4370 *Inorg. Chem.* **1989**, *28*, 4370–4373

Contribution from the Department of Chemistry,
Northern Illinois University, DeKalb, Illinois 60115

Electronic Absorption and MCD Spectra for Isoelectronic Linear Two-Coordinate Bis(tri-*tert*-butylphosphine)metal Complexes of Platinum(0) and Gold(I)

Huey-Rong C. Jaw and W. Roy Mason*

Received June 12, 1989

Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for $Pt(P(t\text{-}Bu)_3)_2$ in CH_3CN and in *n*-hexane solution for $[Au(P(t\text{-}Bu)_3)_2]ClO_4$ in CH_3CN solution. The intense bands observed from 2.4 to 4.5 μm^{-1} for the Pt(0) complex and from 4.0 to 5.0 μm^{-1} for the isoelectronic Au(I) complex are assigned as d → p/metal to ligand charge-transfer (MLCT) transitions to Π_u and Σ_u^+ spin–orbit states of $5d \rightarrow 1\pi_u$ excited configurations. The red shift in the spectra for the Pt(0) complex compared to the spectra for the Au(I) complex is interpreted in terms of lower metal orbital stability and a smaller 5d–6p energy separation for Pt(0). Detailed spectral assignments lead to the conclusion of minimal involvement of the 5d orbitals in M–P bonding for both complexes.

Introduction

Linear two-coordinate complexes are important for metal ions of the closed-shell nd^{10} electron configuration, especially for $5d^{10}$ ions. For example, numerous two-coordinate Au(I) and Hg(II) complexes with a variety of ligand types are well-known. In contrast however two-coordination for isoelectronic Pt(0) is not common.[1,2] Instead Pt(0) has a higher tendency than Au(I) to expand its coordination number to 3 (trigonal planar) or 4 (tetrahedral) by adding additional ligands.[3] However, if the ligands are sufficiently bulky, the tendency toward higher coordination number for Pt(0) diminishes and two-coordination is observed.[2] Among the best examples of two-coordinate Pt(0) complexes are bis(trialkylphosphine)platinum(0) complexes, $Pt(PR_3)_2$, where R = *tert*-butyl,[4,5] cyclohexyl,[6] isopropyl,[7] etc. (these bulky phosphine ligands all have cone angles[8] $\gtrsim 160°$). These complexes are of particular interest because in spite of the bulkiness and steric requirements of their ligands they behave as typical coordinately unsaturated metal centers: they undergo addition reactions[1] with reagents such as H_2,[2,9] O_2,[2,9] HX,[9] H_2O,[7] RX,[6,9,10] SO_2,[11] CS_2,[11] alkenes, and acetylenes.[1,6,7] In fact, the mechanism of H_2 addition to $Pt(PR_3)_2$ complexes has been investigated recently by ab initio calculations on the two-coordinate "model" complex $Pt(PH_3)_2$.[12,13] Further, under certain conditions the $Pt(PR_3)_2$ complexes undergo intermolecular substitution reactions that lead to the formation of Pt cluster complexes. For example, the reaction of $Pt(P(t\text{-}Bu)_3)_2$ with CO or CS_2 results in the trinuclear $[Pt(P(t\text{-}Bu)_3)(\mu\text{-}CO)]_3$ or $[Pt(P(t\text{-}Bu)_3)(\mu\text{-}CS_2)]_3$ complex, respectively.[10,11] In spite of these interesting features little is known about the electronic structure, optical spectra, and low-energy excited states for the $Pt(PR_3)_2$ complexes or their comparison with analogous $Au(PR_3)_2^+$ complexes.[14] Some of the MO's and energy levels for the linear $Pt(PH_3)_2$ model complex have been described in the ab initio studies already mentioned,[12,13] and a portion of the electronic absorption spectrum in the region of the lowest energy band has been reported for $Pt(P(i\text{-}Pr)_3)_2$ in *n*-heptane solution.[7] Herein are reported the electronic absorption and magnetic circular dichroism (MCD) spectra for $Pt(P(t\text{-}Bu)_3)_2$ in CH_3CN and *n*-hexane solution in the region 2.2–5.2 μm^{-1}. The $Pt(P(t\text{-}Bu)_3)_2$ complex is air stable,[4] and the crystal structure shows that the molecule is linear in the solid.[5] Spectra are also reported for the $Au(P(t\text{-}Bu)_3)_2^+$ cation in order to provide a direct isoelectronic isostructural comparison between two-coordinate Pt(0) and Au(I) complexes.

Experimental Section

Preparation of Compounds. Bis(tri-*tert*-butylphosphine)platinum(0), $Pt(P(t\text{-}Bu)_3)_2$, was prepared following a literature procedure:[10] $P(t\text{-}Bu)_3$ (Strem Chemicals, Inc.) and K_2PtCl_4 were refluxed in absolute ethanol containing KOH for 30 h. The solvent was removed, and the residue was extracted with hot hexane. The product was obtained by evaporation of the hexane solvent; it was recrystallized from hexane to give fine off-white crystals. Bis(tri-*tert*-butylphosphine)gold(I) perchlorate, $[Au(P(t\text{-}Bu)_3)_2]ClO_4$, was prepared by treating a CH_3CN solution of $[Au(CH_3CN)_2]ClO_4$[15] with a slight excess of $P(t\text{-}Bu)_3$. A white solid was obtained on removal of the solvent. This product was washed with hexane and ether and then recrystallized from CH_3CN/ether and dried under vacuum. Both compounds gave satisfactory elemental analysis and were air stable. *Caution: potential perchlorate hazard for* $[Au(P(t\text{-}Bu)_3)_2]ClO_4$*!*

Spectral Measurements. Absorption spectra were determined by using a Cary 1501 spectrophotometer. MCD and absorption spectra were measured simultaneously and synchronously along the same light path by a spectrometer described earlier.[16] A magnetic field of 7.0 T was provided by a superconducting magnet (Oxford Instruments SM2-7, fitted with a room-temperature bore tube). Spectral grade solvents were used throughout. All spectra were corrected by subtracting solvent blank. The solutions of the Pt(0) or Au(I) complex showed no changes over the times required for the spectral measurements, and Beer's law was found to hold for both complexes to within experimental uncertainty. Even though $Pt(P(t\text{-}Bu)_3)_2$ has a low solubility in CH_3CN (<0.1 mg/mL at room temperature), concentrations sufficient to obtain good quality spectra in this solvent were easily obtained.

Results and Discussion

Electronic Absorption and MCD Spectra. The electronic absorption and MCD spectra for $Pt(P(t\text{-}Bu)_3)_2$ and $[Au(P(t\text{-}Bu)_3)_2]ClO_4$ in CH_3CN are shown in Figures 1 and 2. Quantitative spectral data are collected in Table I, along with data for $Pt(P(t\text{-}Bu)_3)_2$ in *n*-hexane solution. The hexane spectra were of comparable quality to the CH_3CN spectra and did not reveal any additional features. The lowest energy band at 2.6 μm^{-1} (band I) for $Pt(P(t\text{-}Bu)_3)_2$ compares favorably in position and intensity with the band reported for $Pt(P(i\text{-}Pr)_3)_2$ at 2.53 μm^{-1} in *n*-heptane.[7] Both MCD and absorption spectra for the $Au(P(t\text{-}Bu)_3)_2^+$ cation are similar to those for $Au(PEt_3)_2^+$ and other two-coordinate Au(I) complexes with π-acceptor ligands studied earlier in this laboratory.[14,17,18] A comparison of the absorption and MCD spectra

---

(1) Roundhill, D. M. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987, Vol. 5, p 351.

(2) Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191 and references cited therein.

(3) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776.

(4) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

(5) Moynihan, K. J.; Chieh, C.; Goel, R. G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 3060.

(6) Fornies, J.; Green, M.; Spencer, J. L.; Stone, G. F. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006.

(7) Yoshida, T.; Matsuda, T.; Okano, T.; Tetsumi, K.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

(8) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(9) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134.

(10) Goel, R. G.; Ogini, W. O.; Srivastava, R. C. *J. Organomet. Chem.* **1981**, *214*, 405.

(11) Ritchey, J. M.; Moody, D. C.; Ryan, R. R. *Inorg. Chem.* **1983**, *22*, 2276.

(12) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 6928.

(13) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482.

(14) Savas, M. M.; Mason, W. R. *Inorg. Chem.* **1987**, *26*, 301.

(15) Bergerhoff, G. *Z. Anorg. Allg. Chem.* **1964**, *327*, 139.

(16) Mason, W. R. *Anal. Chem.* **1982**, *54*, 646.

(17) Chastain, S. K.; Mason, W. R. *Inorg. Chem.* **1982**, *21*, 3717.

(18) Mason, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 5182.

0020-1669/89/1328-4370$01.50/0

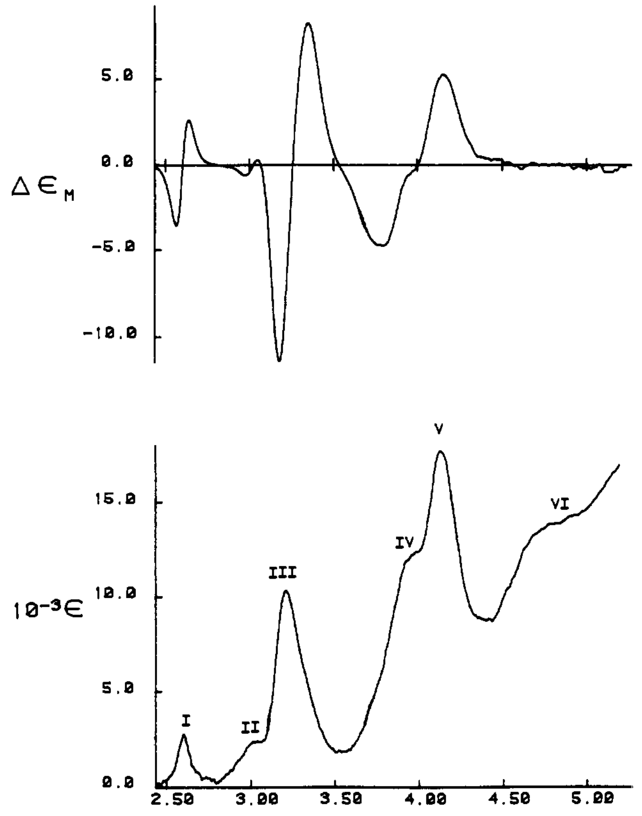

Figure 1. Electronic absorption (lower curve) and MCD (upper curve) spectra for $Pt(P(t\text{-}Bu)_3)_2$ in acetonitrile. The units of $\Delta\varepsilon_M$ are M^{-1} cm^{-1} T^{-1}.

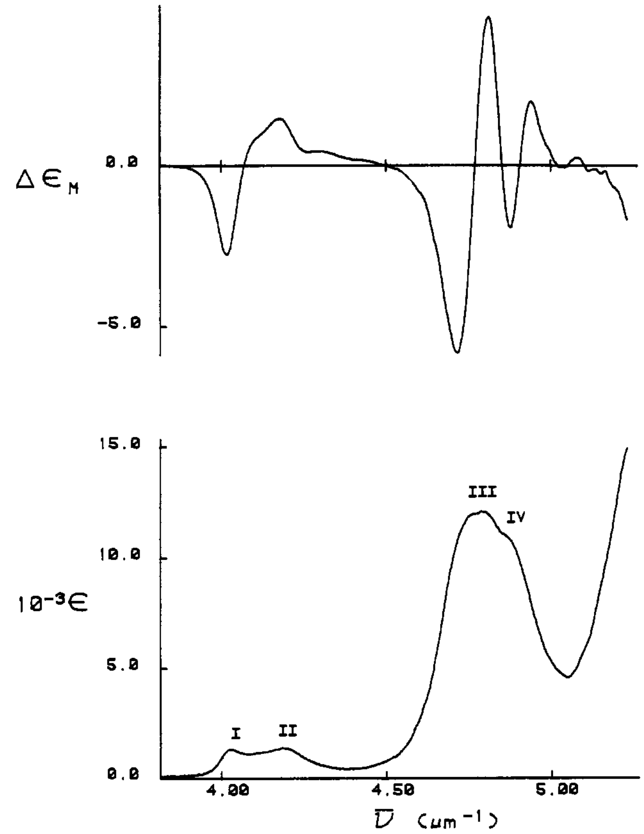

Figure 2. Electronic absorption (lower curve) and MCD (upper curve) spectra for $[Au(P(t\text{-}Bu)_3)_2]ClO_4$ in acetonitrile. The units of $\Delta\varepsilon_M$ are M^{-1} cm^{-1} T^{-1}.

Table I. Spectral Data

band no.	absorption: $\bar{\nu}$, µm^{-1}	absorption: λ, nm	absorption: ε, (M cm)$^{-1}$	MCD: $\bar{\nu}$, µm^{-1}	MCD: $\Delta\varepsilon_M$, (M cm T)$^{-1}$
		$Pt(P(t\text{-}Bu)_3)_2$ in CH_3CN			
I	2.60	384.2	3 100	^{b} 2.56	-3.54
				2.60	0
				2.64	+2.70
II	3.03^a	330.5	3 020	^{b} 2.98	-0.64
				3.02	0
				3.05	+0.34
III	3.21	311.6	11 600	^{b} 3.17	-11.44
				3.26	0
				3.35	+8.21
IV	3.97^a	252.5	14 600	3.77	-4.68
V	4.13	240.2	19 200	4.15	+5.24
VI	4.79^a	208.2	13 030		
		$Pt(P(t\text{-}Bu)_3)_2$ in Hexane			
I	2.60	384.2	4 500	^{b} 2.57	-2.47
				2.61	0
				2.64	+1.77
II	3.03^a	330.5	4 070	^{b} 2.98	-0.47
				3.03	0
				3.06	+0.22
III	3.21	311.1	15 700	^{b} 3.18	-6.55
				3.27	0
				3.36	+4.24
IV	3.99^a	250.4	17 000	3.78	-2.62
V	4.15	241.4	24 000	4.17	+2.76
VI	4.71	212.3	8 850		
		$[Au(P(t\text{-}Bu)_3)_2]ClO_4$ in CH_3CN			
I	4.03	248.4	1 430	4.02	-2.77
II	4.18	239.2	1 480	4.18	+1.48
III	4.78	209.2	12 100	^{b} 4.71	-5.89
				4.77	0
				4.81	+4.67
IV	4.86^a	205.7	11 100	^{b} 4.87	-2.00
				4.90	0
				4.94	+2.02

^{a}Shoulder. ^{b}*A* term.

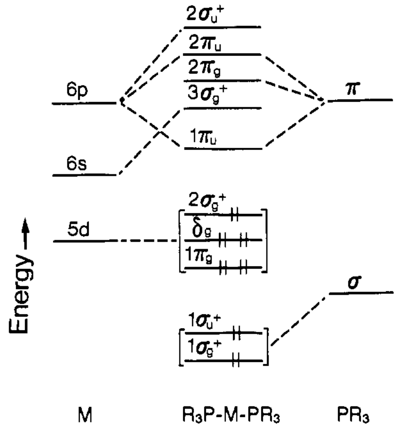

Figure 3. MO energy levels for $D_{\infty h}$ $M(PR_3)_2$ complexes.

for $Pt(P(t\text{-}Bu)_3)_2$ and $Au(P(t\text{-}Bu)_3)_2^+$ shows some similarity in pattern for the lowest energy band systems (bands I–III) between the two complexes, but the Pt(0) spectra are substantially red shifted compared to the Au(I) spectra (band I is lower in energy by 1.43 µm^{-1}, and band III is lower by 1.57 µm^{-1} in the Pt(0) complex). The similarity in pattern and the red shift between the isoelectronic Pt(0) and Au(I) complexes suggest a common interpretation, but one which must reflect differences in metal orbital stability. In the next section an interpretive model is briefly described followed in subsequent sections by a detailed spectral interpretation for each complex.

Molecular Orbitals, Excited States, and MCD Terms. The electronic structural model formulated from the study of $Au(PEt_3)_2^+$ and other two-coordinate Au(I) complexes with π-acceptor ligands[14,17,18] can be used as a basis for the interpretation of the absorption and MCD spectra for $Au(P(t\text{-}Bu)_3)_2^+$ and with only minor modification can also be used for the $Pt(P(t\text{-}Bu)_3)_2$ spectra. To briefly review the features of this model, Figure 3

Table II. Excited Configurations and States

excited confign[a]	no spin–orbit coupling	strong spin–orbit coupling[b]	calcd $\bar{A}_1/\bar{D}_0$
$(2\sigma_g^+)(1\pi_u)$	$a^1\Pi_u$	Π_u	+1
	$a^3\Pi_u$	Π_u	+1
		Σ_u^+	
		(Σ_u^-)	
		(Δ_u)	
$(1\pi_g)^3(1\pi_u)$	$1\Sigma_u^+$	Σ_u^+	
	$^3\Sigma_u^+$	(Σ_u^-)	
		Π_u	+2
	$^1\Sigma_u^-$	(Σ_u^-)	
	$^3\Sigma_u^-$	Σ_u^+	
		Π_u	+2
	$^1\Delta_u$	(Δ_u)	
	$^3\Delta_u$	(Δ_u)	
		(Φ_u)	
		Π_u	0
$(\delta_g)^3(1\pi_u)$	$^1\Phi_u$	(Φ_u)	
	$^3\Phi_u$	(Φ_u)	
		(Γ_u)	
		(Δ_u)	
	$b^1\Pi_u$	Π_u	+1
	$b^3\Pi_u$	Π_u	+1
		Σ_u^+	
		(Σ_u^-)	
		(Δ_u)	

[a] Notation as in Figure 3; filled orbitals omitted. Ground state: ... $(1\pi_g)^4(\delta_g)^4(2\sigma_g^+)^2$, $^1\Sigma_g^+$. [b] Dipole-forbidden spin–orbit states in parentheses.

presents a schematic one-electron MO energy level diagram for the $D_{\infty h}$ $M(PR_3)_2$ complexes (the z axis is taken along the molecular axis). The $5d^{10}$ electron configuration gives complexes that are diamagnetic and have totally symmetric ground states, $^1\Sigma_g^+$. The lowest energy empty orbital in each case is $1\pi_u$, which is a combination of metal $6p_{x,y}$ and ligand π orbitals. Thus, the lowest excited configurations result from 5d → $1\pi_u$ excitations and are visualized as having both d → p and metal to ligand charge-transfer (MLCT) character. Table II summarizes the states of the 5d → $1\pi_u$ configurations. Electric dipole allowed transitions are restricted to Σ_u^+ (z polarized) and Π_u (x,y polarized) excited states, but because spin–orbit coupling is strong for Pt(0) and Au(I) ($\zeta_{5d} \sim 0.4\ \mu m^{-1}$), the singlet and triplet zero-order states will become intermixed. For example, the various $\Pi_u(i)$ spin–orbit states will be eigenvectors of the form in eq 1,

$$|\Pi_u(i)\rangle = a_i|a^1\Pi_u\rangle + b_i|a^3\Pi_u\rangle + c_i|^3\Sigma_u^+\rangle + d_i|^3\Delta_u\rangle + e_i|^3\Sigma_u^-\rangle + f_i|b^3\Pi_u\rangle + g_i|b^1\Pi_u\rangle \quad (1)$$

where a_i–g_i are mixing coefficients among the singlet and triplet states of Table II in the absence of spin–orbit interaction. An analogous eigenvector can be written for the $\Sigma_u^+(i)$ spin–orbit states. The energies and eigenvector coefficients can be obtained by diagonalizing the appropriate spin–orbit energy matrices by using the energies of the zero-order states and the spin–orbit coupling constant ζ as input.[17,18]

The MCD spectra for the linear $M(PR_3)_2$ complexes are expected to consist of contributions from *A* terms (Π_u states) and *B* terms (Σ_u^+ or Π_u states); *C* terms are absent for these diamagnetic complexes.[19] MCD *A* terms result from the magnetic field induced Zeeman splitting of the degenerate $\Pi_u(i)$ excited states and can be predicted from the $\bar{A}_1/\bar{D}_0$ ratio given for space-averaged nonisotropic molecules in eq 2, where μ_B = Bohr

$$\bar{A}_1/\bar{D}_0 = -\frac{1}{\sqrt{2}\mu_B}\langle\Pi_u(i)\|\mu\|\Pi_u(i)\rangle \quad (2)$$

magneton, $\bar{D}_0 = {}^1/_3|\langle\Sigma_g^+\|\mathbf{m}\|\Pi_u(i)\rangle|^2$, the dipole strength of the transition, and $\mathbf{m} = e\mathbf{r}$ and $\mu = -\mu_B(\mathbf{L} + 2\mathbf{S})$, the electric and magnetic moment operators, respectively. Values of $\bar{A}_1/\bar{D}_0$ for the states of the 5d → $1\pi_u$ configurations can be estimated by approximating the orbitals as pure 5d or 6p metal atomic orbitals and evaluating the reduced matrix element (RME) of eq 2 by standard techniques.[19] These values are included in Table II. MCD *B* terms result from the field-induced mixing between Σ_u^+ and Π_u states or between two different Π_u states. For example, the $\bar{B}_0$ parameter for a transition to a $\Sigma_u^+(i)$ state is given by eq 3, where $\Delta W_{ji} = W_{\Pi_u(j)} - W_{\Sigma_u^+(i)}$, the energy difference between

$$\bar{B}_0(\Sigma_u^+(i),\Pi_u(j)) = \mathrm{Re}\left[\frac{-2}{3\mu_B}\sum_j\frac{\langle\Sigma_u^+(i)\|\mu\|\Pi_u(j)\rangle}{\Delta W_{ji}} \times \langle\Sigma_g^+\|\mathbf{m}\|\Sigma_u^+(i)\rangle\langle\Pi_u(j)\|\mathbf{m}\|\Sigma_g^+\rangle\right] \quad (3)$$

the $\Pi_u(j)$ and $\Sigma_u^+(i)$ states. In favorable cases, estimates of signs and relative magnitudes of $\bar{B}_0$ parameters can be made because only states close in energy make significant contributions due to the inverse ΔW_{ji} dependence.[17]

$Au(P(t\text{-}Bu)_3)_2^+$ Spectra. The interpretation of the absorption and MCD spectra for $Au(P(t\text{-}Bu)_3)_2^+$ in terms of the model described above is straightforward and closely parallels that for $Au(PEt_3)_2^+$.[14] The intense bands III (maximum at 4.78 μm^{-1}) and IV (shoulder near 4.86 μm^{-1}) are assigned as transitions to the lowest energy Π_u spin–orbit states of predominantly singlet character, $\Pi_u(b^1\Pi_u)[(\delta_g)^3(1\pi_u)]$ and $\Pi_u(a^1\Pi_u)[(2\sigma_g^+)(1\pi_u)]$, respectively. These two transitions are predicted to have positive *A* terms (see Table II), and the observed MCD spectrum shows two distinct positive *A* terms centered at 4.77 and 4.90 μm^{-1}, respectively. The *B*-term contributions from magnetic interaction between these two close-lying Π_u states are expected to be small because they depend upon integrals of the type $\langle 2\sigma_g^+|\mu|\delta_g\rangle$, which are zero for pure atomic 5d orbitals ($2\sigma_g^+ \sim d_{z^2}$ and $\delta_g \sim d_{xy}$, $d_{x^2-y^2}$). Therefore, there should be very little pseudo-*A*-term (*B* terms of opposite signs for close-lying states) contribution to the MCD in the region of bands III and IV. It is noteworthy that these two bands are analogous to two bands near the same energy for $Au(PEt_3)_2^+$, but there the intensity pattern in reversed: a shoulder and weaker MCD band is observed at 4.78 μm^{-1}, while a maximum and strong positive *A* term is observed at 4.88 μm^{-1}.[14] On the basis of intensity and band shape, it appears that the relative energy of the two transitions is reversed between $Au(PEt_3)_2^+$ and $Au(P(t\text{-}Bu)_3)_2^+$. This observation can be interpreted as a lower energy placement of the weakly antibonding $2\sigma_g^+$ orbital compared to the strictly nonbonding δ_g orbitals in the $P(t\text{-}Bu)_3$ complex, which in turn would imply a lower σ-donor ability for $P(t\text{-}Bu)_3$ than PEt_3 toward Au(I). The steric requirements of the bulky *t*-Bu groups may be responsible for a lower donor ability of the ligand in spite of the greater Brønsted basicity of $P(t\text{-}Bu)_3$ compared to PEt_3 (pK_a for PR_3H^+ for *t*-Bu, 11.4; that for Et, 8.69).[20] However the two excited states are separated by only 0.1–0.13 μm^{-1} in either case and it must be admitted that the effect is small.

The lower energy weaker bands in the spectrum of $Au(P(t\text{-}Bu)_3)_2^+$, band I at 4.03 μm^{-1} and band II at 4.18 μm^{-1}, are assigned as transitions to the Π_u and Σ_u^+ spin–orbit states of $a^3\Pi_u$ and $b^3\Pi_u$ parentage (see Table II). The unsymmetrical MCD in the region of band I is interpreted as a combination of a positive *A* term for the lowest energy $\Pi_u(1)$ state and a positive pseudo-*A* term from the interaction of $\Pi_u(1)$ and the lowest energy, close-lying $\Sigma_u^+(1)$ state. In contrast to *B* terms for the predominantly singlet Π_u states, the *B* terms for the lowest $\Sigma_u^+(1)$ and $\Pi_u(1)$ states are large and of opposite sign and therefore are expected to give rise to a significant positive pseudo-*A* term.[17,18] The Σ_u^+ and Π_u spin–orbit states of both $a^3\Pi_u$ and $b^3\Pi_u$ will be strongly intermixed, but calculations place the lowest energy $\Sigma_u^+(1)$ and $\Pi_u(1)$ states close

---

(19) Piepho, S. B.; Schatz, P. N. *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism*; Wiley-Interscience: New York, 1983. This reference describes the standard (Stephens) definitions and conventions that are used here.

(20) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

in energy (within bandwidths) and near the energy of band I and the other pair of states $\Pi_u(2)$ and $\Sigma_u^+(2)$ to higher energy, though not so close together, near the energy of band II.[17] This interpretation of bands I and II for $Au(P(t\text{-}Bu)_3)_2^+$ is analogous to that advanced[14] for the two lowest energy bands at 3.98 and 4.20 μm^{-1} for $Au(PEt_3)_2^+$.

$Pt(P(t\text{-}Bu)_3)_2$ Spectra. The absorption and MCD spectra for $Pt(P(t\text{-}Bu)_3)_2$ can also be interpreted in terms of 5d → $1\pi_u$ transitions, which parallel those for $Au(P(t\text{-}Bu)_3)_2^+$ when allowance is made for differences in metal orbital stability between the two complexes. For example, the notable red shift in the lowest energy bands of the Pt(0) complex compared to the Au(I) complex can be easily rationalized by the d → p/MLCT nature of the transitions. The occupied $2\sigma_g^+$, δ_g, and $1\pi_g$ "metal" orbitals are expected to be less stable relative to the empty $1\pi_u$ "ligand" orbitals for the Pt(0) complex leading to lower energy MLCT than that for the Au(I) complex. The 5d → 6p atomic orbital energy separation is also lower for Pt(0) ($\sim$3.0 μm^{-1} compared to $\sim$6.3 μm^{-1} for Au(I) in the free ions[21]), which will cause a red shift in the d → p component of each transition. The overall shift observed (1.4–1.5 μm^{-1}) must reflect changes in composition of the $1\pi_u$ orbital and thus the proportion of d → p and MLCT character for the transitions, which unfortunately cannot be separated in any easy way. The relatively lower energy 6p orbitals for Pt(0) however would argue for a greater d → p component for the Pt(0) complex, but the symmetries and number of excited states will be unchanged. Furthermore, unless there is a significant reordering of the occupied orbitals in the Pt(0) complex or electron repulsion differences (assumed to be small) change drastically, the pattern of lowest energy transitions is expected to be similar to that for Au(I) complex only red-shifted. Therefore, the intense band III at 3.21 μm^{-1} for $Pt(P(t\text{-}Bu)_3)_2$ is assigned as unresolved transitions to the spin–orbit Π_u states, which are predominantly $a^1\Pi_u$ and $b^1\Pi_u$. The two positive A terms expected are likewise assumed to be unresolved, simply adding to reinforce each other to give the strong term centered at 3.26 μm^{-1}. This assignment is analogous to that proposed above for bands III and IV for $Au(P(t\text{-}Bu)_3)_2^+$, where the two Π_u states are assumed to be close in energy, but there the transitions are just resolved. Similarly, band I at 2.60 μm^{-1} for $Pt(P(t\text{-}Bu)_3)_2$ is assigned as the unresolved transitions to the lowest energy $\Pi_u(1)$ and $\Sigma_u^+(1)$ spin–orbit states of $a^3\Pi_u$ and $b^3\Pi_u$ parentage. The magnitude of the observed positive A term at 2.60 μm^{-1} is too large to be explained by the A term for the $\Pi_u(1)$ state alone. Estimates of $\bar{A}_1/\bar{D}_0$ from the experimental spectra (by the method of moments[19]) give +2.1 ± 0.1, whereas the $\bar{A}_1/\bar{D}_0$ for a Π_u state from $a^3\Pi_u$ or $b^3\Pi_u$ should have a value closer to +1 (see Table II). The larger observed $\bar{A}_1/\bar{D}_0$ is therefore consistent with a significant pseudo-A-term contribution predicted earlier[17] for the lowest energy $\Pi_u(1)$ and $\Sigma_u^+(1)$ spin–orbit states. Finally, the shoulder at 3.03 μm^{-1} (band II) for $Pt(P(t\text{-}Bu)_3)_2$ exhibits a weak positive A term in the MCD, which would be consistent with the transition to $\Pi_u(2)$, the second spin–orbit Π_u state of $a^3\Pi_u$ and $b^3\Pi_u$ parentage. The transition to $\Sigma_u^+(2)$ is also expected in this energy region but is assumed to be unresolved. The earlier calculation predicted smaller B terms for $\Pi_u(2)$ and $\Sigma_u^+(2)$ because the states are not so close in energy and there are contributions of differing sign from other states both at higher and lower energies.

The intense band V at 4.13 μm^{-1} and the weaker shoulder band IV near 3.97 μm^{-1} for $Pt(P(t\text{-}Bu)_3)_2$ lie 0.7–0.9 μm^{-1} higher in energy than band III and have no observed counterparts in the $Au(P(t\text{-}Bu)_3)_2^+$ spectrum below the measurement limit of 5.2 μm^{-1}. These bands are logically assigned as transitions to states of the higher $(1\pi_g)^3(1\pi_u)$ configuration (Table II). On the basis of intensity, band V is assigned as the transition to the Σ_u^+ spin–orbit state that is predominantly $^1\Sigma_u^+$. The MCD is consistent with this assignment in that the maximum in the MCD spectrum is very near the maximum of band V and therefore is properly interpreted as a positive B term. The broad MCD minimum at 3.77 μm^{-1} is significantly lower in energy than the shoulder band IV, but a term assignment is rendered uncertain by the incomplete resolution in the absorption spectrum. The shoulder and broad MCD likely signal the presence of one or more unresolved transitions to states of the $(1\pi_g)^3(1\pi_u)$ configuration, which are predominantly triplet in origin. Reasonable candidates expected[17] lower in energy than the $\Sigma_u^+(^1\Sigma_u^+)$ state are $\Pi_u(^3\Sigma_u^+)$ and $\Pi_u(^3\Sigma_u^-)$. Both are predicted to have positive A terms and to have nonzero B terms from interaction with the $\Sigma_u^+(^1\Sigma_u^+)$ state. The observed MCD suggests that a negative B-term contribution dominates, but a more precise interpretation is not possible from the present results.

A broad high-energy band with substantial intensity is observed for $Pt(P(t\text{-}Bu)_3)_2$ as a shoulder near 4.8 μm^{-1} in CH_3CN or as a maximum at 4.71 μm^{-1} in *n*-hexane. This band is characterized by zero MCD in both solvents. The lack of measurable MCD indicates a transition to a state with no magnetic moment or angular momentum. There are no such states among the 5d → $1\pi_u$ configurations. A charge transfer to solvent (CTTS) type of transition seems unlikely because there is only a very small solvent dependence between two rather different solvents. The transition could possibly be an internal ligand transition, but is it difficult to visualize such a transition that would both be allowed and have no excited-state angular momentum. One possibility that would be consistent with the results is the transition $1\sigma_u^+ \rightarrow 3\sigma_g^+$, a ligand σ to metal 6s charge transfer (LMCT), which would produce a Σ_u^+ excited state that would not have an excited-state magnetic moment (zero A term) or mix effectively with other states (zero B term). The absence of this transition to lower energy for the Au(I) complex can be explained by assuming a greater σ donation by the $P(t\text{-}Bu)_3$ ligand toward the positively charged metal ion, which would increase the bonding $1\sigma_u^+$–antibonding $3\sigma_g^+$ energy separation.

Concluding Remarks. The d → p/MLCT 5d → $1\pi_u$ excited configurations are adequate for interpreting the absorption and MCD spectra for both $Pt(P(t\text{-}Bu)_3)_2$ and $Au(P(t\text{-}Bu)_3)_2^+$, except for the highest energy band VI for the Pt(0) complex. The red shift in the spectra from Au(I) to Pt(0) is expected from differences in metal orbital stability, and a greater proportion of the d → p component is suggested for the Pt(0) complex due to relatively lower energy 6p orbitals. The red-shifted Pt(0) spectra permit the observation of transitions to states of the $(1\pi_g)^3(1\pi_u)$ configuration, which have not been observed previously for Au(I) complexes in the spectral region accessible to measurement (<5.2 μm^{-1}). Among the lower energy bands (I–III) there is a slightly larger energy separation between band III and band I for the Au(I) complex (0.75 μm^{-1}) compared to the Pt(0) complex (0.61 μm^{-1}), which can be ascribed to slightly larger spin–orbit interaction, but the absorption and MCD spectra are analogous for the two complexes. The assignments suggest the ordering of the occupied 5d orbitals in both cases is $2\sigma_g^+ \approx \delta_g > 1\pi_g$, assuming electron repulsion differences are small. Thus, the $5d_{z^2}$ orbital is not strongly involved in P → M σ bonding and the $5d_{xz}$,$5d_{yz}$ π orbitals are stabilized slightly, which can be interpreted as due to M → P back-bonding, but the stabilization is not very large. The conclusion of minimal 5d orbital involvement in bonding in two-coordinate Au(I) complexes reached in earlier studies[14,17,18] applies equally well to $Pt(P(t\text{-}Bu)_3)_2$ studied here. The 6s and $6p_z$ orbitals undoubtedly bear the strongest burden of Pt–P bonding, as suggested by the recent calculations for $Pt(PH_3)_2$.[13]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

(21) Moore, C. E. *Natl. Bur. Stand. Circ.* (*U.S.*) **1958**, *No. 467*, Vol. III.