g (54%) of crystalline $(C_6F_5)_2Co{\cdot}2PEt_3$, whose physical and spectroscopic properties are consistent with those previously reported.

Reaction with Benzyl Bromide. A slurry of **2** (0.2812 g, 40.5 mmol, of lithium; 6.7343 g, 52.5 mmol, of naphthalene; 2.2540 g, 17.6 mmol, of cobalt chloride) was prepared and the product separated and washed with three 30-mL portions of diethyl ether. The metal powder in 30 mL of fresh glyme was treated at room temperature with 5.46 g (32 mmol) of benzyl bromide, causing a brisk exotherm after a brief induction period. After 14 h the products were quantitatively determined by GC as bibenzyl (63%) and toluene (6%) with use of a known quantity of *n*-nonane as an internal standard and application of response factor corrections.

Reaction with Phenyl Halides: Phenyl Iodide. Method 1. A slurry of **2** (0.2472 g, 35.6 mmol, of lithium; 5.9647 g, 46.5 mmol, of naphthalene; 1.9765 g, 15.4 mmol, of cobalt chloride) was prepared and the product washed once with glyme. It was then treated in 25 mL of glyme was 4.5955 g (22.5 mmol) of phenyl iodide. Quenches were taken periodically by withdrawing 1-mL samples and treating the samples with 2 drops of 1 M HCl. The samples were then quantitatively analyzed by GC with use of *n*-dodecane as an internal standard and application of response factor corrections. After 1 min, 59% of the phenyl iodide remained. After 20 h (last 3 h at reflux), 61% remained. No biphenyl was observed until the reaction mixture was refluxed, after which an 11% yield of that compound was found.

Method 2. A slurry of **1** (0.3166 g, 45.6 mmol, of lithium; 0.5889 g, 4.6 mmol, of naphthalene; 2.5429 g, 19.8 mmol, of cobalt chloride) was prepared and the powder washed once with 25 mL of glyme. It was then treated in 30 mL of glyme with 6.3406 g (31.1 mmol) of phenyl iodide. Quenches were taken as described in method 1 (vide supra) and showed 64% of the phenyl iodide remained unchanged after 1 min at room temperature. After 26 h (3 h at reflux) 60% of the phenyl iodide remained. No biphenyl was observed at any time.

Preparation of Tetraphenylethylene: Method 1. A slurry of **1** (0.3516 g, 50.7 mmol, of lithium; 1.3021 g, 10.2 mmol, of naphthalene; 7.7919 g, 24.9 mmol, of cobalt chloride) was prepared and the powder washed with 160 mL of glyme in two portions. The slurry in 20 mL of glyme was treated with 3.70 g (15 mmol) of dichlorodiphenylmethane, causing a brief mild exotherm. After 20 h, GC analysis revealed that only a trace of Ph_2CCl_2 remained in the green solution. The organic products were extracted from 3 M HCl with chloroform, washed with several portions of water, and dried over magnesium sulfate. After concentration in vacuo recrystallization of the residues from benzene–ethanol gave 1.58 g (63%) of pale yellow crystalline tetraphenylethylene, identified by its mixed melting point with an authentic sample and high-resolution mass spectroscopy.

Method 2. A slurry of **1** (0.1853 g, 26.7 mmol, of lithium; 0.2254 g, 1.8 mmol, of naphthalene; 4.002 g, 12.8 mmol, of cobalt iodide) was chilled to −78 °C, and 1.05 g (13 mmol) of cyclohexene and 1.48 g (6.2 mmol) of dichlorodiphenylmethane were added. After it was stirred for 48 h at room temperature, the mixture was refluxed for 3 h and worked up as described in method 1 to give 0.53 g (51%) of tetraphenylethylene.

Method 3. A slurry of **1** (0.2154 g, 31.0 mmol, of lithium; 0.1840 g, 1.4 mmol, of naphthalene; 4.5599 g, 14.6 mmol, of cobalt iodide; 45 mL of THF) was prepared. The metal powder was isolated by filtration under argon and dried in vacuo overnight. The cobalt powder (3.678 g) was slurried in 20 mL of distilled hexanes and treated with 2.72 g (11 mmol) of dichlorodiphenylmethane at room temperature, causing the formation of a green solution. After the mixture was stirred for 48 h, the products were worked up as previously described to give 0.80 g (42%) of tetraphenylethylene.

Reaction of Cobalt with Diiodomethane. A slurry of **1** (1.9500 g, 6.2 mmol, of cobalt iodide; 0.5009 g, 12.8 mmol, of potassium; 0.7878 g, 6.2 mmol, of naphthalene; 20 mL of THF) was treated with 5.2331 g (19.5 mmol) of diiodomethane and 0.0714 g of *n*-tridecane (GC standard). After 14 h ethylene was identified by mass spectroscopy in the gases above the reaction mixture. Analysis of the reaction mixture by GC showed that 57% of the diiodomethane remained unchanged.

X-ray Photoelectron Spectroscopy (XPS). Samples for XPS studies were sealed under argon in glass ampules. These were opened in an argon-filled drybox, and the metal powder was dusted onto aluminum-backed tape and transferred into the vacuum chamber of the XPS system (PHI Model 550) by means of a controlled-atmosphere specimen-transfer device (PHI Model 04-100). This device allows sample introduction with minimal contamination of the sample by air or moisture.

The spectra were obtained with use of a Mg anode for X-ray excitation with a vacuum of 10^{-9} torr. Sputtering was effected with a differentially pumped ion gun with an energy of 5 KeV and an ion current density of 5 A cm^{-2}. Results from several experiments are collected in Table IV.

Acknowledgment. We thank Professor T. A. George for the use of some of the high-pressure equipment used in this work and P. Ries and Professor C. J. Eckhardt for assistance in obtaining X-ray data. We thank Dr. Ashley Taylor for assistance in the surface analyses. Funding for this work was provided by the U.S. Army Research Office.

Registry No. Co, 7440-48-4; CO, 630-08-0; $(C_6F_5)_2Co{\cdot}2PEt_3$, 60528-59-8; nitrobenzene, 98-95-3; iodopentafluorobenzene, 827-15-6; iodobenzene, 591-50-4; benzyl bromide, 100-39-0; dichlorodiphenylmethane, 2051-90-3; diiodomethane, 75-11-6.

Contribution from the Department of Chemistry,
University of Texas at El Paso, El Paso, Texas 79968-0513

Potential Lanthanide Ion Selective Reagents. 3.[1,2] Metal Complex Formation with 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N*,*N'*-diacetic Acid

C. Allen Chang* and Ven O. Ochaya

Received June 19, 1985

Stability constants for the ligand 1,7-diaza-4,10,13-trioxacyclopentadecane-*N*,*N'*-diacetic acid (dapda or K21DA) with the lanthanides and several other metal ions have been determined at 25 °C in aqueous 0.1 M $(CH_3)_4NCl$ medium by a potentiometric method. The results obtained are compared to those obtained for a similar ligand of larger cavity size, 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic acid (dacda or K22DA), which has been previously studied and reported.[1] The stability of dapda is found to reach a peak at Eu(III) with the lanthanide series and is rationalized in terms of the matching of the ligand properties with metal ion characteristics. The transition-metal ions Ni(II), Cu(II), and Zn(II) all form stronger dapda (as compared to dacda) complexes due to a better match of the ligand cavity size and metal ion radius.

The past 20 years has witnessed a rapid growth in our knowledge and applications of the rare-earth elements. It was estimated that the total consumption of lanthanides was ~1.6 × 10^3 metric tons in the early 1960s, which escalated to more than 20 × 10^3 metric tons in 1975.[3] Also, their use was mainly in lighter flints, carbon arc electrodes, and glass polishing powders in the early 1960s; in recent years, it has changed to applications

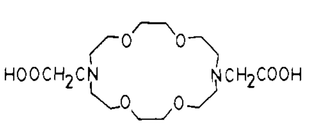
---

[1] Part 1: Chang, C. A.; Rowland, M. E. *Inorg. Chem.* **1983**, *22*, 3866–3869.

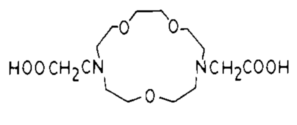
[2] Part 2: Chang, C. A.; Ochaya, V. O.; Sekhar, V. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1724–1725.

[3] Haskin, L. A.; Paster, T. P. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr., Eyring, L., Ed.; North-Holland: Amsterdam, 1979; Vol. 3, pp 71–76.

0020-1669/86/1325-0355$01.50/0 © 1986 American Chemical Society



1. dacda (K22DA)



2. dapda (K21DA)

Figure 1. Structures of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic acid (**1**, dacda) and 1,7-diaza-4,10,13-trioxacyclopentadecane-*N*,*N'*-diacetic acid (**2**, dapda).

in metallurgy, catalysts and chemicals, glasses and ceramics, and electronics. Significiant future applications might include addition to nuclear rods to absorb thermal neutrons, production of solid electrolytes for fuel cells that can convert hydrogen directly into electricity, and use as substrates for the bubble domain memory device, possibly the basis for the next generation of computers.

Due to the remarkable similarities of lanthanide charges and radii, the separation of lanthanide elements has been a sophisticated chemical process. In many cases, it has made rare-earth concentrates an exploitable byproduct of other industries, e.g., the phosphate fertilizer industry. Although lanthanide reserves appear adequate to meet anticipated needs into the distant future, more economic processes are yet to be developed. On the other hand, the separation of lanthanides from nuclear fission products remains a difficult challenge.

Currently, lanthanide elements are commercially separated by ion-exchange techniques on a large scale.[4] The separation depends primarily on the hydrated ionic radius: La should be the most tightly bound lanthanide and Lu the least; hence, the elution order is Lu → La. However, selective separation of a particular lanthanide element cannot be easily performed. To achieve such a purpose (as well as many others), we have been interested in the design and synthesis of lanthanide (Ln) ion selective reagents. Macrocyclic compounds with ionizable functional side groups are of primary interest because they possess at least two selectivity factors, i.e. charge density and cavity size, in addition to structural aspects. Several recent examples such as lithium-selective ionophores[5,6] and specific uranophile[7,8] are all macrocycles.

In a previous paper, we reported the stability constants of complexes of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic acid (Figure 1, dacda or K22DA) with several metal ions.[1] It was shown that, except for a few transition- and post-transition-metal ions such as Cu(II), Pb(II), and Cd(II), dacda shows unique selectivity toward lanthanide ions as a group. Also, for the first time in aqueous solution for a multidentate ligand, the stability constants for Ln–ligand complexes decrease with increasing atomic number for heavy lanthanides and remain roughly unchanged for the lighter lanthanides. In this paper, we report the stability constants of metal complexes of 1,7-diaza-4,10,13-trioxacyclopentadecane-*N*,*N'*-diacetic acid (Figure 1, dapda or K21DA), which has a smaller (15-membered) ring, and it is shown that for the first time, through a systematic approach, the ligand is selective toward the Eu(III) ion among all the lanthanide elements.

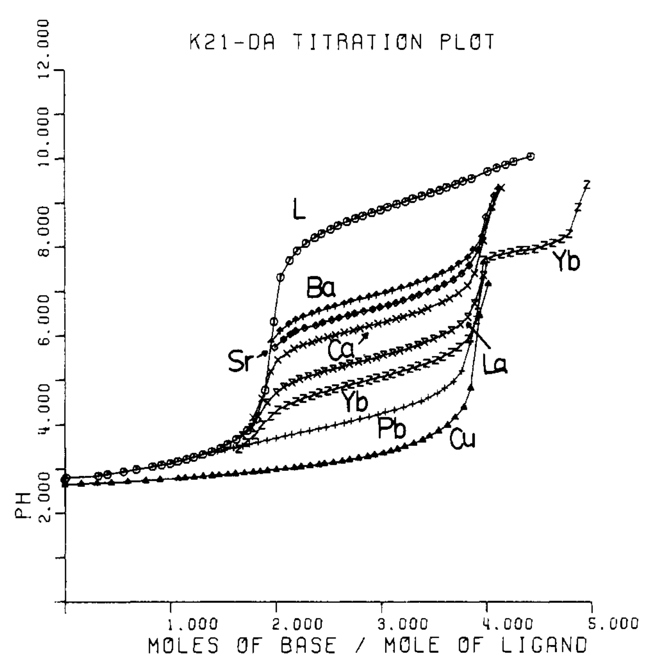


Figure 2. Potentiometric equilibrium curves of dapda·2HCl and 1:1 ratios of dapda with several metal ions. [M] = [dapda] = 1.2×10^{-3} M; 25.0 ± 0.1 °C; $\mu = 0.10$, $(CH_3)_4NCl$.

Experimental Section

Materials and Standard Solutions. The ligand, 1,7-diaza-4,10,13-trioxacyclopentadecane-*N*,*N'*-diacetic acid (dapda, H_2L), was prepared according to the method of Kulstad and Malmsten.[9] The procedure is as that used for the preparation of dacda reported in an earlier publication.[1] The white precipitate collected was recrystallized in 80% ethanol–water solution. (Yield: 0.76 g, 40.7%).

Recrystallization of the compound in ca. 4 M HCl ethanolic solution yields the crystalline dihydrochloride salt, which shows a sharp characteristic carbonyl absorption band at 1715 cm^{-1}, indicating the presence of protonated carboxylic acid groups. ^1H NMR (Me_4Si, δ 0): δ 3.71 (t, 8 H), 3.85 (s, 4 H), 3.95 (t, 8 H), 4.21 (s, 4 H). ^{13}C NMR (Me_4Si, δ 0): δ 53.89, 54.79, 55.21, 63.12, 63.43, 69.81. Anal. Calcd for $C_{14}H_{26}N_2O_7 \cdot 2HCl$: C, 41.28; H, 6.93; N, 6.88. Found (Galbraith): C, 40.97; H, 6.78; N, 6.77.

A 1×10^{-2} M ligand stock solution was prepared and standardized as previously described.[1] Likewise, the standard metal salt solutions having concentrations of about 0.01 M were prepared.

Potentiometric Titrations. All titrations were carried out at constant ionic strength of 0.10 M $(CH_3)_4NCl$. Boiled deionized water was used for all experiments. A Model 750 Fisher Accumet Selective Ion Analyzer in conjunction with a Fisher combination electrode was employed to monitor the pH (±0.001 pH unit). The sample solution was prepared by pipetting exact amounts of each stock solution into a titration vessel so that the final mixture was 1.2×10^{-3} M in both the ligand and the metal salt. The water-jacketed titration vessel with a 25-mL capacity was purchased from Brinkmann together with a five-hole cover. Electrode, buret, and temperature probe were fitted into these holes. The vessel was always kept at 25.0 ± 0.1 °C by using a constant-temperature circulating bath from Van Waters and Rogers. Prior to each titration, the pH meter was standardized at pH 4.00 and 7.00 ± 0.02 by using Fisher buffer solutions. $(CH_3)_4NOH$ solution was delivered from a 5-mL buret with a reading accuracy of ±0.01 mL. All titrations were performed three to four times without any slow-equilibrium problem, and reproducible results were obtained. Oxygen-free nitrogen gas was bubbled through the titrate solution on several occasions, and no significant difference was found if the step was neglected. The activity coefficient, f_{H^+}, was calcuated by titrating a HCl solution of known concentration with 0.10 M KNO_3 by using 0.10 M KOH solution. The measured pH was then converted to hydrogen ion concentration, $[H^+]$, according to the equation $-\log [H^+] = pH + \log f_{H^+}$. A value of 13.791 was employed for the pK_w at 25 °C, ionic strength 0.10. All equilibrium calculations were performed by using computer programs described elsewhere.[10] Data points in the metal buffer region of 20–80% metal complexation

---

(4) Powell, J. E. In "Handbook on the Physics and Chemistry of Rare Earths"; Gschneidner, K. A., Jr., Eyring, L., Ed.; North-Holland: Amsterdam, 1979; Vol. 3, pp 81–109.

(5) Olsher, U. *J. Am. Chem. Soc.* **1982**, *104*, 4006–4007.

(6) Kitazawa, S.; Kimura, K.; Yano, H.; Shono, T. *J. Am. Chem. Soc.* **1984**, *106*, 6978–6983.

(7) Tabushi, I.; Kobuke, Y.; Ando, K.; Kishimoto, M.; Ohara, E. *J. Am. Chem. Soc.* **1980**, *102*, 5947–5948.

(8) Tabushi, I.; Kobuke, Y.; Yoshizawa, A. *J. Am. Chem. Soc.* **1984**, *106*, 2481–2482.

(9) Kulstad, S.; Malmsten, L. A. *Acta Chem. Scand., Ser. B* **1979**, *B33*, 469–474.

(10) Chang, C. A.; Douglas, B. E. *J. Coord. Chem.* **1981**, *11*, 91–97.

Table I. Stability Constants of Metal Complexes of 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N*,*N*′-diacetic Acid (dapda or K21DA) and 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-diacetic Acid (dacda or K22DA)[a]

	ionic radii,[b] Å	log $K_{ML}{}^{M}$ K21DA (dapda)	log $K_{ML}{}^{M}$ K22DA (dacda)
Mg^{2+}	0.89	7.42 ± 0.09	
Ca^{2+}	1.12	8.74 ± 0.04	8.39
Sr^{2+}	1.26	7.91 ± 0.04	8.29
Ba^{2+}	1.42	7.31 ± 0.04	7.63
Ni^{2+}	0.69	12.23 ± 0.10	7.39
Cu^{2+}	0.73	16.02 ± 0.50	14.49
Zn^{2+}	0.74	14.08 ± 0.20	8.42
Cd^{2+}	1.10	12.95 ± 0.04	11.07
Pb^{2+}	1.29	12.91 ± 0.10	13.55
La^{3+}	1.160	10.11 ± 0.06	12.21
Ce^{3+}	1.143	10.89 ± 0.08	12.23
Pr^{3+}	1.126	11.31 ± 0.05	12.22
Nd^{3+}	1.109	11.60 ± 0.07	12.21
Sm^{3+}	1.079	11.72 ± 0.09	12.12
Eu^{3+}	1.066	11.85 ± 0.11	12.02
Gd^{3+}	1.053	11.66 ± 0.10	11.93
Tb^{3+}	1.040	11.52 ± 0.10	11.70
Dy^{3+}	1.027	11.55 ± 0.07	11.57
Ho^{3+}	1.015	11.34 ± 0.08	11.18
Er^{3+}	1.004	11.15 ± 0.06	11.30
Tm^{3+}	0.994	10.79 ± 0.09	11.10
Yb^{3+}	0.985	10.76 ± 0.03	10.90
Lu^{3+}	0.977	10.33 ± 0.09	10.84
Y^{3+}	1.019	10.85 ± 0.02	
Ga^{3+}	0.62	13.96 ± 0.16	

[a] $K_{ML}{}^{M}$ = [ML]/[M][L]; ionic strength = 0.10; 25.0 ± 0.1 °C. [b] Data taken from ref 18. Coordination numbers are assumed to be 8 except for the cases of the Ga^{3+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} ions, where 6 is assumed.

were employed for the calculation of stability constants. The averaged values are presented together with the standard deviation calculated from those valid data points.

Results and Discussion

Ligand Protonation Constants. The ligand potentiometric titration curve (L of Figure 2) shows two buffer regions. The higher one from pH 7 to pH 10 corresponds to the simultaneous dissociation of two protons attached to the nitrogen atoms. The two calculated pK_a values, 9.02 ± 0.05 and 8.79 ± 0.03 for the nitrogen protons, are higher than those of dacda. The third protonation constant with a value of 2.95 ± 0.06 is estimated from the titration data.

Stability of Metal Chelates. Some representative metal complex formation equilibrium curves are also shown in Figure 2. All of these curves are lower in pH than that of the ligand titration without metal ion, indicating competition between metal ions and protons for binding with the ligand. For most metal ions except Cu(II), Zn(II), and Pb(II), complexation occurs only after the acetic acid protons are removed. The complexation reactions for these metal ions are best described by

$$M^{n+} + H_2L \rightleftarrows ML^{(n-2)+} + 2H^+ \qquad (1)$$

For the Cu(II), Zn(II), and Pb(II) ions, the stability of complex formation is greater so that the following reaction occurs:

$$M^{n+} + H_4L^{2+} \rightleftarrows ML^{(n-2)+} + 4H^+ \qquad (2)$$

This is demonstrated by the calculated average protonation number, $\bar{h}$, defined by eq 3.

$$\bar{h} = \text{(total dissociable hydrogen ion concentration bound to ligand species)}/\text{(total ligand concentration)} \qquad (3)$$

For those ions involved in eq 2, $\bar{h}$ is always less than 2, even when no base was added. Because the complexation process must expel the two nitrogen protons from the ligand, the fact $\bar{h} < 2$ would mean that complexation indeed occurred before any base was added. Table I lists the calculated log *K* values for the metal ions chosen for study as compared with those obtained for complexes of dacda.

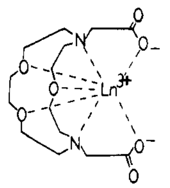


Figure 3. Possible structure of lighter lanthanide–dapda complexes.

The divalent alkaline-earth-metal ions form dapda complexes with intermediate stability. Because the 15-membered ring cavity size of dapda is smaller (which fits well with the ionic size of Mg^{2+}), significant complex formation is observed between Mg^{2+} and dapda. This is in contrast to the Mg^{2+}–dacda system, in which no detectable complex formation is observed. Also, strong Ca^{2+}–dapda complex formation is found, indicating a better match between properties of the ligand and the metal ion. On the other hand, the cavity size of dapda is too small for Sr^{2+} and Ba^{2+}; significant measurable decreases of dapda complex formation constants as compared to those of dacda are observed.

A similar study was reported for the determination of formation constants of dapda with several alkaline-earth-metal ions under identical experimental conditions except KNO_3 was used to adjust ionic strength.[11] It turned out that the protonation constants of dapda of the earlier report are 0.4–0.6 log unit lower and the formation constants of dapda–alkaline-earth-metal complexes are 0.6–0.7 log unit lower as compared to ours. Because of cavity size of dapda is still large enough to complex K^+ ion (although the potentiometric determination of the stability constant would be difficult), the data of the earlier report cannot be the true protonation constants and stability constants due to the competition reactions during the titration processes. However, the trend observed in the previous study is still consistent with ours.

In case of all lanthanide ions, it is observed that strong Ln^{3+}–dapda complexes are formed, i.e. log $K_{ML}{}^{M}$ values are between 10.1 and 11.9. Most important is that Eu(III) ion forms the strongest complex. This is different from the data observed for dacda complexes, in which lighter lanthanide complexes are more stable.[1] Also, by comparing the corresponding formation constants of a particular lanthanide ion, it is seen that the dacda complex is usually more stable than the dapda complex except in a few cases (see Table I) in which no significant differences are found. Thus, the selectivity of dapda toward Eu(III) among all the lanthanide ions must be attributed to the *less unfavorable match* between the properties of the ligand and the metal ion. It is important to note that selectivity does not have to be achieved with superior stability. Sometimes, sacrifice of the stability may allow the presence of selectivity.

The cavity size of dapda is approximately the same as that of 15-crown-5 (diameter 1.7–2.2 Å), which is definitely too small for the lighter lanthanide ions. Note that Eu(III) forms a sandwich compound with 15-crown-5.[12] Thus, the structure of lighter Ln complexes is more likely the one depicted in Figure 3 in which a cis-carboxylate configuration is proposed.[13] On the other hand, structural aspects are not clear for the heavier Ln–dapda complexes. However, the ability to form ternary complexes with the acetylacetonate ion indicates that their structures are all similar.[14] We are in the process of unraveling the structural nature of these complexes.

Another interesting point observed from the potentiometric equilibrium titration curves of Ln–dapda complexes is that only the Yb–dapda complex shows a clearly detectable water hydrolysis buffer region, with a pK_h = 7.93 ± 0.05. The reason other

---

(11) Tazaki, M.; Mita, K.; Takagi, M.; Ueno, K. *Chem. Lett.* **1982**, 571–574.
(12) Bunzli, J.-C. G.; Wessner, D. *Isr. J. Chem.* **1984**, *24*, 313–322.
(13) Spirlet, M.-R.; Rebizant, J.; Loncin, M.-F.; Desreux, J. F. *Inorg. Chem.* **1984**, *23*, 4278–4283.
(14) Chang, C. A.; Garg, B. S.; Manchanda, V. K.; Ochaya, V. O.; Sekhar, V. C. *Inorg. Chim. Acta*, in press.

Ln–dapda complexes do not exhibit this same property is not certain.

The four transition-metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} and the post-transition-metal ion Pb^{2+} all form strong complexes with dapda. Except for Pb^{2+}, which has a larger ionic radius, the other four all form dapda complexes that are stronger than dacda complexes. Inversion of the Irving–Williams series is also observed for the Ni^{2+} and Zn^{2+} complexes.[15] Both trends are consistent with the data obtained for the underivatized structural analogues 1,7-diaza-4,10,13-trioxacyclopentadecane (K21) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (K22). The compound K21 has a smaller size in which the two coordinating nitrogen atoms can relatively easily form a stable complex with any of the transition-metal ions without large compensation of the energy needed for conformational change for complexation.

The structures of Cu(II) complexes of 12-, 15-, and 18-membered diaza-crown-*N*,*N'*-diacetic acids have been discussed.[16] X-ray diffraction data are only reported for the 18-membered compound.[17] However, it is proposed that for the Cu^{II}–dapda complex the Cu(II) ion is contained inside the ring. This is consistent with very stable Cu^{II}–dapda complex formation.

Acknowledgment. This material was prepared with the support of U.S. Department of Energy Grant No. DE-FG05-84ER13292; however, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE.

Registry No. dapda, 81963-61-3.

---

(15) Luboch, E.; Cygan, A.; Biernat, J. F. *Inorg. Chim. Acta* **1983**, *68*, 201–204.

(16) Kolinski, R. A.; Mrozinski, J. *Polyhedron* **1983**, 2, 1217–1220.

(17) Uechi, T.; Ueda, I.; Tazaki, M.; Takagi, M.; Ueno, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chems.* **1982**, *B38*, 433–436.

(18) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas 76129

Preparation of P-N-H and P-P Compounds from a Silylated Aminomethylenephosphine

Bei-Li Li and Robert H. Neilson*

Received April 29, 1985

Secondary amines react with the silylated aminomethylenephosphine $(Me_3Si)_2NP{=}CHSiMe_3$ (**1**) by a complex process involving Si–N bond cleavage as well as addition to the P=C bond. Thus, treatment of **1** with Et_2NH yields either the N–H phosphine $Me_3SiN(H)P(NEt_2)CH_2SiMe_3$ (**2**) or the unexpected P^V–P^{III} product $Me_3SiN{=}P(NEt_2)(CH_2SiMe_3){-}P(CH_2SiMe_3)N(SiMe_3)_2$ (**3**), depending upon the reaction stoichiometry. In two separate experiments with mechanistic implications (a) **2** was prepared from the reaction of Et_2NH with $(Me_3Si)_2NP(NEt_2)CH_2SiMe_3$ (**1a**), the presumed intermediate in the Et_2NH/**1** reaction, and (b) **3** was prepared directly by addition of the N–H compound **2** to the methylenephosphine **1**. Compound **2** is smoothly oxidized by CCl_4 to the *P*-chlorophosphoranimine $Me_3SiN{=}P(Cl)(NEt_2)CH_2SiMe_3$ (**4**) or is deprotonated by *n*-BuLi. The ambident anion thus formed reacts with the chlorophosphines Ph_2PCl and $(Me_3Si)_2NP(Cl)CH_2SiMe_3$ to yield the P–P products $Me_3SiN{=}P(NEt_2)(CH_2SiMe_3){-}PPh_2$ (**5**) and compound **3**, respectively.

Introduction

The chemistry of 2-coordinate, acyclic P^{III} compounds containing the P=C double bond, the methylenephosphines, is of considerable current interest.[1] Four major types of reactions of such compounds have been studied: (1) addition and cycloaddition reactions of the P=C bond, (2) complexation of transition metals to the phosphorus lone pair and/or the P–C π bond, (3) oxidation to the 3-coordinate P^V state, and (4) nucleophilic substitution at the 2-coordinate P^{III} center. Our recent studies,[2,3] in particular, have shown that methylenephosphines bearing the disilylamino group, e.g., $(Me_3Si)_2NP{=}CHSiMe_3$ (**1**),[4] actually exhibit all of these reaction pathways.

In addition, the Si–N bonds in compounds such as **1** are potentially reactive sites. The general lack of Si–N reactions in these 2-coordinate phosphines is rather surprising since many examples of silyl group rearrangement and/or elimination processes have been observed in 3- and 4-coordinate Si–N–P systems.[5] We report here, however, the observation of Si–N bond cleavage as part of a complex series of reactions between **1** and diethylamine. Some related preparative chemistry is also described.

Results and Discussion

The reactions of the 2-coordinate phosphines $(Me_3Si)_2NP{=}ESiMe_3$ (E = CH, N) with protic reagents generally occur either by simple 1,2-addition to the double bond[4] or by oxidative addition to the highly electrophilic phosphorus center.[6] Therefore, we expected to find one or both of these pathways operating in the reaction of **1** (E = CH) with secondary amines R_2NH (R = Et, *n*-Bu, *i*-Pr). A preliminary study of such reactions, however, in NMR-tube experiments, revealed an unexpected degree of complexity. The formation of the Si–N cleavage product Me_3SiNR_2 and mixtures of phosphorus-containing compounds was consistently observed. As a representative example, the reaction of **1** with Et_2NH was selected for more detailed study on a preparative scale.

In a typical experiment, Et_2NH was added to a CH_2Cl_2 solution of **1** at 0 °C with subsequent warming to room temperature. The

---

(1) For example, see the following and references cited therein: (a) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731. (b) van der Knaap, Th. A.; Klebach, Th. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* **1984**, *40*, 765. (c) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015. (d) Xie, Z.-M.; Wisian-Neilson, P.; Neilson, R. H. *Organometallics* **1985**, *3*, 339.

(2) Li, B.-L.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 3665.

(3) Ford, R. R.; Li, B.-L.; Neilson, R. H.; Thoma, R. J. *Inorg. Chem.* **1985**, *24*, 1993.

(4) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679.

(5) See, for example: (a) Ford, R. R.; Goodman, M. A.; Neilson, R. H.; Roy, A. K.; Wettermark, U. G.; Wisian-Neilson, P. *Inorg. Chem.* **1984**, *23*, 2063. (b) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 289 and 623.

(6) Markovski, L. N.; Romanenko, V. D.; Ruban, A. V. *Phosphorus Sulfur* **1980**, *9*, 221.

0020-1669/86/1325-0358$01.50/0 © 1986 American Chemical Society