and kinetically irreversible cathodic wave in the vicinity of −2 V vs. SCE.

Table VIII presents UV–vis data obtained for the homoleptic six-coordinate complexes; traces recorded for the d^6 complexes **1**, **4**, **8**, and **12** are shown in Figure 4. On the basis of assignments made by Mann et al. for $Cr(CNC_6H_5)_6$ and $[Mn(CNC_6H_5)_6]Cl$,[5] the two lowest energy bands for each complex are assigned as metal-to-ligand charge-transfer (MLCT) transitions of the type $d\pi \rightarrow \pi^*_v$, where π^*_v is the π^*_{CN} orbital which is lowered in energy by interaction with the phenyl-ring π^* orbitals.[52] Spectra of the Cr(0) and Mn(I) complexes are similar to their phenyl isocyanide analogues.[5] In Figure 4 and Table VIII, one can see that the $d\pi$–π^*_v bands for the d^6 compounds increase in energy in the following order: Cr(0) < Mn(I) < Fe(II) ~ Co(III). The spectra of the Fe(II) and Co(III) complexes are surprisingly similar, despite the difference in charge. For the Co(III) complex **12**, the $d\pi$–π^*_v energy gap is smaller than expected perhaps because of the absence of significant $d\pi$–π^*_{CN} back-bonding and/or lowering of the π^*_{CN} energies by σ-inductive effects caused by the strong electron-withdrawing ability of the Co^{3+}. The Cr(I) and Mn(II) complexes **2** and **5** afford blue-shifted spectra as compared with **1** and **4**, in accord with the MLCT nature of the transitions.[5]

Four-Coordinate Homoleptic Complexes. All the complexes of DiNC and *t*-BuDiNC prepared heretofore have employed the ligands either as chelating ligands at pseudooctahedral metal sites (i.e., with C–M–C angles of ca. 90°)[1-4] or as bridging ligands.[1] The following studies were carried out to determine if these ligands are able to chelate to pseudotetrahedral metal centers. If they did coordinate, a C–M–C angle in the chelate ring of 109° would require considerable distortion of the ligand from its normal geometry. However, if the ligand is not distorted, the C–M–C angle is likely to be close to 90°.

Reactions between $Ni(CO)_4$ and *t*-BuDiNC or DiNC afford the complexes $Ni(CO)_2(t\text{-BuDiNC})$ (**13**) and $Ni(CO)_2(DiNC)$ (**14**) in moderate yields (eq 5). The fully substituted complex $Ni(t\text{-BuDiNC})_2$ (**15**) is obtained from the reaction

$$\mathrm{Ni(CO)_4} + t\text{-BuDiNC} \rightarrow \underset{\mathbf{13}}{\mathrm{Ni(CO)_2}(t\text{-BuDiNC})} + 2\mathrm{CO} \tag{5}$$

between $Ni(CO)_4$ and additional *t*-BuDiNC (eq 6) (or via the

$$\mathrm{Ni(CO)_4} + 2t\text{-BuDiNC} \rightarrow \mathrm{Ni}(t\text{-BuDiNC})_2 + 4\mathrm{CO} \tag{6}$$

reaction of $Ni(CO)_2(t\text{-BuDiNC})$ with *t*-BuDiNC in $CHCl_3$ solution). Isoelectronic $[Cu(t\text{-BuDiNC})_2]BF_4$ (**16**) is synthesized by displacement of four CH_3CN ligands from $[Cu(CH_3CN)_4]BF_4$ by *t*-BuDiNC. The dicarbonyl derivatives **13** and **14** each exhibit two ν(CN) and two ν(CO) bands similar in energy to those of $Ni(CO)_2(CNC_6lH_5)_2$.[53] The mononuclearity of $Ni(CO)_2(t\text{-BuDiNC})$ was confirmed by an osmometric molecular weight determination, and $Ni(CO)_2(DiNC)$ is presumed to be mononuclear as well. The tetrasubstituted complexes $Ni(t\text{-BuDiNC})_2$ (**15**) and $[Cu(t\text{-BuDiNC})_2]BF_4$ (**16**) each exhibit a single, strong ν(CN) band at 2040 and 2169 cm^{-1}, respectively. Each complex is readily soluble in organic solvents such as $CHCl_3$. This observation, along with the known mononuclear structure of $Ni(CO)_2(t\text{-BuDiNC})$, suggests that **15** and **16** possess mononuclear, rather than polymeric, structures. It is clear that the *t*-BuDiNC ligand does chelate to normally tetrahedral metals. However, the exact structures of the complexes must await an X-ray diffraction investigation.

Acknowledgment. Support of this work by the National Science Foundation (Grant CHE78-07913 and CHE-8100419) is gratefully acknowledged. The authors thank Dr. Robert E. McCarley and Dr. William Beers for access to the electrochemical apparatus and for assistance in its operation.

Registry No. **1**, 87711-97-5; **2**, 87711-99-7; **3**, 87712-01-4; **4**, 87712-03-6; **5**, 87712-05-8; **6**, 87712-06-9; **7**, 87760-31-4; **8**, 87712-08-1; **9**, 87712-10-5; **10**, 87712-11-6; **11**, 87712-12-7; **12**, 87712-14-9; **13**, 87712-15-0; **14**, 87712-16-1; **15**, 87712-17-2; **16**, 87712-19-4; $CrCl_3(THF)_3$, 10170-68-0; $AgPF_6$, 26042-63-7; $Mn(CO)_5Cl$, 14100-30-2; $AlCl_3$, 7446-70-0; $CoCl_2$, 7646-79-9; $Ni(CO)_4$, 13463-39-3; $[Cu(CH_3CN)_4]BF_4$, 15418-29-8; Br_2, 7726-95-6.

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(53) (a) van Hecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966**, *5*, 1960. (b) Bigorgne, M. *Bull. Soc. Chim. Fr.* **1963**, 295.

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Synthesis and Structure of the Lithium Bromide–Pentamethyldiethylenetriamine 1:1 Adduct

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Reaction of BrBu-*n* with LiBu-*n*(PMDETA) affords in high yield (PMDETA)LiBr (**1**) (PMDETA = $Me_2N(CH_2)_2NMe(CH_2)_2NMe_2$), which forms dimeric aggregates in the solid. Crystals are triclinic, of space group $P\bar{1}$, with $a = 14.887$ (7) Å, $b = 11.737$ (6) Å, $c = 8.631$ (7) Å, $\alpha = 73.43$ (6)°, $\beta = 77.64$ (5)°, $\gamma = 80.93$ (4)°, and $Z = 2$ dimers. The unit cell contains a pair of dimeric aggregates possessing "bridging" bromine atoms; the metal–halogen distances within each centrosymmetric aggregate are unsymmetric. Li–Br: 2.51 (1) and 3.20 (2) Å, aggregate **1**; 2.57 (1) and 2.87 (1) Å, aggregate **2**.

Introduction

Permethylated amines readily form metal N-chelate complexes with main group 1 halides, with a feature of high solubility of the derived complexes in organic solvents.[1] Although solution properties of these complexes have been studied in depth by using NMR techniques, there being postulated solvent–complex interactions in order to account for ^1H chemical shift variations of CH_3 and CH_2 resonances,[2] no detail of the nature of these compounds in the solid is

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(1) A. W. Langer, Jr., and W. R. Moser, *Catal. Org. Synth.*, 219 (1978).

(2) A. W. Langer, *Adv. Chem. Ser.*, No. **130**, 113 (1974).

available. Accordingly, a structure determination on a selected complex of the type (tertiary amine)MX, viz. (PMDETA)LiBr (**1**) (PMDETA ≡ pentamethyldiethylenetriamine), has been undertaken.

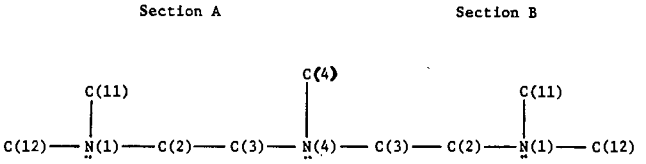
Experimental Section

Synthesis of LiBr(PMDETA) (1). To a stirred cooled (0 °C) solution of LiBu-*n* in hexane (2.5 cm^3, 1.6 M, 4.0 mmol) was added PMDETA (0.7 g, 4.0 mmol) followed by slow addition of a hexane solution of BrBu-*n* (0.60 g, 4.4 mmol, 10 cm^3 of $\mathrm{C_6H_{14}}$). A white crystalline precipitate formed, which was collected, washed with pentane (3 × ~5 cm^3), and dried in vacuo: yield 0.93 g (90%); mp 80–81 °C dec. Anal. Calcd for $\mathrm{C_9H_{23}BrLiN_3}$: C, 41.55; H, 8.91; N, 16.15. Found: C, 41.11; H, 8.81; N, 16.11. All manipulations were carried out under a dinitrogen atmosphere; PMDETA, hexane, and pentane were purified by distillation over KOH, $\mathrm{CaH_2}$, and $\mathrm{LiAlH_4}$, respectively.

Crystallography

Crystal Data: $\mathrm{C_{18}H_{46}Br_2Li_2N_6}$, M_r = 520.3, triclinic, space group $P\bar{1}$ (C_i^1; No. 2) (justified on the basis of successful solution and refinement); a = 14.887 (7) Å, b = 11.737 (6) Å, c = 8.631 (7) Å, α = 73.43 (6)°, β = 77.64 (5)°, γ = 80.93 (4)°, V = 1404 (2) Å^3, $D_{\mathrm{calcd}}(Z = 2)$ = 1.23 g cm^{-3}, $F(000)$ = 544, specimen size 0.25 × 0.42 × 0.48 mm (prism) (capillary), μ_{Mo} = 28.5 cm^{-1}, T = 295 K.

Structure Determination. A unique data set was measured to $2\theta_{\max}$ = 45° with a Syntex P2$_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode with graphite-monochromated Mo Kα radiation (λ = 0.7106_9 Å); 3694 independent reflections were obtained of which 2263 with $I > 3\sigma(I)$ were considered "observed" and used in the least-squares refinement after solution of the structure by direct methods and the application of an analytical absorption correction. For the non-hydrogen atoms, anisotropic thermal parameters were refined; for hydrogen atoms, x, y, z, and U were constrained as estimates, U_{H} being set at $1.25\bar{U}_{ii}$ (parent C, $\mathrm{CH_2}$) and $1.5\bar{U}_{ii}$(parent C, methyl). Residuals at convergence were R (R') = 0.047 (0.055), reflection weights being $(\sigma^2(F_o) + 0.0005F_o^2)^{-1}$. Neutral complex scattering factors were used.[3] Computation was carried out on a Perkin-Elmer 3240 instrument using the X-RAY 76 program system.[4] Atom numbering with each ligand (**1**, **2**) is as follows: each molecule, having pseudo-*m* symmetry in its asymmetric unit, is divided into two segments, A and B. Hydrogen atom numbering follows that of the



$$\begin{array}{ccccccccc} & \mathrm{C(11)} & & & \mathrm{C(4)} & & & \mathrm{C(11)} & \\ & | & & & | & & & | & \\ \mathrm{C(12)}- & \ddot{\mathrm{N}}\mathrm{(1)} & -\mathrm{C(2)}- & \mathrm{C(3)}- & \ddot{\mathrm{N}}\mathrm{(4)} & -\mathrm{C(3)}- & \mathrm{C(2)}- & \ddot{\mathrm{N}}\mathrm{(1)} & -\mathrm{C(12)} \end{array}$$

parent atom suffixed A, B, or C.

Discussion

Compound **1**, an extremely moisture-sensitive material, was prepared by a salt-elimination reaction between LiBu-*n*, activated with PMDETA, and Bu-*n*-Br in hexane, rather than direct complexation of base to the salt substrate.[2] The reaction takes advantage of the increase in reactivity of LiBu-*n* in the presence of a tertiary amine, ascribed to an increase in carbanionic character;[5] the reaction should have potential for the synthesis of lithium halide–tertiary amine complexes in general, particularly for polydentate bases, since it has been demonstrated that increasing the number of chelate rings enhances (base)LiBu-*n* reactivity. This is exemplified by (TMEDA)LiBu-*n* (TMEDA = tetramethylethylenediamine) being less reactive than (PMDETA)LiBu-*n*.[6]

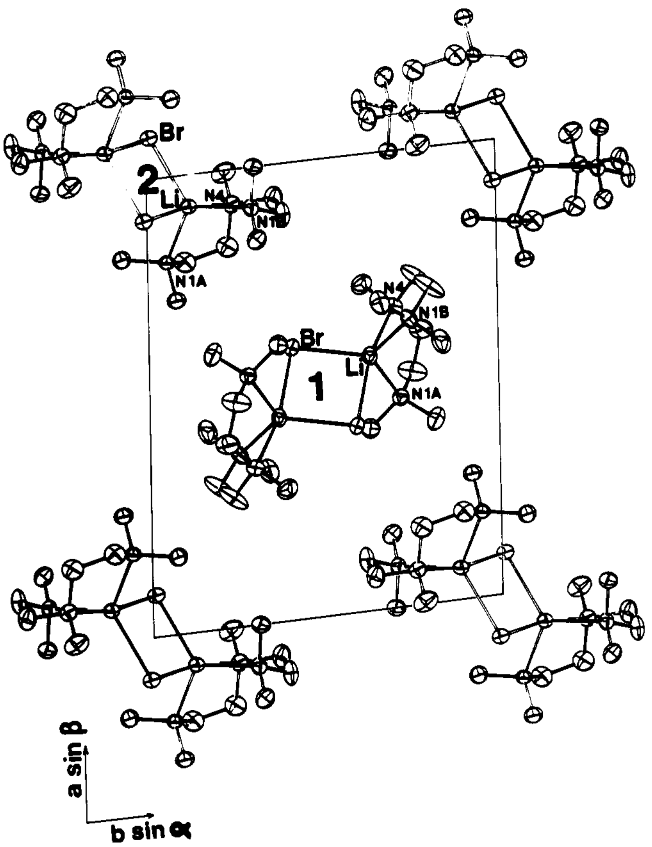


Figure 1. Unit cell contents projected down *c*, showing the non-hydrogen atoms with thermal ellipsoids at the 20% probability level.

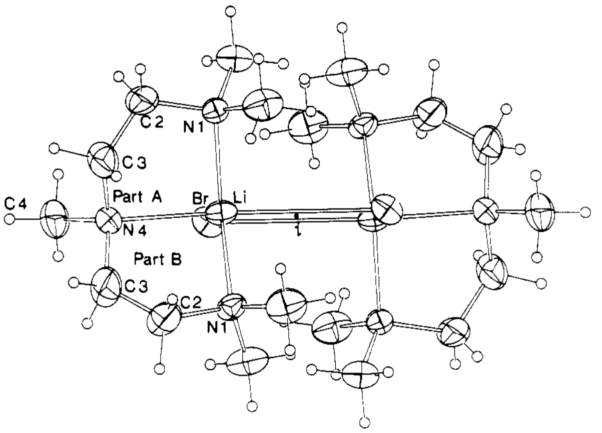


Figure 2. Projection of aggregate **1**, showing the hydrogen atoms with arbitrary radius 0.1 Å.

The thermal stability of **1**, melting with decomposition at 80–81 °C, contrasts with (TMEDA)LiX (X = halide) complexes, which can be prepared only at reduced temperatures, the difference in stability being consistent with enthalpy considerations.[2]

^{7}Li and ^{1}H NMR data support the existence of tight "ion pairs" in solution.[2] Complex **1** and related compounds, e.g. (*i*-HMTT)LiBr (*i*-HMTT = $[\mathrm{N((CH_2)_2NMe_2)_3}]$), are monomeric in benzene at low concentrations with solvent–complex association for increasing concentration (ca. >0.2 M). Furthermore, all complexes studied in $\mathrm{CH_2Cl_2}$ have been assumed to be monomeric.[2] Attempts to determine the molecular weight of **1** in $\mathrm{CH_2Cl_2}$ (ebullioscopy) were unsuccessful. In

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(3) "International Tables for X-ray Crystallography", Vol. 4, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974.

(4) "The X-RAY System—Version of March, 1976", Technical Report TR-446, Computer Science Center, University of Maryland, College Park, MD, 1976.

(5) K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", W. B. Saunders, Philadelphia, PA, 1977, p 827.

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Table I. Non-Hydrogen Atom Coordinates

	aggregate **1**			aggregate **2**		
	x	*y*	*z*	*x*	*y*	*z*
Li	0.5552 (9)	0.6313 (10)	0.0563 (14)	0.9302 (8)	0.1198 (11)	0.0981 (15)
Br	0.59378 (6)	0.40893 (7)	0.13513 (10)	1.09144 (5)	0.00868 (7)	0.12712 (9)
			Amine Ligand Section A			
N(1)	0.4569 (4)	0.7175 (5)	0.2222 (7)	0.8130 (4)	0.0549 (5)	0.2872 (6)
C(11)	0.3969 (6)	0.6296 (8)	0.3264 (10)	0.8309 (6)	−0.0743 (7)	0.3429 (10)
C(12)	0.4006 (7)	0.8175 (8)	0.1363 (11)	0.7272 (5)	0.0810 (7)	0.2230 (10)
C(2)	0.5105 (7)	0.7524 (11)	0.3227 (12)	0.8086 (6)	0.1073 (8)	0.4222 (9)
C(3)	0.6000 (6)	0.7793 (9)	0.2513 (13)	0.8310 (6)	0.2293 (8)	0.3706 (11)
N(4)	0.6580 (4)	0.7009 (6)	0.1601 (7)	0.9232 (4)	0.2434 (5)	0.2666 (7)
C(4)	0.7130 (6)	0.6105 (8)	0.2641 (12)	0.9950 (6)	0.2218 (9)	0.3636 (12)
			Amine Ligand Section B			
C(3)	0.7175 (8)	0.7659 (12)	0.0175 (12)	0.9260 (7)	0.3639 (8)	0.1557 (11)
C(2)	0.6917 (8)	0.8049 (11)	−0.1285 (11)	0.8869 (7)	0.3883 (7)	0.0113 (11)
N(1)	0.6251 (4)	0.7458 (5)	−0.1716 (7)	0.9105 (4)	0.2987 (5)	−0.0802 (7)
C(11)	0.6685 (7)	0.6623 (8)	−0.2622 (11)	0.8385 (6)	0.3143 (8)	−0.1808 (11)
C(12)	0.5678 (7)	0.8365 (8)	−0.2726 (11)	1.0001 (6)	0.3068 (8)	−0.1892 (11)

Table II. Lithium Atom Environments[a]

	$r_{\text{Li-L}}$	N(1A)	N(4)	N(1B)	Br′
Br	2.51 (1), 2.57 (1)	120.2 (5), 117.9 (5)	103.9 (4), 98.8 (5)	122.1 (5), 122.1 (5)	87.7 (4), 91.5 (4)
N(1A)	2.16 (1), 2.19 (1)		81.8 (5), 80.4 (5)	117.7 (6), 118.8 (5)	95.6 (5), 96.1 (5)
N(4)	2.28 (2), 2.31 (2)			80.5 (5), 79.8 (5)	167.8 (5), 169.6 (5)
N(1B)	2.19 (1), 2.24 (1)				90.4 (5), 93.5 (5)
Br′	3.20 (2), 2.87 (1)				

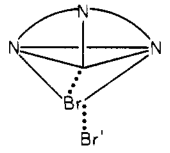
Li–Br–Li′ = 92.3 (4) Å (aggregate **1**), 88.5 (4) Å (aggregate **2**)

[a] The two values in each entry are for aggregates **1** and **2**, respectively. $r_{\text{Li-L}}$ is the lithium–ligand distance (Å); the other values in the matrix are the angles subtended at lithium by the two relevant atoms (deg). Primed atoms are generated by the intraaggregate inversion center.

the solid, however, we find **1** to be dimeric.

The unit cell contents confirm the stoichiometry of the complex as (PMDETA)LiBr, two formula units of which comprise the asymmetric unit of the structure. Examination of the unit cell contents (Figure 1), however, shows the presence of dimeric aggregates about crystallographic centers of symmetry, so that the asymmetric unit comprises two halves of two independent aggregates of the type (PMDETA)-LiBr_2Li(PMDETA).

The environments about each of the two independent lithium atoms are very similar (Table II). In each case the angular geometry is a very fair approach to trigonal bipyramidal, with three Li–N contacts, two of which, corresponding to the outer nitrogen atoms of the ligand, are equal while the third is rather longer. The two outer nitrogen atoms lie in the equatorial plane of the trigonal bipyramid with the central nitrogen axial. The third equatorial position is occupied by a Li–Br contact at 2.51 (1) and 2.57 (1) Å, and the other axial position by a centrosymmetrically generated contact to the bromine at a rather greater distance (3.20 (2), 2.87 (1) Å) (cf. the ionic radius sum for Li^+Br^- of 0.60 + 1.95 = 2.55 Å).[7] We thus find three close contacts in the equatorial plane and two longer axial ones, with the Li environment having local *m* symmetry:



This disposition of the five atoms about the metal atom, with the three nitrogen atoms of the tridentate ligand coordinating *fac* so that we find one halide axial and one equatorial, is parlleled by the dispositions observed in studies of complexes of the type MX_2(PMDETA) for other metals, notably those of the first transition series, typified by the structure of CoCl_2(PMDETA).[8] In its interaction with the lithium,

Table III. Ligand Geometries

	aggregate/section			
	1/A	**1**/B	**2**/A	**2**/B
	Distances/Å			
N(1)–C(11)	1.445 (10)	1.418 (12)	1.454 (9)	1.476 (12)
N(1)–C(12)	1.446 (10)	1.458 (11)	1.454 (10)	1.458 (9)
N(1)–C(2)	1.469 (15)	1.457 (16)	1.451 (12)	1.447 (11)
C(2)–C(3)	1.388 (13)	1.329 (15)	1.443 (14)	1.425 (15)
C(3)–N(4)	1.444 (12)	1.446 (11)	1.476 (10)	1.465 (9)
N(4)–C(4)	1.449 (11)		1.443 (13)	
	Angles/deg			
Li–N(1)–C(11)	107.3 (6)	102.5 (6)	107.7 (5)	116.6 (6)
Li–N(1)–C(12)	112.4 (6)	117.7 (6)	111.8 (5)	102.5 (5)
Li–N(1)–C(2)	106.7 (6)	107.8 (6)	107.6 (6)	108.1 (5)
C(11)–N(1)–C(12)	108.4 (6)	108.1 (7)	107.5 (6)	108.3 (6)
C(11)–N(1)–C(2)	109.4 (6)	112.4 (7)	109.6 (6)	107.4 (6)
C(12)–N(1)–C(2)	112.6 (8)	108.4 (7)	112.5 (6)	114.1 (7)
N(1)–C(2)–C(3)	117.2 (9)	121.1 (10)	113.8 (6)	116.0 (7)
C(2)–C(3)–N(4)	118.2 (10)	121.6 (11)	113.0 (7)	107.6 (6)
Li–N(4)–C(3)	103.3 (6)	104.9 (7)	102.8 (6)	104.9 (6)
Li–N(4)–C(4)	115.6 (6)		117.6 (6)	
C(3)–N(4)–C(4)	110.8 (7)	110.0 (7)	111.8 (6)	108.9 (7)
C(3)–N(4)–C(3)	112.0 (8)		110.6 (6)	

Table IV. Selected Amine Torsion Angles (deg) (Esd's Typically 0.7°)

	aggregate/section			
	1/A	**1**/B	**2**/A	**2**/B
N(1)–C(2)–C(3)–N(4)	−44.6	−26.1	−56.9	−45.0
C(4)–N(4)–C(3)–C(2)	−93.4	144.7	−86.1	157.3
Li–N(4)–C(3)–C(2)	31.0	19.8	41.0	30.7
Li–N(1)–C(2)–C(3)	30.0	15.8	37.9	31.7
C(2)–C(3)–N(4)–C(3)	143.3	−91.6	152.4	−79.5

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(7) E.g.: L. J. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, New York, 1960, p 514.

however, PMDETA has thus far been structurally characterized only in the more usual four-coordinate covalent stereochemistry, exemplified in $[(o\text{-}C_6H_4CH_3(CHSiMe_3))(Li(PMDETA))]$;[9] in the latter, Li–N are only slightly shorter than the present values (Table II), being 2.17 (1), 2.23 (1), and 2.18 (1) Å, with the angles contained by the ligand being 84.1 (4), 84.8 (3), and 114.2 (4)°.

Acknowledgment. We gratefully acknowledge receipt of a grant in support of this work from the Australian Research Grants Committee.

Registry No. 1, 87729-09-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, thermal parameters, and hydrogen atom parameters (14 pages). Ordering information is given on any current masthead page.

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[8] M. di Vaira and P. L. Orioli, *Inorg. Chem.*, **8**, 2729 (1969).

[9] M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, to be submitted for publication in *J. Chem. Soc., Dalton Trans.*

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University of Southern California, Los Angeles, California 90089-1062

Preparation and Structural Characterization of $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$: Conformational Flexibility in the M_2P_4 Core Structure of Bis(diphenylphosphino)methane Complexes

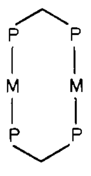
DOUGLAS M. HO and ROBERT BAU*

Received March 16, 1983

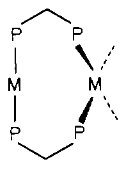
The bis(diphenylphosphino)methane (dpm) silver compounds $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ have been synthesized and characterized by IR and ^1H NMR spectroscopy and X-ray diffraction. The molecules are found to contain $[Ag_2(dpm)_2]^{2+}$ core structures with the two silver atoms bridged by the dpm ligands to give eight-membered $Ag_2P_4C_2$ rings. The $[Ag_2(dpm)_2]^{2+}$ units exist in a range of conformational forms subject to the nature of additional ligands present (e.g., NO_3^-). In $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$, the $[Ag_2(dpm)_2]^{2+}$ units are significantly folded along the Ag···Ag axes in the solid state (P–Ag–P angles from 138 to 152°). ^1H NMR data on $[Ag_2(dpm)_2(NO_3)_2]$ in acetonitrile, however, are consistent with a nonfolded structure for the $[Ag_2(dpm)_2]^{2+}$ dication in solution. Crystallographic details are as follows. For $[Ag_2(dpm)_2(NO_3)_2]$: monoclinic space group $C2/c$, $a = 12.687$ (4) Å, $b = 16.997$ (3) Å, $c = 22.627$ (6) Å, $\beta = 100.73$ (3)°, $Z = 4$, $R = 5.0\%$ for 2669 nonzero reflections with $F^2 > 3\sigma(F^2)$. For $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$: triclinic space group $P\bar{1}$, $a = 13.703$ (3) Å, $b = 14.516$ (2) Å, $c = 13.402$ (2) Å, $\alpha = 112.21$ (1)°, $\beta = 96.82$ (2)°, $\gamma = 83.56$ (1)°, $Z = 1$, $R = 5.6\%$ for 4555 nonzero reflections.

Introduction

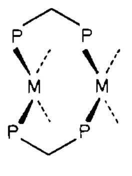
A key feature in the chemistry of dinuclear bis(diphenylphosphino)methane (dpm) complexes is the relatively stable, intrinsic $M_2(dpm)_2$ framework. In general, this has consisted of trans-bound, bridging dpm ligands to give a planar M_2P_4 core structure (I) with the two metal atoms held in close proximity to each other (regardless of whether a metal–metal bond is present or not). This feature is presumably one of the chief reasons for the unusual bonding, reactivity, and catalytic properties of $M_2(dpm)_2$ compounds. The stable $M_2(dpm)_2$ framework, while accepting some conformational changes when interacting with small molecules, places much of the burden for any structural adjustment on the substrate species themselves and on any additional ligands present. This adjustment may be expressed in terms of unique bonding interactions or chemical reactivity. For example, the unusual $\mu_2\text{-}\eta^1,\eta^2$ bridge-binding (σ, π) mode for carbon monoxide was first discovered in the homobimetallic dpm complex $[Mn_2(dpm)_2(CO)_5]$,[1] while the rare "unsupported" bridging CO linkage (i.e., without concomitant M–M bonding) can be found in the compounds $[M_2(dpm)_2(\mu\text{-}CO)X_2]$ (M = Pd, Pt; X = Cl, Br, I).[2-4] Further, the bridging CO ligands in the latter complexes can be removed and reinserted reversibly, a phenomenon currently unique to $(dpm)_2$ compounds. Catalytic hydrogenation[5-7] and water gas shift activity[7,8] involving $M_2(dpm)_2$ species have also been reported.



I



II



III

Bis(diphenylphosphino)methane compounds containing alternate forms for the $M_2(dpm)_2$ framework on the other hand are rather uncommon but have also been recently isolated and characterized. $[Pt_2(dpm)_2(CH_3)_3]^{+}$[9] and $[Pt_2(dpm)_2(CH_3)_4]$,[10] for instance, have been found to contain cis-bound phosphorus donor atoms to give the new structural types II and III, respectively. In fact, the discovery of still other structural forms (in addition to types I–III) seems highly probable in light of more recent efforts to systematically synthesize *hetero*bimetallic dpm complexes.[11-15] The M_2P_4 core structure of

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