B_{2u}{}^{CN}$
	$^3B_{2u}{}^{CN}$	$3B_{1u}{}^{CN},3B_{3u}{}^{CN}(3A_u{}^{CN})$
$(b_{1g})(1b_{1u}{}^P)$	$^1A_u{}^P$	$(4A_u{}^P)$
	$^3A_u{}^P$	$4B_{1u}{}^P,4B_{2u}{}^P,4B_{3u}{}^P$
$(b_{1g})(1b_{1u}{}^{CN})$	$^1A_u{}^{CN}$	$(4A_u{}^{CN})$
	$^3A_u{}^{CN}$	$4B_{1u}{}^{CN},4B_{2u}{}^{CN},4B_{3u}{}^{CN}$

[a] Filled orbitals omitted. [b] Forbidden states in parentheses.

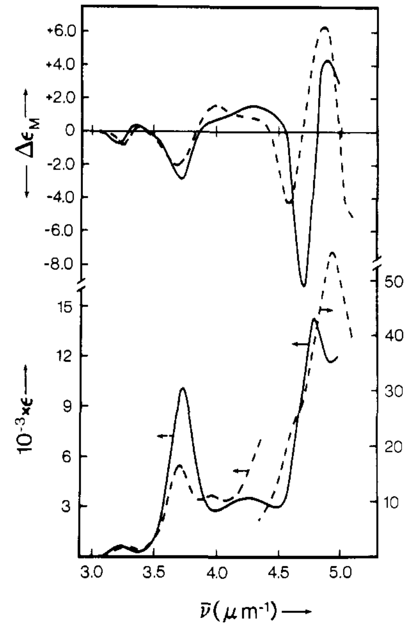

Figure 2. Absorption (lower curves) and MCD (upper curves) spectra for $[Pt(P(OEt)_3)_4](ClO_4)_2$ (—) and $[Pt(DEPE)_2](ClO_4)_2$ (- - -) in acetonitrile.

Results and Discussion

Absorption and MCD spectra were determined for acetonitrile solutions at room temperature. Figures 2–5 present typical spectra, and detailed spectral data are collected in Table II. In each case, except for $Ni(DEPE)_2^{2+}$, and possibly $Pd(DEPE)_2^{2+}$, Beer's law was obeyed within experimental error (≤5%) and the solutions were found to be stable over a period of days. The deviations from Beer's law for $Ni(DEPE)_2^{2+}$ were considerable, and spectra obtained in acetonitrile and dichloromethane solutions were different. Beer's law was followed in dichloromethane, but when a dichloromethane solution of $Ni(DEPE)_2^{2+}$ was titrated with acetonitrile, the spectrum changed systematically with increasing acetonitrile

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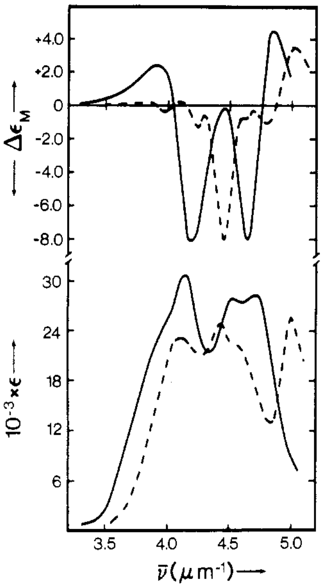

Figure 3. Absorption (lower curves) and MCD (upper curves) spectra for $[Pd(DEPE)_2][PF_6]_2$ (—) and *trans*-$[Pd(P(n\text{-}Bu)_3)_2(CN)_2]$ (---) in acetonitrile.

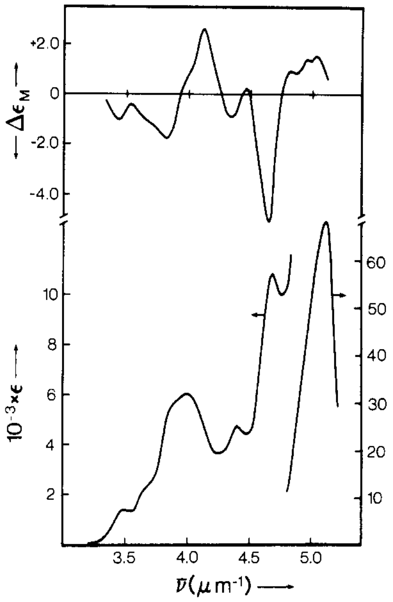

Figure 4. Absorption (lower curves) and MCD (upper curve) spectra for *trans*-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$ in acetonitrile.

concentration and exhibited isosbestic points at 2.85 and 3.25 μm^{-1}. When the solvent composition was ca. 20% acetonitrile, the spectrum appeared the same as in pure acetonitrile. Finally, when a titrated solution was evaporated to dryness and the solids were redissolved in dichloromethane, the spectrum was the same as before titration. These observations are consistent with a reversible reaction of $Ni(DEPE)_2^{2+}$ with acetonitrile (eq 1). The structure of the product complex is

$$Ni(DEPE)_2^{2+} + CH_3CN \rightleftharpoons Ni(DEPE)_2(CH_3CN)^{2+} \quad (1)$$

not known, but it may be a five-coordinate complex, since trigonal-bipyramidal five-coordination is known for Ni(II) complexes containing phosphine ligands.[17,18] The departure of $Pd(DEPE)_2^{2+}$ from Beer's law was observed to be much smaller. The spectral band shape was unchanged, but absorptivities decreased 10–12% as concentrations were reduced from 2.8×10^{-4} to 1.4×10^{-5} M. In contrast, the changes in absorptivities as a function of concentration for $Pt(DEPE)_2^{2+}$ were <2–5%. The origin of the changes for $Pd(DEPE)_2^{2+}$ is not known but is likely very different from that of the large changes observed for $Ni(DEPE)_2^{2+}$. The small changes for the Pd(II) complex may be due to a concentration-dependent ion-pair formation between $Pd(DEPE)_2^{2+}$ and the counterion, which could affect the absorptivities of the complex slightly.

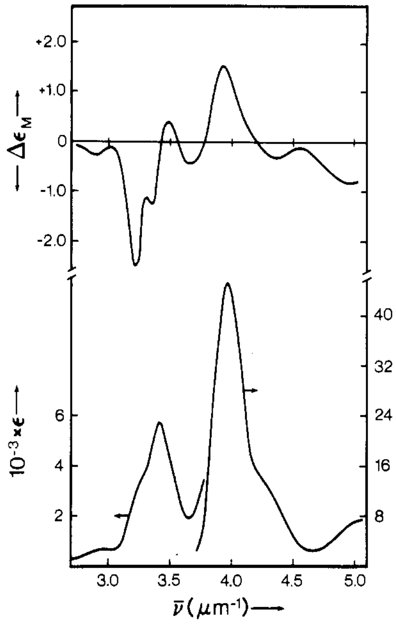

Figure 5. Absorption (lower curves) and MCD (upper curve) spectra for *trans*-$[Ni(PEt_3)_2(CN)_2]$ in acetonitrile.

Spectral Assignments. MP_4 Complexes. Figure 2 and the data of Table II show that the pattern among the absorption and the MCD spectra for the Pt(II) complexes that contain four P-donor ligands are quite similar. Further, these patterns are remarkably similar to those observed for the $Pt(CN)_4^{2-}$ ion,[7a] *cis*-$[Pt(PEt_3)_2(CH_3)_2]$[10] (the CH_3 ligands are σ-donor ligands and are transparent in the UV), and the $Pt(CNR)_4^{2+}$ ion[7b] and thus appears to be quite characteristic of MLCT for Pt(II). The spectral assignments therefore can be easily made by use of the model used to interpret the absorption and MCD spectra of $Pt(CN)_4^{2-}$.[7a,19] This model includes spin–orbit coupling in the excited states derived from the configurations involving the $1a_{2u}$ orbital. These assignments are included in Table II; the notation there indicates the symmetry of the spin–orbit excited state, together with the zero-order state from which the state is derived in parentheses. The lowest energy band, band I, in each case is assigned to $A_{1g} \rightarrow 1E_u(^3A_{2u})$, and it has associated with it a positive *A* term[20] in the MCD, which is predicted by the MLCT model. Band II is assigned as $A_{1g} \rightarrow 1A_{2u}(^1A_{2u})$ and displays a prominent negative *B* term[20] again consistent with prediction.[8] Band IV, which is resolved in the absorption spectrum for $Pt(P(OEt)_3)_4^{2+}$ at 4.78 μm^{-1} but appears as a shoulder on the more intense band V for the other complexes, exhibits a strong positive *A* term as predicted[7a,19] by the MLCT model for an assignment $A_{1g} \rightarrow 2E_u(^1E_u)$. On the basis of its lower energy and intensity compared to those of band IV, band III is assigned to tran-

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[20] For a review of MCD spectroscopy and the conventions used here see: Stephens, P. J. *Adv. Chem. Phys.* **1976**, *35*, 197. In particular the *sign* of the *B* terms as used here refers to the *sign* of the observed $\Delta\epsilon_M$ and implies the same sign for the B_0 parameter which would be derived from a moment analysis of the spectral band.

sitions to the spin–orbit states of ^3E_u. The broadness of band III for $Pt(P(OEt)_3)_4^{2+}$ (see Figure 2) likely signals a slightly larger separation of the $3E_u(^3E_u)$ and $2A_{2u}(^3E_u)$ states; the $2A_{2u}(^3E_u)$ state is predicted from spin–orbit calculations[7a,8,19] to be at higher energy than $3E_u(^3E_u)$. Although the MLCT model predicts a weak positive *A* term and a weak positive *B* term for the transitions to $^3E_u(^3E_u)$ and $2A_{2u}(^3E_u)$, respectively,[7a,8,19] the observed MCD for band III is not well enough resolved to show these individual terms, probably because of their expected small magnitude. Finally at high energy an intense band, band V, is observed for each complex except $Pt(P(OEt)_3)_4^{2+}$, where only a rising absorbance is seen. This band cannot be accommodated by the excited configurations involving $1a_{2u}$ and has no counterpart in the $Pt(CN)_4^{2-}$ spectrum below 5.2 μm^{-1}. The MCD in the region of this intense band is quite weak and not very informative. An assignment to an excited state involving the next higher energy ligand-based MO, $2e_u$, seems plausible. The lowest energy configuration would be $(a_{1g})(2e_u)$, giving rise to spin–orbit states derived from the ^1E_u and ^3E_u zero-order states. In view of the band intensity the assignment $A_{1g} \rightarrow E_u[^1E_u,(a_{1g})(2e_u)]$ is reasonable. This E_u state is expected to exhibit an *A* term, but its magnitude will be determined by several two-centered integrals of the form $\langle 2e_u x|l_z|2e_u y\rangle$, where the $2e_u x$ and $2e_u y$ orbitals involve primarily 3d orbitals on different P ligands. Such two-center integrals are expected to be small, and thus the weak observed MCD is in keeping with expectation for the assignment.

The MCD spectrum for the $Pd(DEPE)_2^{2+}$ ion (Figure 3) exhibits two very prominent features: a negative *B* term associated with band II at 4.1 μm^{-1} and a positive *A* term for band IV at 4.7 μm^{-1}. These two terms can be interpreted by assignment of bands II and IV to transitions to the predominantly singlet states $1A_{2u}(^1A_{2u})$ and $2E_u(^1E_u)$, respectively, analogous to corresponding features in the MCD spectra of the Pt(II) complexes. Bands I (a shoulder on the low-energy side of band II) and III are assigned to transitions to the $1E_u(^3A_{2u})$ and $3E_u(^3E_u)$ states, respectively, even though the absorptivities are quite high for transitions to predominantly spin-forbidden states. The high absorptivities are rationalized by the close proximity of these states to the allowed $1A_{2u}(^1A_{2u})$ and $2E_u(^1E_u)$ states, respectively; the bandwidths of the predominantly allowed transitions are sufficiently large that a considerable absorptivity contribution will be present at the energies of the weaker transitions to $1E_u(^3A_{2u})$ and $3E_u(^3E_u)$. The MCD for band III is quite weak, and that for band I does not show the expected positive *A* term, presumably because it is also weak. The broad unresolved $\Delta\epsilon_M$ observed in the region of band I is likely due to other weaker transitions on the low-energy side of band I. It would not be unreasonable, for example, to expect ligand field (LF) transitions (e.g. $a_{1g}(z^2) \rightarrow b_{1g}(x^2 - y^2)$ etc.) at such energies for Pd(II). On the whole the $Pd(DEPE)_2^{2+}$ spectrum is compressed (bands I–IV span $\sim$0.8 μm^{-1}) and blue shifted (by $\sim$0.7 μm^{-1}) compared to the more expanded $Pt(DEPE)_2^{2+}$ spectrum (bands I–IV span $\sim$ 1.35 μm^{-1}). These trends are consistent with the MLCT assignments since the Pd(II) 4d orbitals are expected to be more stable than the Pt(II) 5d orbitals and the spin–orbit splitting of the MLCT states for Pd(II) is expected to be less than for Pt(II).

The structure of the $Ni(DEPE)_2^{2+}$ ion in acetonitrile is not known and may be a distorted five-coordinate complex involving solvent coordination (see eq 1). The intense absorptions exhibited in the spectra are probably MLCT since the bands fall in the same energy region as those of $Ni(CN)_4^{2-}$;[19] however, the MCD is quite different. *Two negative A* terms are observed at 2.5 and 3.9 μm^{-1}, whereas the $Ni(CN)_4^{2-}$ ion shows only *positive A* terms.[19] Further, the MLCT model for a planar D_{4h} ion involving the $1a_{2u}$ excited configurations cannot account for two negative *A* terms. Thus the MCD suggests a distinctly different structure in acetonitrile, but in the absence of knowledge of this structure, a detailed interpretation of the spectra is not possible.

trans-$[M(PR_3)_2(CN)_2]$ Complexes. Compared to those of the PtP_4 complexes discussed above, the absorption and MCD spectra of *trans*-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$ in acetonitrile solution (Figure 4) are more complicated. Similar results were obtained for the absorption spectrum in cyclohexane solution (Table II) and also for the absorption spectrum of the related *trans*-$[Pt(PEt_3)_2(CN)_2]$ complex in acetonitrile.[21] The increased complexity of the *trans*-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$ spectrum compared to those of the PtP_4 complexes can be ascribed to the presence of the two different π-acceptor ligands in the complex. Thus the transitions may be assigned as $5d \rightarrow CN^-$ or $5d \rightarrow P(n\text{-}Bu)_3$.[22] For example the lowest energy transition in the PtP_4 complexes appears at 3.2–3.3 μm^{-1} while that of $Pt(CN)_4^{2-}$ is observed at 3.54 μm^{-1} in acetonitrile.[7a] Consequently band I at 3.49 μm^{-1} in *trans*-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$ is assigned as $5d \rightarrow P(n\text{-}Bu)_3$ and band II at 3.69 μm^{-1} as $5d \rightarrow CN^-$ since the lowest energy MLCT in the PtP_4 complexes occurs at lower energy than that in $Pt(CN)_4^{2-}$; both transitions are slightly blue shifted compared to the PtP_4 or $Pt(CN)_4^{2-}$ spectra. Similar comparisons to the PtP_4 and $Pt(CN)_4^{2-}$ spectra lead to the assignments given in Table II. The MCD below 4.7 μm^{-1} appears very much like a superposition of the MCD spectral patterns observed here for the PtP_4 complexes and that observed for $Pt(CN)_4^{2-}$.[7a,19] All terms in the D_{2h} complex are *B* terms[20] because all states in D_{2h} are nondegenerate. However, as was shown with lower symmetry cyanoammine complexes of Pt(II),[7a] close-lying states can produce *B* terms of opposite sign that appear to be an *A* term; these terms are called *pseudo-A* terms.[20] In particular the states in D_{2h} correlating with the E_u states of D_{4h}, nB_{2u} and nB_{3u} (see Table I), are expected to exhibit pseudo-*A* terms of the same sign as the E_u state of D_{4h}. Thus the transitions $A_g \rightarrow 2B_{3u}{}^{CN},3B_{2u}{}^{CN}(^1B_{3u}{}^{CN},{}^1B_{2u}{}^{CN})$ and $A_g \rightarrow 2B_{3u}{}^{P},3B_{2u}{}^{P}(^1B_{3u}{}^{P},{}^1B_{2u}{}^{P})$ are both expected to give positive pseudo-*A* terms. It should be noted that the two pseudo-*A* terms and the states from which they arise will be virtually independent of one another because the transitions involve orbitals centered on different ligands. Thus to a first approximation a simple superposition of terms would be expected in the observed MCD. Above 4.7 μm^{-1} only a single very intense band (band VII) is observed at 5.04 μm^{-1} (ϵ = 74 000), which is analogous to band V exhibited by the PtP_4 complexes. It is probable that this intense band obscures the $A_g \rightarrow 2B_{3u}{}^{P},3B_{2u}{}^{P}$ transition, which is expected at about 4.85 μm^{-1} by comparison with the PtP_4 complexes. The MCD in the region of band VI shows a strong negative *B* term but is anomalously weak above 4.7 μm^{-1}. This observed MCD may result from a partial cancellation of the positive portion of a lower energy pseudo-*A* term by the negative portion of an adjacent higher energy one. Thus the strong negative *B* term is assigned as $A_g \rightarrow 2B_{3u}{}^{CN}$, the negative part of the expected positive pseudo-*A* term, while the weaker MCD features to higher energy are assigned to the superposition of the terms from the remaining $3B_{2u}{}^{CN}$, $2B_{3u}{}^{P}$, and $3B_{2u}{}^{P}$ states.

The interpretation of the absorption and MCD spectra for *trans*-$[Pd(P(n\text{-}Bu)_3)_2(CN)_2]$ (Figure 3) is made difficult by the lack of a thorough understanding of the spectrum of Pd-

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[21] Ozkan, M. A.; Isci, H., unpublished results, 1981.

[22] As pointed out by a reviewer, the $P(n\text{-}Bu)_3$ and CN^- acceptor orbitals may be intermixed but split by the lower symmetry of the complex since the orbital energies are evidently close. In any case there will be two excited states of the same symmetry for each pair of intermixed orbitals. The degree of $P(n\text{-}Bu)_3$–CN^- intermixing cannot be inferred from our results.

Table II. Spectral Data[a]

	absorption			
band no.	λ, nm	$\bar{\nu}$, μm^{-1} (ε, M^{-1} cm^{-1})	MCD $\bar{\nu}$, μm^{-1} ($\Delta\epsilon_M$, M^{-1} cm^{-1} T^{-1})[b]	excited state(s)
			$[Pt(P(OEt)_3)_4](ClO_4)_2$	
I	309	3.24 (770)	3.21 (−0.78) 3.27 (0) 3.33 (+0.32) $\}^c$	$1E_u(^3A_{2u})$
II	268	3.73 (10 000)	3.71 (−2.99)	$1A_{2u}(^1A_{2u})$
III	237	4.23 (3200)	4.29 (+1.56)	$3E_u(^3E_u)$, $2A_{2u}(^3E_u)$
IV	209	4.78 (14 400)	4.70 (−9.22) 4.80 (0) 4.88 (+4.42) $\}^c$	$2E_u(^1E_u)$
			$[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$	
I	309	3.24 (520)	3.19 (−0.76) 3.26 (0) 3.30 (+0.20) $\}^c$	$1E_u(^3A_{2u})$
II	268	3.73 (7900)	3.74 (−2.86)	$1A_{2u}(^1A_{2u})$
III	244	4.10 (3100)	4.14 (+2.48)	$3E_u(^3E_u)$, $2A_{2u}(^3E_u)$
IV	208	4.80 (17 800)[d]	4.67 (−4.67) 4.80 (0) 4.95 (+2.34) $\}^c$	$2E_u(^1E_u)$
V	192	5.20 (39 500)		$E_u[^1E_u,(a_{1g})(2e_u)]$
			$[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$	
I	308	3.25 (440)		$^1E_u(^3A_{2u})$
II	266	3.76 (6900)		$1A_{2u}(^1A_{2u})$
III	242	4.14 (2600)		$3E_u(^3E_u)$, $2A_{2u}(^3E_u)$
IV	208	4.80 (16 400)[d]		$2E_u(^1E_u)$
V	193	5.17 (35 800)		$E_u[^1E_u,(a_{1g})(2e_u)]$
			$[Pt(DEPE)_2](ClO_4)_2$	
I	304	3.29 (700)	3.23 (−0.78) 3.30 (0) 3.35 (+0.28) $\}^c$	$1E_u(^3A_{2u})$
II	270	3.71 (4900)	3.68 (−2.20)	$1A_{2u}(^1A_{2u})$
III	251	3.98 (3100)	3.99 (+1.52)	$3E_u(^3E_u)$, $2A_{2u}(^3E_u)$
IV	215	4.65 (21 000)[d]	4.57 (−4.31) 4.69 (0) 4.86 (+6.34) $\}^c$	$2E_u(^1E_u)$
V	203	4.93 (55 000)		$E_u[^1E_u,(a_{1g})(2e_u)]$
			$[Pt(DEPE)_2](PF_6)_2$	
I	304	3.29 (700)		$1E_u(^3A_{2u})$
II	270	3.71 (4900)		$1A_{2u}(^1A_{2u})$
III	251	3.98 (3300)		$3E_u(^3E_u)$, $2A_{2u}(^3E_u)$
IV	215	4.65 (20 000)[d]		$2E_u(^1E_u)$
V	203	4.93 (53 000)		$E_u[^1E_u,(a_{1g})(2e_u)]$
			$[Pd(DEPE)_2](PF_6)_2$	
I	253	3.95 (24 000)[d]	3.90 (+2.47)	$1E_u(^3A_{2u})$
II	242	4.13 (31 000)	4.18 (−8.21)	$1A_{2u}(^1A_{2u})$
III	221	4.53 (29 000)	4.47 (0)	$3E_u(^3E_u)$, $2A_{2u}(^3E_u)$
IV	211	4.73 (29 500)	4.65 (−8.07) 4.76 (0) 4.86 (+4.61) $\}^c$	$2E_u(^1E_u)$
			$[Ni(DEPE)_2](PF_6)_2$[e]	
I	386	2.59 (1000)	2.37 (+0.12) 2.52 (0) 2.72 (−0.22) $\}^c$	
II	333	3.00 (800)[d]	3.01 (−0.35)	(see text)
III	252	3.97 (34 500)	3.77 (+2.09) 3.92 (0) 4.13 (−3.82) $\}^c$	
			trans-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$	
I	286	3.49 (1400)	3.44 (−1.08)	$1B_{3u}^P(^3B_{1u}^P)$
			3.53 (−0.42)	$1B_{2u}^P(^3B_{1u}^P)$
II	271	3.69 (2500)	3.68 (−1.10)[d]	$1B_{2u}^{CN}$,$1B_{3u}^{CN}(^3B_{1u}^{CN})$
III	253	3.95 (5800)[d]	3.81 (−1.83)	$1B_{1u}^P(^1B_{1u}^P)$
IV	249	4.02 (6000)	4.01 (+0.93)[d]	$1B_{1u}^{CN}(^1B_{1u}^{CN})$
			4.11 (+2.68)	$2B_{2u}^{CN}$,$3B_{3u}^{CN}(^3B_{2u}^{CN},{}^3B_{3u}^{CN})$
V	227	4.41 (4800)	4.34 (−0.98) 4.45 (+0.26) $\}$	$2B_{2u}^P$,$3B_{3u}^P(^3B_{3u}^P,{}^3B_{2u}^P)$
VI	213	4.69 (12 000)	4.62 (−5.07)	$2B_{3u}^{CN}(^1B_{3u}^{CN})$
			4.80 (+0.94) 4.96 (+1.44) $\}$	$3B_{2u}^{CN}(^1B_{2u}^{CN})$, $2B_{3u}^P(^1B_{3u}^P)$, $3B_{2u}^P(^1B_{2u}^P)$
VII	198	5.06 (74 000)	5.03 (+1.52)	$B_{3u}^P[^1B_{3u}^P,(a_g)(1b_{3u}^P)]$

Table II (*Continued*)

band no.	absorption λ, nm	absorption $\bar{\nu}$, μm^{-1} (ε, M^{-1} cm^{-1})	MCD $\bar{\nu}$, μm^{-1} (Δε$_M$, M^{-1} cm^{-1} T^{-1})^b	excited state (s)
			trans-[Pt(P(*n*-Bu)$_3$)$_2$(CN)$_2$]^f	
I	286	3.50 (1860)^d		$1B_{2u}^P,1B_{3u}^P(^3B_{1u}^P)$
II	277	3.61 (2100)		$1B_{2u}^{CN},1B_{3u}^{CN}(^3B_{1u}^{CN})$
III	255	3.92 (6900)		$1B_{1u}^P(^1B_{1u}^P)$
IV	247	4.05 (5700)^d		$1B_{1u}^{CN}(^1B_{1u}^{CN})$
V	230	4.34 (5100)		$2B_{2u}^{CN},3B_{3u}^{CN}(^3B_{2u}^{CN},^3B_{3u}^{CN})$
VI	213	4.69 (10 500)		$2B_{3u}^{CN}(^1B_{3u}^{CN})$
VII	196	5.10 (60 000)		$B_{3u}^P[^1B_{3u}^P,(a_g)(1b_{3u}^P)]$
			trans-[Pd(P(*n*-Bu)$_3$)$_2$(CN)$_2$]	
I	244	4.10 (22 700)	3.96 (−0.38)	$1B_{3u}^P(^3B_{1u}^P)$
			4.11 (+0.13)	$1B_{2u}^P(^3B_{1u}^P)$
			4.24 (−1.32)	$1B_{2u}^{CN},1B_{3u}^{CN}(^3B_{1u}^{CN})$
II	228	4.43 (24 800)	4.45 (−8.01)	$1B_{1u}^P(^1B_{1u}^P)$
III	221	4.55 (22 200)^d	4.63 (−0.88)	$1B_{1u}^{CN}(^1B_{1u}^{CN})$
			4.78 (−1.10)	$2B_{3u}^P(^1B_{3u}^P)$
IV	200	5.00 (25 500)	5.02 (+3.52)	$3B_{2u}^P(^1B_{2u}^P)$
			trans-[Ni(PEt$_3$)$_2$(CN)$_2$]	
I	339	2.95 (900)	2.89 (−0.28)	$\left.\begin{matrix}1B_{2u}^{CN},1B_{3u}^{CN}\\1B_{2u}^P,1B_{3u}^P\end{matrix}\right\}(^3B_{1u}^P,^3B_{1u}^{CN})$
II	308	3.25 (3000)^d	3.22 (−2.53)	$1B_{1u}^P(^1B_{1u}^P)$
III	293	3.41 (5700)	3.34 (−1.25)	$1B_{1u}^{CN}(^1B_{1u}^{CN})$
			3.48 (+0.39)	$2B_{2u}^{CN},3B_{3u}^{CN}(^3B_{2u}^{CN},^3B_{3u}^{CN})$
			3.65 (−0.45)	$2B_{3u}^P(^1B_{3u}^P)$
IV	252	3.97 (45 300)	3.92 (+1.52)	$3B_{2u}^P(^1B_{2u}^P)$
V	234	4.27 (13 300)^d	4.38 (−0.34)	$2B_{3u}^{CN}(^1B_{3u}^{CN})$
			4.55 (−0.18)	$3B_{2u}^{CN}(^1B_{2u}^{CN})$

[a] Acetonitrile solution, room temperature. [b] $\Delta A/(ClH)$, where ΔA = differential absorbance, C = molar concentration, l = path length in cm, and H = magnetic field in Tesla. [c] A term. [d] Shoulder. [e] Beer's law failure (see text); ε and Δε$_M$ values are approximate. [f] Cyclohexane solution.

$(CN)_4^{2-}$. Both absorption and MCD spectra for $Pd(CN)_4^{2-}$ show overlapping features with incomplete resolution.[19] However, a comparison of the cyanophosphine complex to the $Pd(DEPE)_2^{2+}$ complex investigated here is useful since the spectra show some similar characteristics. Thus a very prominent negative B term for band II at 4.4 μm^{-1} appears analogous to that of band II for $Pd(DEPE)_2^{2+}$. A reasonable assignment for band II is therefore $A_g \rightarrow 1B_{1u}^P(^1B_{1u}^P)$. Similarly the positive pseudo-A term for band IV at 5.0 μm^{-1} is analogous to the strong A term for band IV of $Pd(DEPE)_2^{2+}$ and is logically assigned as the analogous $A_g \rightarrow 2B_{3u}^P,3B_{2u}^P(^1B_{3u}^P,^1B_{2u}^P)$ transitions. The observation that bands II and IV of *trans*-[Pd(P(*n*-Bu)$_3$)$_2$(CN)$_2$] are both blue shifted by the same amount (~0.3 μm^{-1}) compared to their counterparts in the $Pd(DEPE)_2^{2+}$ spectrum tends to support these assignments. The MCD in the region of band I at 4.1 μm^{-1} of the *trans*-[Pd(P(*n*-Bu)$_3$)$_2$(CN)$_2$] spectrum is more complicated than for $Pd(DEPE)_2^{2+}$ and shows at least two weak features. This may signal separate 4d → CN$^-$ and 4d → P(*n*-Bu)$_3$ transitions like the separate transitions observed for the Pt(II) cyanophosphine complex. Following this line of interpretation, band III at 4.5 μm^{-1} is assigned to $A_g \rightarrow 1B_{1u}^{CN}$. However, the interpretation of the weak MCD in the region of band III is less clear. It is probable that adjacent overlapping terms resulting in cancellation is responsible for the weak MCD. Thus the $A_g \rightarrow 2B_{2u}^{CN},3B_{3u}^{CN}(^3B_{2u}^{CN},^3B_{3u}^{CN})$ transitions are expected at only slightly higher energy than band III and should give a positive pseudo-A term between the negative B term of band II and the positive pseudo-A term of band IV. The overlap of these terms could account for the weak observed MCD for band III. A more detailed interpretation will require better resolved spectra.

The absorption and MCD spectra of *trans*-[Ni(PEt$_3$)$_2$(CN)$_2$] (Figure 5) parallel those of $Ni(CN)_4^{2-}$,[19] but they exhibit greater complexity in detail, similar to the Pt(II) cyanophosphine case. Thus an interpretation involving separate 3d → CN$^-$ and 3d → PEt$_3$ MLCT transitions can be applied in a straightforward manner. Band I at 2.95 μm^{-1}, which is weak and broad, is assigned to the unresolved predominantly spin-forbidden transitions to both CN$^-$ and PEt$_3$, while the more intense bands II at 3.2 μm^{-1} and III at 3.4 μm^{-1} are assigned to the spin-allowed $A_g \rightarrow 1B_{1u}^P(^1B_{1u}^P)$ and $A_g \rightarrow 1B_{1u}^{CN}(^1B_{1u}^{CN})$, respectively. The intense negative B term for band II is reminiscent of the term observed for the same transition in the Pd(II) cyanophosphine complex, while the unsymmetrical pseudo-A term for band III is similar to the MCD for the corresponding band in $Ni(CN)_4^{2-}$.[19] Band IV at 3.97 μm^{-1} (ϵ = 45 300) is more intense than the corresponding band at 3.7 μm^{-1} in $Ni(CN)_4^{2-}$ (ϵ = 11 400). Therefore band IV is likely due to $A_g \rightarrow 3B_{2u}^P,2B_{3u}^P(^1B_{2u}^P,^1B_{3u}^P)$ while band V at 4.27 μm^{-1} (ϵ = 13 300) is tentatively assigned as the $A_g \rightarrow 3B_{2u}^{CN},2B_{3u}^{CN}(^1B_{2u}^{CN},^1B_{3u}^{CN})$ transitions.

Electronic Structural Features. From the foregoing assignments it is clear that a model involving only the lowest energy MLCT excited configurations can be used satisfactorily to interpret the principal absorption and MCD features of the square-planar P-donor complexes investigated here. This interpretation implies the energy ordering of the occupied d orbitals as $nd_{z^2} > nd_{xz}, nd_{yz}$, taking the standard assumption that electron repulsion differences between the MLCT states are negligible. The stabilization of the π-bonding nd_{xz}, nd_{yz} orbitals relative to the weakly σ-antibonding or nearly nonbonding nd_{z^2} is consistent with metal to ligand π interaction. In fact a qualitative estimate of the P-donor ligand π-acceptor ability can be obtained from spectral energy differences $\Delta_{\pi-\sigma}$ between the transitions involving $nd_{xz},nd_{yz}(d_\pi \rightarrow L)$ and that involving $nd_{z^2}(d_\sigma \rightarrow L)$. Some relevant data are collected in Table III. The data show that $\Delta_{\pi-\sigma}$ varies as $P(OR)_3 > PR_3 > CNEt > CN^-$ for the Pt(II) complexes. It should be noted that the smaller $\Delta_{\pi-\sigma}$ values for the Pd(II) complexes cannot be compared directly with those of Pt(II) because there is a

Table III. Comparative MLCT Energies (μm^{-1})[a]

complex	$d_\sigma \rightarrow L$[b]	$d_\pi \rightarrow L$[c]	$\Delta_{\pi-\sigma}$
	Pt(II) Complexes		
$Pt(P(OEt)_3)_4^{2+}$	3.71	4.80	1.09
$[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$	3.74	4.80	1.06
$[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$	3.76[d]	4.80[d]	1.04
$Pt(DEPE)_2^{2+}$	3.68	4.69	1.01
trans-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$			
P	3.81	*h*	
CN	4.01	*h*	
cis-$[Pt(PEt_3)_2(CH_3)_2]$[e]	3.66	4.63	0.97
$Pt(CNEt)_4^{2+}$ [f]	3.93[d]	4.83[d]	0.90
$Pt(CN)_4^{2-}$ [g]	3.85[d]	4.55[d]	0.70
	Pd(II) Complexes		
$Pd(DEPE)_2^{2+}$	4.18	4.76	0.58
trans-$[Pd(P(n\text{-}Bu)_3)_2(CN)_2]$			
P	4.45	*h*	
$Pd(CNEt)_4^{2+}$ [f]	4.56[d]	5.16[d]	0.60

[a] From MCD data. [b] $1A_{2u}(^1A_{2u})$ in D_{4h} or $1B_{1u}(^1B_{1u})$ in D_{2h}. [c] $2E_u(^1E_u)$ in D_{4h} or $3B_{2u},2B_{3u}(^1B_{2u},^1B_{3u})$ in D_{2h}. [d] From absorption data. [e] $B_1(^1B_1)$ and $B_2,A_1(^1B_2,^1A_1)$ in C_{2v}.[10] [f] Reference 7b. [g] Reference 7a. [h] Band location uncertain.

component of the energy difference due to the spin–orbit splitting of the A_{2u} and E_u states, which of course is larger for Pt(II) than Pd(II). Thus for Pd(II) $\Delta_{\pi-\sigma}$ is about the same for PR_3 and CNEt, implying comparable π-acceptor ability.

It is interesting that separate *n*d → P donor and *n*d → CN^- transitions could be resolved in the cyanophosphine complexes studied here. This resolution indicates separate configurations involving the different ligand-based orbitals. However, the energy difference between these ligand-based orbitals is quite small, being less than ~0.2 μm^{-1} for Pt(II) and Pd(II) and slightly larger for Ni(II). Furthermore, the change in energy of the MLCT spectrum, as judged by the $d_\sigma \rightarrow L$ transition, and the change in spread of the spectrum, as judged by $\Delta_{\pi-\sigma}$, over a range of ligands is not very large. For example, the Pt(II) the $d_\sigma \rightarrow L$ transition shifts less than 0.36 μm^{-1} while $\Delta_{\pi-\sigma}$ changes only by 0.39 μm^{-1} for the complexes of Table III. The lack of strong dependence of transition energies on the nature of the ligand, which is apparent here, has been cited[6,9] as an indication of considerable $(n + 1)p_z$ character in the "ligand" LUMO. We believe this is a valid point but should not be taken to the extreme of minimizing the ligand contribution to the LUMO. There is a nonnegligible ligand contribution as clearly evidenced by the resolution of separate transitions to the CN^- and PR_3 ligands of the D_{2h} complexes investigated here. Thus it is reasonable to view the LUMO's in these P-donor M(II) complexes, and probably also the Rh(I) and Ir(I) complexes investigated previously,[1,2,5,6,8,9] as having significant contributions of *both* metal $(n + 1)p_z$ and ligand orbitals and consequently the LUMO as being extensively delocalized over both metal and ligands.

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Registry No. $[Pt(P(OEt)_3)_4](ClO_4)_2$, 88212-05-9; $[Pt(P(OH)(OMe)_2)_2(P(O)(OMe)_2)_2]$, 30053-63-5; $[Pt(P(OH)(OEt)_2)_2(P(O)(OEt)_2)_2]$, 32324-65-5; $[Pt(DEPE)_2](ClO_4)_2$, 88657-18-5; $[Pt(DEPE)_2](PF_6)_2$, 88657-19-6; $[Pd(DEPE)_2](PF_6)_2$, 88657-21-0; $[Ni(DEPE)_2](PF_6)_2$, 88657-22-1; *trans*-$[Pt(P(n\text{-}Bu)_3)_2(CN)_2]$, 15390-91-7; *trans*-$[Pd(P(n\text{-}Bu)_3)_2(CN)_2]$, 88657-23-2; *trans*-$[Ni(PEt_3)_2(CN)_2]$, 14523-37-6.

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Preparation, Structure, and Properties of Central-Carbon-Bonded Diethyl Malonato Complexes of Palladium(II) with Bis(μ-chloro) and μ-Oxalato Bridges

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cis-Bis(diethyl malonato-*C*)palladium(II) complexes have been prepared by the reaction of diethyl malonate with a tetrachloropalladate ion in an alkaline solution. During the preparation of the complex Pd-induced oxidative decomposition of the ligand occurs to yield a (μ-oxalato)palladium(II) complex, whose structure has been determined by a single-crystal X-ray study. The compound, $Na_2[(Pd(C_7H_{11}O_4)_2)_2Cl_2]K_2[(Pd(C_7H_{11}O_4)_2)_2(C_2O_4)]\cdot4H_2O$, crystallizes in the monoclinic space group *Cc*, with cell constants $a = 28.331$ (3) Å, $b = 16.212$ (1) Å, $c = 22.510$ (2) Å, $\beta = 122.21$ (1)°, and $Z = 4$. The structure has been solved by heavy-atom methods, and least-squares refinements have led to $R = 0.056$ and $R_w = 0.076$ for 4691 reflections with $F_0 > 2\sigma(F_0)$. The crystal consists of two kinds of dimeric complexes held together by interaction of the carbonyl oxygen atoms and alkali-metal ions. The bridging oxalate group is approximated to be of D_{2h} symmetry, exhibiting $\nu_{CO}(B_{2u})$ at 1618 cm^{-1}. The (diethyl malonato-*C*)palladium(II) compounds react with methanol to give diethyl bis(hydroxymethyl)malonate in a moderate isolated yield.

Introduction

Since the first synthesis of a carbon-bonded β-diketonato Pd(II) complex by Kawaguchi and co-workers,[1a] extensive work has been carried out on such a type of Pd(II) compounds with β-diketones and β-ketoacetic esters.[1] In contrast, only a limited number of Pd(II) compounds with malonic esters have been isolated and characterized so far,[2] although diethyl malonate is a very useful reagent for C–C bond formation in reactions with organopalladium compounds.[3] Our attention was thus drawn to the neglected Pd(II) compounds with un-

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