value would be in favor of **10′** (strong O–H···N interaction) rather than **10″**.

Comparison between the Reactivities of 1 and 2. It is particularly noteworthy that the two closely related phosphoranes **1** and **2**, which differ only by the number of methylene groups, exhibit a quite different reactivity toward **6**: **2** reacts *instantaneously* with 1 equiv of **6** to yield the P–O–C sequence containing adduct **9** whereas **1** reacts *slowly* with 1 equiv of **6** to give the P–C–O sequence containing compound **10**.

This difference may be assigned to the presence, for **2**, of the open tautomeric form cyclamphosphine. It is generally assumed that the initial site of attack of tertiary phosphine on activated ketone is located on oxygen, producing a phosphonium–carbanion 1:1 intermediate, which reacts rapidly with a second ketone to give dioxaphospholane.[2a] The observed reactivity of **2** may thus be attributed to the aminophosphine open form **2′** and would involve phosphorus, its most nucleophilic site, leading to the intermediary compound **14**. This may evolve to give **9** either (i) by intramolecular nucleophilic addition of the free nitrogen site on the phosphorus followed by transprotonation (Scheme II, route I) or (ii) by direct abstraction of the N-bound proton by the carbanion site followed by an intramolecular attack of the amide on the phosphonium site (route II).

The presence of the NH tentacle in the intermediate **14** probably inhibits the formation of a dioxaphospholane, which might have been expected if **2′** behaved as a typical tertiary phosphine. Protonation of the carbanion and ring closure are probably more rapid than condensation with a second equivalent of ketone.

It should be noted that the presence of **13** in the crude mixture in about 15% cannot arise only from the slow transformation of **9**. It may be taken to indicate that intermediate B (route II) is formed: this intermediate evolves either to **9**, by addition on the phosphonium site, or to **13** by nucleophilic attack at the POC carbon and formation of the P=O bond.

On the other hand, **1** seems to exhibit the expected P–H reactivity of phosphoranes toward **6** with the formation of the phosphorane alcohol **10**. However, it has been proposed that the hydrospirophosphoranes react by their open form,[3c] yielding a P–C–O compound, by the attack of phosphorus on the carbonyl carbon atom. This cannot be the case for **1**: its open form **1′** is structurally and electronically very close to **2′**; therefore, we would have expected the formation of the P–O–C compound analogous to **9** through attack of phosphorus on the carbonyl oxygen atom.

Furthermore, the basicity of the apical nitrogen atoms in **1**[1a,c] and the acidity of the P–H bond in phosphoranes have also been established.[7] These results may be taken to indicate that the conjugated base of **1**, cyclenphosphoranide anion **11**,[8] might react with **6**, through attack at the carbon atom of the ketone, to give **12** as depicted in Scheme III. This seems to be confirmed by the fact that **11**, obtained quantitatively by deprotonation with LiMe,[9] reacts instantaneously with **6** to give **10** (after hydrolysis). By this work, we have contributed to establishing that the hydrophosphorane/phosphoranide acid–base equilibrium must be taken into account in the reactivity of tetracyclic tetraaminophosphoranes, especially when the phosphorane/phosphine tautomeric equilibrium is not operating.

Experimental Section

Compounds **1** and **2** were prepared according to Richman's method.[10]

$C_{18}H_{26}N_4POF_3$ (9). A 0.183-g (1.05-mmol) sample of **6** (Aldrich) in 20 mL of hexane is added, at −70 °C, to a solution of **2** (0.249 g, 1.10 mmol) in 40 mL of hexane. The reaction mixture is immediately filtered and concentrated, and a crystallization in pentane at −30 °C yields 0.317 g (70%) of **9** as white needles. **9** is soluble in all common organic solvents but evolves into **13** in a few weeks in CH_2Cl_2, $CHCl_3$, or toluene. Anal. Calcd for $C_{18}H_{26}N_4POF_3$ (M_r 402): C, 53.73; H, 6.51; N, 13.92; P, 7.69. Found: C, 53.07; H, 6.54; N, 13.93; P, 7.69. $^{31}P\{^1H\}$ NMR (toluene): δ −56 (s). ^{19}F NMR (C_6D_6): δ −75.9 (d, $^3J_{FH} = 7.5$ Hz). ^1H NMR (C_6D_6): δ 7.4 (m, C_6H_5), 5.7 (dq, $^3J_{HF} = 7.5$ Hz, $^3J_{HP} = 15$ Hz, H-(CCF_3Ph)), 2.8 (m, CH_2N), 1.55 (m, $CH_2(CH_2N)_2$). MS (chemical ionization with NH_3; *m/e*): MH^+ (100%).

$C_{16}H_{22}N_4POF_3$ (10). A 0.126-g (0.70-mmol) sample of **6** in 20 mL of pentane is added dropwise to a solution of **1** (0.145 g, 0.70 mmol) in 50 mL of pentane, at −70 °C. The reaction mixture is then allowed to warm to room temperature and stirred for 4 h. The solvent is evaporated, and crystallization in CH_2Cl_2 by slow evaporation yields 0.230 g (85%) of **10** as white parallelepipedic crystals. Compound **10** is very soluble in CH_2Cl_2 and $CHCl_3$ and quite soluble in pentane, toluene, and CH_3CN; mp 145 °C. Anal. Calcd for $C_{16}H_{22}N_4OPF_3$ (M_r 374): C, 51.34; H, 5.92; N, 14.97; P, 8.27. Found: C, 51.24; H, 5.88; N, 15.01; P, 8.28. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −35 (q, $^3J_{PF} = 3$ Hz). ^{19}F NMR ($CDCl_3$): δ −71.8 (d, $^3J_{FP} = 3$ Hz). ^1H NMR ($CDCl_3$): δ 8.9 (d, $J_{HP} = 20$ Hz, H(O or N)), 7.5 (m, C_6H_5), 2.8 (m, CH_2N). ^{13}C NMR ($CDCl_3$): δ 138.6, 127.5, 126.9 (C_6H_5); 126.5 (q, $^1J_{CF} = 285$ Hz, CF_3); 79.0 (dq, $^1J_{CP} = 135$ Hz, $^2J_{CF} = 27$ Hz, $C(CF_3(Ph)OH)$); 43, 42.5 (d, d, $^2J_{CP} = 10$ Hz, $^2J_{CP} = 9$ Hz, CH_2N). MS (chemical ionization with NH_3, *m/e*): MH^+ (46%).

Synthesis of 10 from 11. A 0.35-mL aliquot of a 1.6 N solution of CH_3Li in ether is added dropwise to 0.102 g (0.51 mmol) of **1** in 10 mL of THF at −45 °C to give **11** (^{31}P NMR (THF): δ 4.5). A 0.100-g (0.57-mmol) sample of **6** in 5 mL of THF is added to the reaction mixture at −45 °C to give **12**, which is immediately hydrolyzed by about 0.5 mL of H_2O. The solvent is pumped away, and the crude mixture is washed with 3 × 10 mL of toluene. The toluene is evaporated to yield 0.165 g of **10** (87%).

Registry No. **1**, 64317-97-1; **2**, 64317-99-3; **6**, 434-45-7; **9**, 112460-78-3; **10**, 112460-80-7; **11**, 112460-81-8; **13**, 112460-79-4.

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(7) Garrigues, B.; Boyer, D.; Munoz, A. *Can. J. Chem.* **1984**, *62*, 2170.

(8) Riess, J. G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Quin, L., Verkade, J. G., Eds.; Verlag Chemie: Weinheim, FRG; in press.

(9) The reaction is selective. A variation of temperature or concentration does not affect the ^{31}P NMR spectrum.

(10) (a) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* **1978**, 4333. (b) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149.

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Emission Properties of Tetrahedral $M(dppp)_2$ Complexes (M = Pd, Pt). Crystal and Molecular Structure of $Pt(dppp)_2$

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Reports on the electronic spectroscopy and photochemistry of d^{10} ML_3 and d^{10}–d^{10} M_2L_6 (L = P-donor) complexes have recently appeared.[1,2] Absorptions attributable to p ← d transitions have been identified, and the lowest emissive excited states have been assigned ($^3[(d_{xy},d_{x^2-y^2})^3(p_z)^1]$, ML_3; $^3[(d\sigma^*)^1(p\sigma)^1]$, M_2L_6).[2] Most of these complexes possess long-lived excited states that are capable of undergoing photooxidative substitution with elimination of a phosphine ligand. In particular, the mononuclear and binuclear palladium complexes photoreact readily with halogenated hydrocarbons and aromatic compounds to produce oxidized species in which two electrons per metal atom have been transferred.[1]

Little is known about the effects of structural perturbations on the excited-state lifetimes and energies of d^{10} species. For this reason, we have measured the lifetimes and electronic spectra of $M(dppp)_2$ (M = Pd, Pt; dppp = bis(diphenylphosphino)propane) complexes in the solid state and in fluid solutions at room temperature and at 77 K, and comparisons of these properties to those of trigonal-planar (d^{10} ML_3) species have been made. In connection with this work, the structure of $Pt(dppp)_2$ has been determined by X-ray crystallography.

Experimental Section

Materials. K_2PtCl_4 and K_2PdCl_4 (Aldrich) and triphenylphosphine and dppp (Strem) were used without further purification. $M(PPh_3)_3$[3] and $M(dppp)_2$[4] (M = Pd, Pt) were prepared according to standard proce-

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(1) Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718.

(2) Harvey, P. D.; Gray, H. B. *J. Am. Chem. Soc.*, in press.

(3) Ittel, S. D. *Inorg. Synth.* **1976**, *17*, 117.

Table I. Crystal and Intensity Collection Data

formula: $PtP_4C_{54}H_{52}$
fw: 1020.00
cryst color: orange
habit: prismatic
a = 18.306 (3) Å
b = 13.322 (2) Å
c = 10.067 (3) Å
β = 109.28 (2)°
V = 2317 (1) Å^3
Z = 2
λ = 0.71073 Å
T = 23 °C

graphite monochromator
space group: $C2/m$
absences: hkl, $h + k = 2n + 1$
cryst size: 0.14 × 0.11 × 0.10 mm
μ = 33.57 cm^{-1} (μr_{max} = 0.34)
CAD-4 diffractometer
θ–2θ scan
2θ range: 2–56°
octants collected: $\pm h,k,l$; $\pm h, -k, l$
no. of rflns measd: 6194
no. of indep rflns: 2903
no. with $F_o^2 > 0$: 2902
no. with $F_o^2 > 3\sigma(F_o^2)$: 2847
goodness of fit for merging data: 0.994

dures. The complexes were purified by triple-recrystallization in benzene/ethanol or benzene/propanol. The purity was checked by elemental analysis and ^{31}P and ^{1}H NMR spectroscopy (500 MHz; 1000 scans). Because $M(PPh_3)_3$ complexes are air-sensitive, they were stored in an oxygen-free drybox when not in use. The complexes are also light-sensitive in the solid state and were stored in the dark.[5] Ethanol, propanol, and 2-MeTHF (Aldrich) were purified according to standard procedures.[6,7] Benzene (B&J) was used without further purification. All syntheses were performed in a nitrogen-flush box, and spectroscopic measurements were made after freeze–pump–thaw degassing of the solutions.

Measurements. The UV–visible spectra were recorded on a Cary 17 spectrometer. The emission and excitation spectra were obtained by using a Perkin-Elmer MMPF-66 spectrofluorimeter. The emission lifetimes were measured on a Quanta Ray Nd-YAG (8-ns fwhm, 355- and 532-nm excitation) laser system.[8]

X-ray Data Collection.[9] A crystal of $Pt(dppp)_2$ obtained from benzene/ethanol was glued onto a glass fiber with epoxy cement and mounted on a CAD-4 diffractometer. Unit cell dimensions were calculated from the setting angles of 25 reflections with 19° < 2θ < 24°. Three check reflections showed no variations greater than counting statistics would predict. Backgrounds were counted at each end of each scan, and an average background as a function of 2θ was calculated and used. Lorentz and polarization factors were applied. No absorption correction was made: after data collection, the crystal was knocked off its fiber before it was measured or the faces were identified.

Statistics strongly indicated a noncentrosymmetric space group. A Patterson map placed the platinum atom at the origin and located the phosphorus atoms of the ligand. The remaining ligand atoms were found (with difficulty, because of false mirror symmetry) in the Fourier map, and the structure was refined to an R value of 0.075 in space group $C2$. It was apparent then that this structure was incorrect. The phenyl rings had badly distorted geometries, and the difference map had many residual peaks of 2.5–3.5 e Å^{-3}. We attempted to improve matters by averaging the data in point group 2 (the original averaging had been in $2/m$) and including F'', but the problems remained. We returned to the original data and calculated a Fourier map for $C2/m$. The ligand atoms could be picked out from their mirror images; refinement led to a final R index of 0.027 and a goodness of fit of 1.14. The final cycles varied positional and anisotropic thermal parameters of all non-hydrogen atoms except four carbon atoms; these were treated isotropically because of the mirror disorder. Hydrogen atoms were included at calculated positions (C–H = 0.95 Å) with isotropic B's 20% greater than those of the carbon atoms to which they are bonded; their parameters were not refined but were adjusted three times. The final refinement included 247 parameters in a single matrix. The final shifts were all less than 0.03σ; the maximum excursions in the final difference map were +0.45 and −0.43 e Å^{-3}. Despite the strong statistical evidence for a noncentrosymmetric structure, and despite the fact that the $C2/m$ structure has a mirror disorder for 29 out of its 30 heavy atoms, the successful refinement to a low value of the R index and a satisfactory goodness of fit, with regular geometry for the ligands, indicates that the choice of space group is correct.

Table II. Final Parameters for Bis[bis(diphenylphosphino)propane]platinum(0)[a] (x, y, z, and U_{eq}[b] $\times 10^4$)

atom	x	y	z	U_{eq} or B, Å^2
Pt	0	0	0	250 (0.4)
P1	443 (1)	989 (1)	1934 (1)	253 (3)
P2	−919 (1)	−879 (1)	655 (1)	272 (3)
C1	−262 (3)	1236 (4)	2851 (5)	350 (11)
C2	−672 (3)	286 (4)	3116 (5)	384 (12)
C3	−1306 (2)	−123 (6)	1794 (4)	2.5 (1)[c]
C11	741 (3)	2264 (4)	1659 (5)	312 (11)
C12	1310 (3)	2363 (4)	1023 (6)	400 (12)
C13	1546 (4)	3287 (5)	703 (7)	522 (16)
C14	1208 (4)	4147 (5)	1021 (7)	545 (17)
C15	651 (4)	4082 (5)	1631 (7)	554 (17)
C16	418 (4)	3143 (5)	1953 (7)	454 (15)
C21	1286 (4)	604 (5)	3464 (7)	2.2 (1)[c]
C22	1426 (4)	−409 (5)	3597 (8)	2.9 (2)[c]
C23	2051 (4)	−807 (6)	4770 (7)	432 (19)
C24	2535 (3)	−153 (7)	5680 (5)	3.3 (1)[c]
C25	2391 (4)	884 (6)	5507 (8)	585 (21)
C26	1760 (4)	1253 (6)	4372 (7)	496 (19)
C31	−645 (3)	−2017 (4)	1770 (6)	374 (12)
C32	70 (4)	−2444 (4)	1978 (7)	490 (16)
C33	325 (5)	−3237 (6)	2892 (10)	724 (24)
C34	−139 (6)	−3616 (6)	3626 (9)	879 (28)
C35	−860 (6)	−3213 (6)	3407 (9)	838 (25)
C36	−1110 (4)	−2426 (5)	2488 (7)	578 (16)
C41	−1829 (3)	−1293 (4)	−677 (5)	339 (11)
C42	−1961 (3)	−2297 (5)	−1087 (6)	453 (14)
C43	−2636 (4)	−2573 (6)	−2151 (7)	584 (17)
C44	−3177 (4)	−1868 (7)	−2807 (7)	671 (20)
C45	−3066 (4)	−884 (6)	−2426 (7)	610 (19)
C46	−2385 (3)	−592 (5)	−1378 (6)	444 (14)

[a] The platinum atom is at a twofold position. The other atoms are in general eightfold positions with population parameters of 0.5. [b] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a^*{}_j)(\vec{a}_i\cdot\vec{a}_j)]$. [c] Isotropic displacement parameter, B.

Table III. Selected Distances (Å) and Angles (deg) in the $Pt(dppp)_2$ Molecule

Pt–P1	2.268 (1)	P2–C3	1.835 (5)
Pt–P2	2.317 (1)	P2–C31	1.854 (6)
P1–C1	1.847 (5)	P2–C41	1.845 (5)
P1–C11	1.832 (5)	C1–C2	1.540 (7)
P1–C21	1.856 (7)	C2–C3	1.547 (7)
P1–Pt–P2	97.9 (1)	P1–C1–C2	113.7 (4)
P1–Pt–P2[a]	116.8 (1)	C3–C2–C1	114.3 (4)
P1–Pt–P1[a]	108.9 (1)	P2–C3–C2	113.3 (4)
P2–Pt–P2[a]	119.3 (1)		

[a] Symmetry related (a twofold axis).

Results and Discussion

The X-ray crystal structures of $Pt(PPh_3)_3$,[10] $Pt_2(dppm)_3$[11] (dppm

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(4) Clark, H. P.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107.

(5) Both $M(PPh_3)_3$ solids give bright yellow crystals after multiple recrystallizations but turn pale gold (Pd) and orange (Pt) in room light.

(6) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, England, 1966.

(7) 2-MeTHF was purified according to the procedure outlined for THF in: Gordon, A. J.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*; Wiley: New York, 1979; p 436.

(8) Nocera, D. G.; Winkler, J. R.; Yocom, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5145.

(9) (a) Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from ref 9b. $R = \sum|F_o - |F_c|| / \sum F_o$, for only $F_o^2 > 0$, and goodness of fit = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of data and p the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned on the basis of counting statistics plus an additional term, $0.02I^2$. Variances of the merged reflections were calculated by standard propagation of error plus another additional term, $0.02\,\langle I\rangle^2$. The secondary extinction parameter[9c] was refined to 0.40 (2) × 10^{-6}. (b) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 71, 149. (c) Larson, E. C. *Acta Crystallogr.* **1967**, *23*, 664.

(10) Albano, V.; Bellon, P. L.; Scatturin, V. *J. Chem. Soc., Chem. Commun.* **1966**, 507.

Table IV. Emission Lifetimes of d^{10} Palladium and Platinum Complexes

	2-MeTHF soln				solid state			
	295 K		77 K		295 K		77 K	
	τ_e, μs	λ_{max}, nm	τ_e, μs	λ_{max}, nm	τ_e, μs	λ_{max}, nm	τ_e, μs	λ_{max}, nm
$Pd(PPh_3)_3$[a,b]	6.61 ± 0.02	635	98 ± 1	590	82 ± 2	613	180 ± 3	592
$Pt(PPh_3)_3$[a,b]	0.69 ± 0.01	705	24.9 ± 0.1	645	6.9 ± 0.2	633	21.7 ± 0.1	677
$Pd(dppp)_2$[b]	≤0.02	620	≤0.02	612	29.4 ± 0.2	622	84 ± 1	632
$Pt(dppp)_2$[b]	≤0.02	620	≤0.02	618	≤0.02	622	0.048 ± 0.002	624

[a] Data in fluid solution are taken from ref 2. [b] Solid-state decays exhibit two additional components (one fast, one slow; ~10% of the total decay). In each case the fast component is ≤0.02 μs.

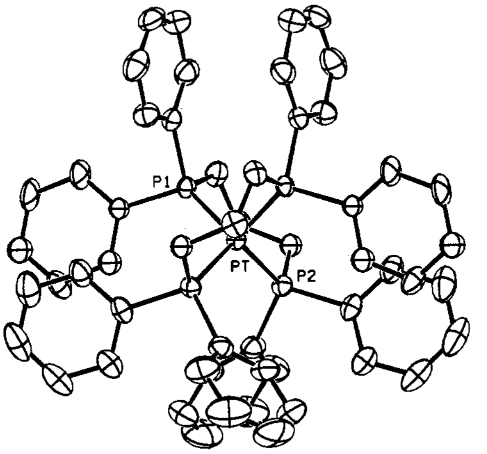

Figure 1. ORTEP drawing of $Pt(dppp)_2$. Thermal ellipsoids are shown at the 50% probability level. Only one of the disordered pair of ligands is shown.

= bis(diphenylphosphino)methane), $Pd(dba)_3$,[12] and $Pd_2(dba)_3$[13,14] (dba = dibenzylideneacetone) are known. The ML_3 units of the molecules are planar, with L-M-L angles approximately equal (in dba, the M—L bond is taken from the middle of the C=C bond).

Crystal and intensity collection data for $Pt(dppp)_2$ are given in Table I, and final parameters are in Table II. The complex has a distorted tetrahedral coordination about the platinum atom, with Pt-P distances of 2.267 (1) and 2.317 (1) Å; the four tetrahedral angles range from 97.9 to 119.3 (1)° (Figure 1). The Pt-P bond distances in $Pt_2(dppm)_3$[11] and $Pt(PPh_3)_3$[10] range from 2.232 (4) to 2.289 (4) Å and from 2.25 (1) to 2.28 (1) Å, respectively. The slightly longer Pt-P bond distances in $Pt(dppp)_2$ may well be related to the internal strain imposed by the ring system. The two diphosphine ligands are not perpendicular but make an angle of 102.9 (1)° with each other. This distortion is not reflected in unusual distances or angles in the ligands themselves, for these are normal[15] (Table III).

Solid samples of $M(dppp)_2$ exhibit very weak orange emissions; $M(PPh_3)_3$ solids are much more strongly luminescent (Figure 2).[16]

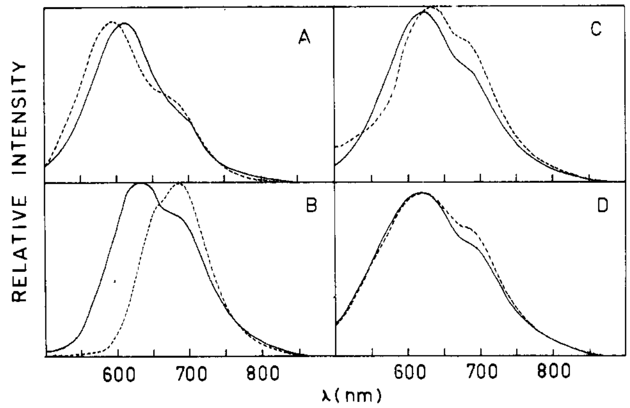

Figure 2. Solid-state emission spectra at 295 (—) and 77 K (---) of $Pd(PPh_3)_3$ (A), $Pt(PPh_3)_3$ (B), $Pd(dppp)_2$ (C), and $Pt(dppp)_2$ (D). Relative intensities follow the order $M(PPh_3)_3 >> M(dppp)_2$. In each case, I(77 K) > I(295 K). In each panel the intensities have been matched to allow a comparison of band shapes.

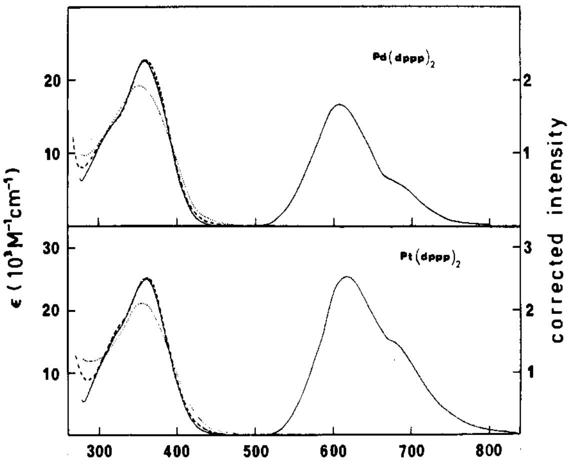

Figure 3. Electronic absorption (295 K, ···; 77 K, —), emission (—), and excitation (---) spectra of $M(dppp)_2$ at 77 K in 2-MeTHF.

The $M(dppp)_2$ emission maxima red-shift slightly, but the band shapes remain roughly the same at low temperature. Emission lifetimes are set out in Table IV.

The solution absorption and emission spectra of $M(PPh_3)_3$ have been interpreted previously.[2] The lowest singlet and triplet excited states have the $[(d_{x^2-y^2},d_{xy})^3(p_z)^1]$ configuration. The UV-visible, excitation, and emission spectra of $M(dppp)_2$ in 2-MeTHF are shown in Figure 3. The lowest energy absorption band (~360 nm, $\epsilon \approx 24000$ M^{-1} cm^{-1} at 77 K) is assigned to the spin-allowed $t_2(\pi^*,p\sigma^*) \leftarrow t_2(d\sigma^*)$ transition.[17]

A relatively short-lived weak orange luminescence also has been detected in $M(dppp)_2$ solutions. Since the energies and band

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(11) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1155.

(12) Mozza, M. C.; Pierpont, C. G. *Inorg. Chem.* **1973**, *12*, 2955.

(13) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J.-J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *64*, 253.

(14) (a) Pierpont, C. G.; Mazza, M. C. *J. Chem. Soc., Chem. Commun.* **1973**, 207. (b) Pierpont, C. G.; Mazza, M. C. *Inorg. Chem.* **1974**, *13*, 1891.

(15) The phenyl rings of the complex are all planar, the maximum deviation from a plane being 0.017 Å (C23), and the C-C distances are normal: they range from 1.347 (10) to 1.447 (10) Å, averaging 1.385 (21) Å. The extreme values are in ring 2, which is most affected by the disorder, but all the rings suffer some perturbation from the atoms of the other half-molecule that are near them. The average deviation of a C-C-C angle from 120° is 1°. The P-C bonds are all normal, with average distance 1.845 (10) Å (Table III). There are a few close contacts (shortest, 2.64 Å, C···C), but they can be eliminated in many cases by the disorder. The molecule appears to be fairly crowded, with many C···C approaches of 3.3-3.5 Å; this crowding may partially be the cause of the distorted tetrahedral coordination, reflecting the best fit the atoms are able to make.

(16) Unlike $M(PPh_3)_3$ and $M_2(dppm)_3$, the $M(dppp)_2$ complexes are air-stable in the solid state and decompose only slowly in oxygenated solutions.

(17) Orio, A. A.; Chastain, B. B.; Gray, H. B. *Inorg. Chim. Acta* **1969**, *3*, 8.

shapes of the emissions are similar for the solid-state and solution spectra, the four-coordinate structure of $M(dppp)_2$ appears to be intact in solution.[18] Because of the low solubility of the $M(dppp)_2$ complexes, absorptions attributable to spin-forbidden transitions could not be established with certainty.[19] The $M(dppp)_2$ emission lifetimes in 2-MeTHF (≤20 ns) are much shorter than those measured for $M(PPh_3)_3$ complexes. Assignment of the emissive state of $M(dppp)_2$ to $^3([t_2(d\sigma^*)]^5[t_2(\pi^*,p\sigma^*)]^1)$ is suggested.

Depopulation of $d\sigma^*$ in the emissive excited state should lead to a distortion toward a square-planar ML_4 structure.[20] It is reasonable to suggest that this distortion is related to the rapid excited-state decay that is observed.

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Registry No. $Pd(PPh_3)_3$, 28516-49-6; $Pt(PPh_3)_3$, 13517-35-6; $Pd(dppp)_2$, 31989-49-8; $Pt(dppp)_2$, 54206-19-8.

Supplementary Material Available: Tables V–VIII, listing thermal parameters, the derived hydrogen positions, and complete distances and angles in the molecule (3 pages); a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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[18] ^{31}P NMR spectra show no resonances attributable to free phosphine (see ref 4). For a number of ML_4 complexes (M = Pd, Pt and L = bulky phosphine ligand), extensive dissociation takes place in solution: Hartley, F. R. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 119.

[19] A very weak band at ~520 nm in each excitation spectrum might represent a triplet ← singlet transition.

[20] Irradiation (≥340 nm) of $Pd(dppp)_2$ in degassed 5% CH_2Cl_2/THF at room temperature gives $[Pd(dppp)_2]Cl_2$ and ethylene (2:1 mole ratio). The photoreaction differs from those reported[1] for $Pd(PPh_3)_3$ and $Pd_2(dppm)_3$ in that no phosphine is eliminated: Harvey, P. D.; Gray, H. B., unpublished results.

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Polynuclear Zinc(II) Complexes with Large Polyazacycloalkanes. Equilibrium Studies and Crystal Structure of the Binuclear $[Zn_2([30]aneN_{10})(NCS)](ClO_4)_3$ Complex

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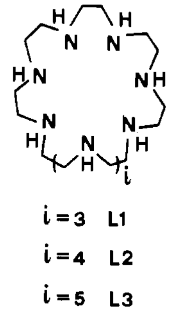
Large polyazacycloalkanes, defined as saturated aza macrocycles with more than six secondary nitrogens as donor atoms, are interesting ligand molecules. The cyclic nature, the elevated number of donor atoms available, and the molecular flexibility make these ligands very versatile for the formation of polynuclear metal complexes. In earlier papers we have reported the synthesis and the copper(II) complexes of many large polyazacycloalkanes.[2–5] In this paper we have investigated the formation equilibria of binuclear zinc(II) complexes of the three large polyazacycloalkanes 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane ($[27]aneN_9$), 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane ($[30]aneN_{10}$), and 1,4,7,10,13,16,19,22,25,28,31-undecazacyclotritriacontane ($[33]aneN_{11}$) (hereafter abbreviated as L1, L2, and L3, respectively). In the case of L2 a solid binuclear zinc(II) complex has been isolated and characterized by X-ray analysis.

Table I. Crystal and Refinement Data

mol formula	$C_{21}H_{50}Cl_3N_{11}O_{12}S_1Zn_2$
mol wt	917.86
a, Å	15.615 (3)
b, Å	13.678 (3)
c, Å	9.473 (2)
α, deg	78.85 (5)
β, deg	82.62 (5)
λ, deg	79.53 (5)
V, $Å^3$	1942.9
Z	2
space gp	$P1^a$
D_{calcd}, g cm^{-3}	1.56
radiation	Mo Kα, graphite monochromated
λ, Å	0.7107
temp, °C	25
μ, cm^{-1}	14.7
scan tech	$\theta/2\theta$
scan speed, deg min^{-1}	2.4
scan width, deg	$1.0 + 0.3 \tan\theta$
scan range, deg	$5.0 < 2\theta < 50.0$
cutoff of obsd data	$3.5\sigma(I)$
no. of obsd. reflcns	2128
no. of refined params	275
R^b	0.109
$R_w{}^c$	0.110

[a] Based on centric distribution of *E* values. [b] $R = \sum||F_0| - |F_c|| / \sum|F_0|$. [c] $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w(F_0)^2]^{1/2}$.



Experimental Section

Synthesis of the Zinc(II) Complex. Well-formed colorless prismatic crystals of the complex $[Zn_2L2]NCS(ClO_4)_3$ were obtained by slow evaporation at room temperature of a solution of L2 (0.01 mol dm^{-3}) containing $Zn(ClO_4)_2$ (0.02 mol dm^{-3}), KCNS (0.02 mol dm^{-3}), and $NaClO_4$ (2 mol dm^{-3}). The solution was maintained at pH ~12. The crystals were collected, rapidly washed with water and methanol, and then dried in vacuo. Anal. Calcd for $Zn_2C_{21}N_{11}H_{50}SCl_3O_{12}$: C, 27.48; H, 5.49; N, 16.79. Found: C, 27.4; H, 5.6; N, 16.7.

Emf Measurements. All potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ (C. Erba ACS grade). Purification and standardization of solutions used in the potentiometric titrations were performed according to the procedure described in ref 6. Hydrochloride salts of L1, L2, and L3 have been obtained as described in ref 4, 5, and 7, respectively. Aqueous solutions of zinc(II) perchlorate were obtained by dissolving the solid hydrate salt in water. The concentration of zinc(II) was determined gravimetrically by the standard method. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, cell, microcomputer, etc.) that has been fully described.[8] Two titration curves for each systems investigated were used.

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