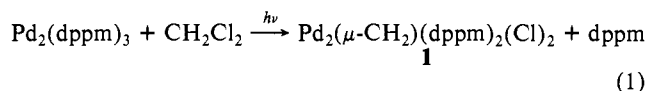


a planar three-coordinate geometry about each metal center on the basis of the crystal structure of $\text{Pt}_2(\text{dppm})_3$ in which the stereochemistry about each metal is essentially identical with that of monomeric $\text{Pt}(\text{PPh}_3)_3$.⁶ The nature of the emissive species in our experiments is clouded by the fact that the monomeric complexes are known to exist in solution as equilibrium mixtures of ML_n ($n = 2-4$) with the position of the equilibrium depending to a large extent upon the steric bulk of L.⁷ On the basis of a number of lines of evidence we believe that the observed solution luminescence in this class of complexes comes from species that are three-coordinate in both the ground and excited states.⁸

The radiative decay rates for all of the complexes in Table I are slow which suggests that the electronic transitions responsible for the observed emission spectra are only weakly allowed. We have observed that organic triplet quenchers will quench the emissive excited states of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dppm})_3$, and $\text{Ni}(\text{P}(\text{O}-\text{tol})_3)_3$ with rates that depend systematically upon the organic triplet energy, indicating that emission from the d^{10} complexes originates from low-lying triplet states. The relative insensitivity of the observed emission spectra to the nature of the phosphine, phosphite, or arsine ligands suggests an excited state that is by and large metal localized in character. This is in accord with our extended Hückel molecular orbital calculations⁹ which indicate that the lowest excited state for the planar ML_3 d^{10} complexes should correspond to the promotion of an $(n)d$ electron to a vacant metal localized $(n+1)p_z$ orbital. An analogy exists between the $d^{10} p \leftarrow d$ excited states and the previously investigated¹⁰ $p \leftarrow d$ excited states of square-planar d^8 complexes. In essence the trigonal symmetry of the d^{10} complexes causes the metal d_{xy} and $d_{x^2-y^2}$ orbitals to become degenerate and to lie lower in energy than the $(n+1)p_z$ level. In contrast for d^8 complexes with four-fold symmetry d_{xy} and $d_{x^2-y^2}$ are split and $d_{x^2-y^2}$ lies above $(n+1)p_z$. As a result the lowest energy excited states for both systems become the $p \leftarrow d$ states. The important difference between the d^8 and d^{10} complexes lies in the lifetimes of the $p \leftarrow d$ excited states. For the d^8 complexes the emissive excited states are immeasurably short lived at room temperature in fluid solution,¹¹ which has been a major factor in preventing the investigation of bimolecular photochemistry of these types of complexes.

Given the microsecond excited-state lifetimes of the complexes in Table I in solution it seemed likely to us that bimolecular photochemical reactions of these complexes could be observed. This is indeed the case as shown in eq 1 where low-energy visible



irradiation of $\text{Pd}_2(\text{dppm})_3$ in the presence of CH_2Cl_2 leads cleanly and quantitatively to the formation of the methylene bridged dimer

(6) (a) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* 1982, 1155. (b) Albano, V.; Bellon, P. L.; Scaturin, V. *J. Chem. Soc., Chem. Commun.* 1966, 507.

(7) (a) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* 1975, 1673. (b) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* 1972, 94, 2669.

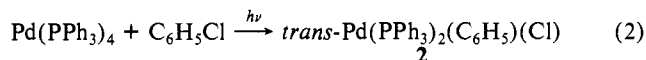
(8) We find that the excited-state lifetimes, emission spectra, and transient absorption spectra of all of the compounds that we have investigated are unaffected by the addition of excess phosphine ligand while quantum efficiencies for emission decrease as the concentration of excess ligand is increased. In addition the emission band shapes are unchanged when the complexes are either imbedded in rigid polymer films or examined as crystalline solids. These results are all consistent with complexes that are three-coordinate in both the ground and excited states. Further details will be presented in the full paper.

(9) Caspar, J. V., unpublished results. For calculational methods, see: (a) Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* 1979, 18, 3407. (b) McKinney, R. J.; Pensak, D. A. *Inorg. Chem.* 1979, 18, 3413.

(10) (a) Geoffroy, G. L.; Gray, H. B.; Hammond, G. S.; Wrighton, M. S. *J. Am. Chem. Soc.* 1974, 96, 3105. (b) Andrews, L. J. *Inorg. Chem.* 1978, 17, 3180. (c) Fordyce, W. A.; Crosby, G. A. *Inorg. Chem.* 1982, 21, 1455.

(11) (a) This product was previously identified from what was thought to be the slow thermal reaction of $\text{Pd}_2(\text{dppm})_3$ with CH_2Cl_2 .^{11b} We believe that this reaction was in fact proceeding photochemically under room light. After 48 h in the dark we find no detectable thermal reaction between the dimer and methylene chloride. (b) Balch, A. L.; Hunt, C. T.; Lee, C.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* 1981, 103, 3764.

1 in which a formal net four-electron oxidation of the dimer has been effected with one visible photon.¹² The monomeric complexes are also photochemically reactive as shown in eq 2 where



the oxidative addition product 2 can be isolated in 20% yield.^{12a} Significantly 2 has been isolated from the thermal reaction of $\text{Pd}(\text{PPh}_3)_4$ with chlorobenzene at 120 °C^{12b} whereas the photochemical reaction proceeds at room temperature. As a variety of catalytic reactions of d^{10} phosphine and phosphite complexes involve initial activation of halocarbons¹³ via oxidative addition, our photochemical results suggest the possibility of expanding the scope of these catalytic reactions to thermally unreactive substrates. We are also investigating the possibility that some of the previously identified radical reaction pathways in the thermal reactions of halocarbons with d^{10} metals may in fact be photochemically initiated.¹⁴

In summary we have identified a new class of $p \leftarrow d$ excited states general to low-valent metal complexes which have potential applications in photocatalysis. In addition to pursuing the photochemistry we are also expanding our studies of the fundamental photophysics and spectroscopy of these complexes and we are trying to assess the generality of these types of excited states for other metals (e.g., Ag(I), Au(I)) and other coordination environments.

Acknowledgment. It is a pleasure to acknowledge Dr. David L. Thorn for valuable discussion, Dr. Ying Wang for aid in carrying out the laser experiments, and S. H. Harvey and A. P. Berry for technical assistance.

(12) (a) The product was identified by comparison with an authentic sample.^{12b} (b) Coulson, D. R. *J. Chem. Soc., Chem. Commun.* 1968, 1530.

(13) (a) Heck, R. F. *Pure Appl. Chem.* 1978, 50, 691. (b) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971.

(14) (a) Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* 1974, 96, 7145. (b) Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Chem. Commun.* 1973, 948.

Synthesis and Characterization of the First Transition-Metal Complex of 1,2:5,6:9,10-Tribenzocyclododeca-1,5,9-triene-3,7,11-triene

Joseph D. Ferrara, Claire Tessier-Youngs, and Wiley J. Youngs*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received May 13, 1985

We wish to report the synthesis and structural and partial spectral characterization of a novel Ni(0) complex of a planar dehydroannulene,¹ complex I (Figure 1). The incorporation of a nickel atom into the cavity of the dehydroannulene II leads to novel chemistry when compared to transition-metal complexes of other unsaturated hydrocarbons²⁻⁵ and provides compelling

(1) (a) Nakagawa, M. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed; Wiley: Chichester, 1978; Part 2, pp 635-712. (b) Sondheimer, F. *Acc. Chem. Res.* 1972, 5, 81-91. (c) Sondheimer, F. *Proc. R. Soc. London, Ser. A* 1967, 297, 173-204. (d) Sondheimer, F. *Pure Appl. Chem.* 1963, 7, 363-388.

(2) (a) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* 1976, 14, 33-61. (b) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* 1976, 14, 245-283. (c) Mingos, D. M. P. In "Comprehensive Organometallic Chemistry"; Wilkinson, G.; Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, pp 1-88.

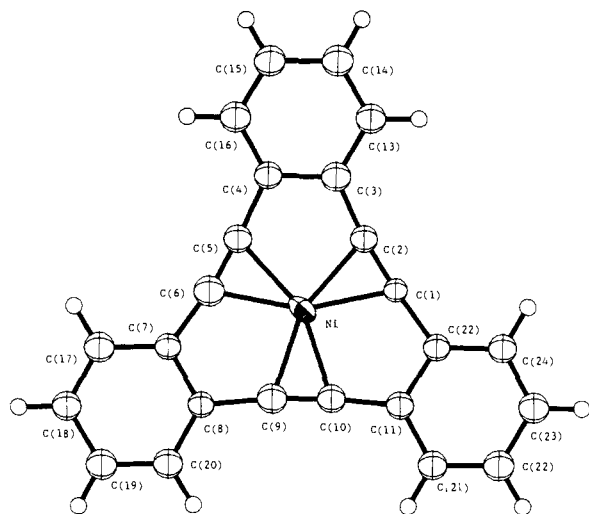


Figure 1. Labeling diagram of $\text{Ni}(\text{C}_{24}\text{H}_{12})$. The hydrogen atoms are drawn arbitrarily small for clarity.

arguments that I may lead to a new class of one-dimensional conductors. The planarity of molecules of I can be compared to that of phthalocyanine⁶ and porphyrin⁷ metal complexes. (Some of these nitrogen donor complexes are one-dimensional conductors when partially oxidized or reduced.) In contrast to the nitrogen donor complexes, complex I contains soft donor atoms; a feature found in the conducting metal chalcogenides. A final parallel to one-dimensional conducting systems^{8,9} is found upon examination

of the molecular packing. Molecules of I stack in a manner reminiscent of the component compounds of the one-dimensional conductor TTF-TCNQ¹⁰ and very similar to undoped nickel(II) phthalocyanine.⁶

All manipulations, unless otherwise stated, were done by using inert atmosphere techniques.¹¹ Reaction of the dehydroannulene II, 1,2:5,6;9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triene¹² (0.100 g, 3.33×10^{-4} mol) with $\text{Ni}(\text{COD})_2^{13}$ (0.092 g, 3.3×10^{-4} mol) in 10 mL of C_6H_6 gives a deep blue solution from which long needle-shaped crystals form. The ¹H and ¹³C spectra¹⁴ indicate the formation of a symmetric monomeric species containing the cyclene II as the only carbon and hydrogen moiety. Elemental analysis¹⁵ of the material is consistent with the formula $\text{Ni}(\text{C}_{24}\text{H}_{12})$. The field desorption mass spectrum gives a molecular weight¹⁶ for the parent ion of 358.2 (5) amu. Benzene and THF solutions of the complex are stable indefinitely under argon or vacuum. Benzene solutions of the complex decompose instantly on exposure to air, while THF solutions are stable for short periods. In contrast, the crystalline solid is air-stable.

The IR spectrum (KBr) of I strongly resembles that of the free cyclene II except for a $\text{C}\equiv\text{C}$ stretching band which occurs as a strong band at $1955 (3) \text{ cm}^{-1}$ in the spectrum of I and as a weak band at 2200 cm^{-1} in the spectrum of II.¹⁷ The ¹³C resonance for the acetylenic carbon at 101.8 ppm, the infrared data, and the crystal structure (vide infra) are consistent with the carbon-carbon triple bonds acting as three two-electron donors.^{18,19} The UV-vis spectrum (THF) in the 800–290-nm region shows a maximum at 587.5 nm ($\epsilon = 2.5 (3) \times 10^3$) and a shoulder at 370 nm ($\epsilon \approx 10^3$). The absence of bands in the visible region in the spectrum of free II and the high extinction coefficient of the 587.5-nm band in the spectrum of the complex suggest that this band is a metal to ligand charge-transfer band. This is consistent with an electron-rich Ni(0) and an easily reducible ligand.^{1b,20}

(3) (a) Green, M.; Grove, D.; Howard, J.; Spencer, J.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 759–760. (b) Nesmeyanov, A. N.; Gusev, A. I.; Pasynskii, A. A.; Amisimov, K. N.; Kolobova, N. E.; Struchkov, Y. T. *J. Chem. Soc., Chem. Commun.* **1969**, 277–278. (c) Pasynskii, A. A.; Skripkin, Y. V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1979**, 165, 39–47. (d) Bokiy, N. G.; Gatilov, Y. T.; Struchkov, Y. T.; Ustynyuk, N. A. *J. Organomet. Chem.* **1973**, 54, 213–219. (e) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, 101, 5094–5095. (f) Laine, R. M.; Moriarty, R. E.; Bau, R. *J. Am. Chem. Soc.* **1972**, 94, 1402–1403. (g) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, 101, 5764–5773. (h) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1983**, 22, 41–44. (i) Maassarani, F.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, 106, 8002–8004. (j) Hey, E.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, 514, 25–38.

(4) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, 10, 1–8. (b) King, R. B.; Haiduc, I.; Eavenson, C. W. *J. Am. Chem. Soc.* **1973**, 95, 2508–2516. (c) King, R. B.; Haiduc, I.; Efraty, A. *J. Organomet. Chem.* **1973**, 47, 145–151. (d) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1977**, 100, 1750–1759. (e) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, 94, 3021–3025. (f) Sakurai, H.; Nakadaira, Y.; Hosomi, A.; Eriyama, Y.; Kazuhiro, H.; Kabuto, C. *J. Am. Chem. Soc.* **1984**, 106, 8315–8316.

(5) (a) Boganovic, B.; Kroner, M.; Wilke, G. *Justus Liebig's Ann. Chem.* **1966**, 699, 1–23. (b) Jonas, K.; Heimbach, P.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1968**, 7, 949–950. (c) Fischer, K.; Jonas, K.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, 12, 565–566. (d) Dietrich, H. *Acta Crystallogr., Sect. B* **1972**, 28, 2807–2814. (e) Brauer, D. J.; Krüger, C. *J. Organomet. Chem.* **1972**, 44, 397–402. (f) Day, V. W.; Abdel-Miguid, S. S.; Dabestani, S.; Thomas, M. G.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, 98, 8289–8291. (g) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, 100, 2090–2096. (h) Rosch, N.; Hoffman, R. *Inorg. Chem.* **1974**, 13, 2656–2666. (i) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, 19, 257–304.

(6) (a) Ibers, J. A.; Page, C. J.; Martinsen, J.; Hoffman, B. M. *Struct. Bonding (Berlin)* **1982**, 50, 1–55. (b) Marks, T. J. *Science (Washington, D.C.)* **1985**, 227, 881–889. (c) Diel, B. N.; Inabe, T.; Jaggi, N. K.; Lyding, J. W.; Schneider, O.; Hannack, M.; Kannewurf, C. R.; Marks, T. J.; Schwartz, L. H. *J. Am. Chem. Soc.* **1984**, 106, 3207–3214. (d) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, 105, 1551–1567. (e) Schramm, C. S.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, 102, 6702–6713. (f) Joyner, R. D.; Kenney, M. E. *J. Am. Chem. Soc.* **1960**, 82, 5790–5791. (g) Nohr, R. S.; Kuznesof, P. M.; Wynne, K. J.; Kenney, M. E.; Siebenman, P. G. *J. Am. Chem. Soc.* **1981**, 103, 4371–4377.

(7) (a) Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1983**, 16, 15–21. (b) Phillips, T. E.; Scaringe, R. P.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, 102, 3435–3443.

(8) (a) Wudl, F. *Acc. Chem. Res.* **1984**, 17, 227–232. (b) Maugh, T. H. *Science (Washington, D.C.)* **1983**, 222, 606–607. (c) Williams, J. M.; Beno, M. A.; Wang, H.; Reed, P. E.; Azevedo, L. J.; Schirber, J. F. *Inorg. Chem.* **1984**, 23, 1792–1793. (d) Greene, R. L.; Street, G. B. *Science (Washington, D.C.)* **1984**, 226, 651–656. (e) Gamble, F. R.; DiSalvo, F. J.; Klemm, R. A.; Geballe, T. H. *Science (Washington, D.C.)* **1970**, 168, 568–570. (f) Gressier, P.; Meerschaut, A.; Guemas, L.; Rouxel, J.; Monceau, P. *J. Solid State Chem.* **1984**, 51, 141–151.

(9) Etemad, S.; Heeger, A. J.; MacDiarmid, A. G. *Annu. Rev. Phys. Chem.* **1982**, 33, 443–470.

(10) Coleman, L. B.; Cohen, M. J.; Sandman, A. J.; Sandman, A. J.; Yamagashi, F. G.; Carito, A. F.; Heeger, A. J. *J. Solid State Commun.* **1973**, 12, 1125–1131.

(11) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; R. E. Krieger Publishing Co.: Malabar, FL, 1982.

(12) Campbell, I. D.; Eglinton, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87–89.

(13) (a) See ref 5a. (b) Purchased from Strem Chemical, vacuum sublimed, and stored under Argon.

(14) The ¹H spectrum shows two sextets (7.66, 6.80 ppm, $J = 3.07 (5) \text{ Hz}$) indicating a symmetric ortho-substitution pattern. Intensity differences between the two multiplets are a solvent effect. The ¹³C spectrum shows four peaks, two with attached protons and two without attached protons. The assignments are as follows (see Figure 1): C(01), 101.8; C(03), 128.2; C(13), 130.0; C(14), 128.1 ppm. All data were recorded on a Varian XL-200 at room temperature in C_6D_6 , internal secondary reference (7.15 (¹H), 128.5 ppm (¹³C)).

(15) Schwarzkopf Microanalytical Laboratory, Analyzed for C, H. Found: 79.5% C, 3.25% H. Calcd: 80.3% C, 3.37% H.

(16) Molecular weight calculated for ⁵⁷Ni¹²C₂₄¹H₁₂ is 358.03 amu.

(17) Staab, H. A.; Graf, F. *Chem. Ber.* **1970**, 103, 1107–1118.

(18) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, 102, 3288–3290.

(19) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 110–113.

(20) (a) Wirz, J. *Helv. Chim. Acta* **1976**, 59, 1647–1654. (b) Mullen, K. *Chem. Rev.* **1984**, 84, 603–646. (c) Results to be published.

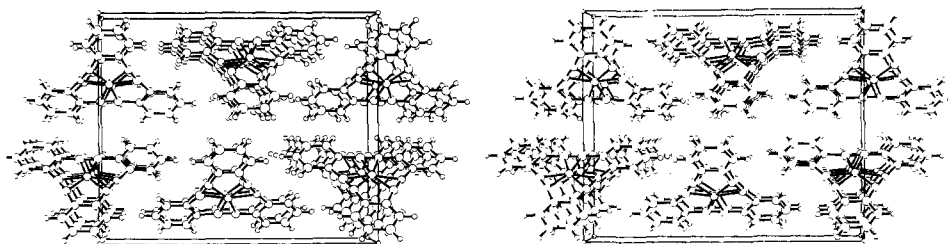


Figure 2. ORTEP stereoview of $\text{Ni}(\text{C}_{24}\text{H}_{12})$ along the c axis with the b axis to the right. The ellipsoids are drawn at the 50% probability level except for the hydrogen atoms which are drawn arbitrarily small for clarity.

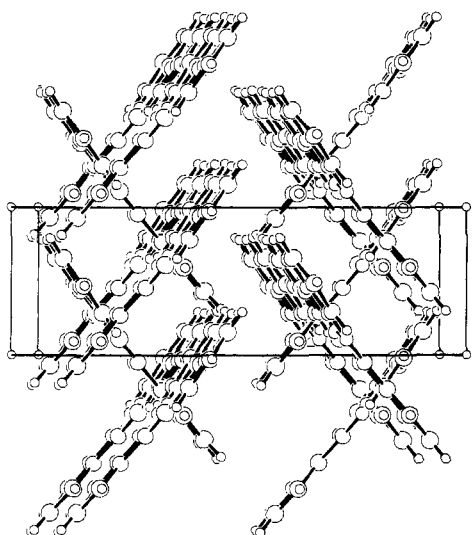


Figure 3. ORTEP packing diagram along the b axis with the a axis to the right.

Crystals suitable for X-ray diffraction studies were obtained on recrystallization from benzene.²¹ Intensity data were collected in air on a Syntex P2₁ single-crystal diffractometer. The structure was solved and refined to a final $R_w = 0.044$ ($I \geq 3\sigma(I)$).²² The molecule is nearly planar with Ni-acetylenic-carbon distances averaging 1.958 (5) Å as compared to 1.899 (19) Å in $\text{Ni}(t\text{-BuN}\equiv\text{C})_2(\text{PhC}\equiv\text{CPh})$.²³ The acetylene linkages are distorted from linearity with C—C≡C angles averaging 173.8 (9)° compared to 178.3 (9)° for the free cyclyne²⁴ and 148.6 (14)° for $\text{Ni}(t\text{-BuN}\equiv\text{C})_2(\text{PhC}\equiv\text{CPh})$. The distortion from linearity is the least that has been reported for any π -bound acetylene complex and may be imposed by the benzo rings. The acetylenic carbon-carbon bond length in the complex is 1.240 (10) Å compared with 1.192 (2) Å in the free cyclyne and 1.284 (16) Å for $\text{Ni}(t\text{-BuN}\equiv\text{C})_2(\text{PhC}\equiv\text{CPh})$. The ORTEP packing diagram along the c axis (Figure 2) shows a slipped-stack arrangement with the benzo groups eclipsed. A view along the b axis (Figure 3) shows a herringbone pattern with an interplanar distance of 3.37 (1) Å. The free cyclyne is also slipped stacked²⁴ with an interplanar spacing of 3.29 Å and the benzo groups staggered.

Further synthetic work will center upon using modified ligands and different metal centers as well as controlled oxidation and reduction. Preliminary reactions with I_2 with TCNQ as oxidizing agents have given several solid phases that are presently under study. Electrochemical, conductometric, spectral, and theoretical

studies are in progress.

Acknowledgment. Special thanks to Drs. W. J. Kroenke and R. P. Lattimer of the BFGoodrich Co., Brecksville, OH, for the FD-MS and to Dr. D. Gervasio and Peter Faguy. Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and an Olin Corporation Charitable Trust Grant of Research Corporation for partial support of this research.

Supplementary Material Available: Tables of data collection and structure solution details, atomic positional and thermal parameters, and structure factors (12 pages). Ordering information is given on any current masthead page.

Stereochemical Course of Phosphoryl Transfer Reactions of P^1, P^1 -Disubstituted Pyrophosphate in Aprotic Solvent. A Model for the Enzyme-Catalyzed "Dissociative" Phosphoryl Transfer

Paul M. Cullis* and Andrew J. Rous

The Department of Chemistry, Leicester University
Leicester LE1 7RH, England

Received May 29, 1985

The evidence in favor of a monomeric metaphosphate intermediate in the reactions of monosubstituted phosphates appears to be persuasive.¹ However, recent stereochemical studies^{1,2} on nucleophilic displacement reactions of phosphate monoesters have demonstrated that they occur with inversion of configuration in *protic* solvents, which argues against a "free" metaphosphate in these instances. A considerable amount of the direct evidence for the intermediacy of monomeric metaphosphate has been obtained in organic solvents (the three-phase test,³ Conant and Swan fragmentation,⁴ phosphorylation of hindered alcohols⁵). It remains a significant possibility that a metaphosphate-like intermediate may have a longer lifetime in organic solvents. We report here one of the first determinations of the stereochemical course of a phosphoryl transfer reaction in an organic solvent. A chiral [¹⁶O,¹⁷O,¹⁸O]pyrophosphate derivative has been used to determine the stereochemical course of the phosphoryl transfer reaction of a P^1, P^1 -disubstituted pyrophosphate. This reaction may represent a good model for the hypothetical enzyme-catalyzed "dissociative" phosphoryl transfer, particularly since such enzyme-catalyzed reactions often involve a pyrophosphate phosphoryl donor.

The dianions of P^1, P^1 -disubstituted pyrophosphates have been shown to be extremely reactive⁶ as compared to the corresponding mono-, P^1, P^2 -di-, and trisubstituted pyrophosphates. This reactivity has been explained in terms of a facile dissociative decomposition to give a metaphosphate intermediate, Scheme Ia. The study

(21) Crystallographic data: Space group, $Pna2_1$, $a = 15.518$ (3) Å, $b = 18.761$ (4) Å, $c = 5.375$ (1) Å; $p_{\text{total}} = 1.528$; $p_{\text{obsd}} = 1.54$; $Z = 4$; FW = 359.07. The intensity data were collected from $3.0 \leq 2\theta \leq 55.0$. Refinement to convergence on the 848 independent reflections, $I \geq 3\sigma(I)$, resulted in final isotropic $R = 0.046$ and $R_w = 0.044$.

(22) The U.C.L.A. Crystallographic Computing Package, Jan 5, 1982.

(23) Dickson, R. S.; Ibers, J. A. *J. Organomet. Chem.* **1972**, *36*, 191-207.

(24) Inrgartinger, H.; Lesisierowitz, L.; Schmidt, G. M. *J. Chem. Ber.* **1970**, *103*, 1119-1131.

(1) Buchwald, S. L.; Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4911 and references cited therein.

(2) Buchwald, S. L.; Knowles, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1438.

(3) Rebek, J.; Gavina, F.; Navarro, C. *J. Am. Chem. Soc.* **1978**, *100*, 8113.

(4) Calvo, K. C.; Westheimer, F. H. *J. Am. Chem. Soc.* **1983**, *105*, 2827.

Satterthwait, A. C.; Westheimer, F. H. "Phosphorus Chemistry Directed Toward Biology"; Stec, W. J., Ed.; Pergamon Press: New York, 1980, p 117.

(5) Ramirez, F.; Marecek, J. F. *Tetrahedron* **1979**, *35*, 1581. Ramirez, F.; Marecek, J. F. *Tetrahedron* **1980**, *36*, 3151.

(6) Brown, D. M.; Hamer, N. K. *J. Chem. Soc.* **1960**, 1155.