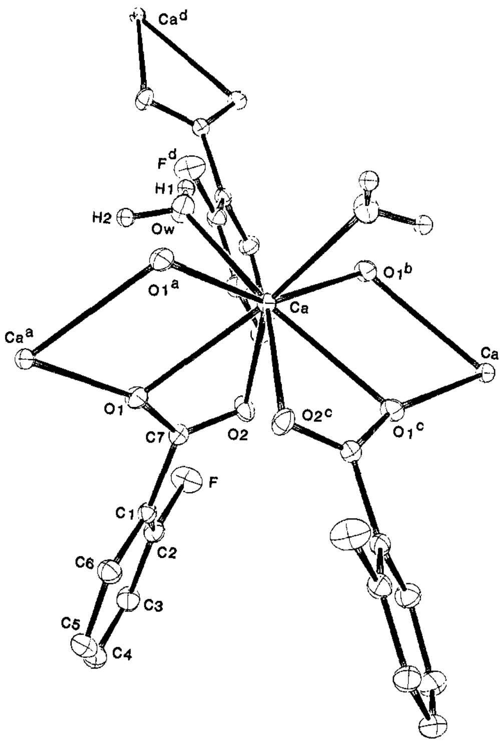

Figure 1. A portion of the structure showing the CaO_8 coordination polyhedron, mode of ligand–Ca^{2+} binding, and the spatial relationship of the O_w–H1···F^d hydrogen bond. The aryl hydrogen atoms have been omitted for clarity. The superscripts refer to the following symmetry-related positions: (a) $-x, -y, 1 - z$; (b) $x, -y, z - 1/2$; (c) $-x, y, 1/2 - z$; (d) $-x - 1/2, 1/2 + y, -z - 1/2$.

gen-containing donors has been demonstrated. For example, this type of binding occurs in the metal complexes of adenosine triphosphate[10] as well as in the Fe^{3+}–OH_2–histidine portion of ferrimyoglobin.[11]

Calcium(II) ion has a high preferential affinity for oxygen donor groups, and we anticipate that in aqueous solution Ca^{2+}···water and Ca^{2+}···carboxylate interactions predominate. Since coordinated water molecules are the most acidic water molecules in solution and in view of the expected polarity of the C–F bond, the formation of weak water-bridged C–F···H_2O···Ca^{2+} interactions, however tenuous, is not unreasonable, especially since this water-mediated coordination survives in the crystal. We are not certain of all the factors whereby a carbon-bound fluorine atom could actually displace a coordinated water molecule or other donor group. There is ample crystallographic evidence that such displacement does occur in many alkali metal salts of fluorocarboxylates. It may very well also prove to occur for large alkaline-earth ions.

For divalent or trivalent transition-metal cations, however, we would expect coordinated water molecules to be more acidic and considerably less labile than for alkali metal ions. In these systems direct C–F···M binding may be relatively less favorable compared to the water-bridged structure, C–F···H_2O···M. We suggest that such outer-sphere coordination of carbon-bound fluorine through a hydrogen bond may play an important role in explaining fluorocitrate inhibition of aconitase.

Registry No. $[Ca(C_7H_4FO_2)_2(H_2O)_2]$, 88686-23-1.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances and angles, and shape parameters and a list of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(11) Nobbs, C. L.; Watson, H. C.; Kendrew, J. C. *Nature (London)* **1966**, *209*, 339.

Synthesis and X-ray Crystal Structure of a Transition-Metal Cluster Involving Framework Phosphorus–Phosphorus Double Bonds

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The synthesis and X-ray crystal structure of the first diphosphene by Yoshifuji and co-workers in 1981 has generated considerable interest in multiple bonding among the heavier main-group 5 elements.[1] So far, structural reports have dealt with compounds having unsupported P–P,[2] P–As,[3] or As–As[4] double bonds and their simple transition-metal complexes.[5] In this paper we report the synthesis and structure of a rare transition-metal cluster involving P–P double bonds. This is the compound $[Ni_5(CO)_6[(Me_3Si)_2CHP{=}PCH(SiMe_3)_2]_2Cl]$ (**1**), which represents a significant development in both transition-metal cluster and diphosphene chemistry.

The synthesis of **1** involved the addition of a solution of $P[CH(SiMe_3)_2]Cl_2$ (1 equiv) in ether to a freshly prepared solution of $Na_2[Ni_6(CO)_{12}]$ (1 equiv).[6] The ether was removed after stirring for 12 h, and the residue was redissolved in *n*-hexane to give a red-brown solution. Filtration and subsequent cooling gave **1** as red-brown crystals in ca. 15% yield (based on phosphorus), IR (Nujol) 2018, 1723 cm^{-1}. ^{31}P NMR indicated that the *n*-hexane solution contained other species in addition to **1**, and work is in progress to characterize these. The singlet seen at 353 ppm (in C_6D_6 relative to 85% H_3PO_4) has been assigned to **1**.

The structure of **1** was determined by X-ray diffraction[7] and is illustrated in Figure 1. The molecular geometry involves four of the five nickel atoms in a butterfly arrangement. These four nickels are bound to terminal carbonyls, and two additional carbonyls triply bridge the underside of each butterfly wing. The two diphosphene ligands bridge two wing tips and hinge metal centers to the fifth nickel atom, Ni(1), which is also bonded to chlorine. The Ni–Ni distances within the butterfly average ca. 2.55 Å while Ni(1)–Ni(3) and Ni(1)–Ni(5) distances are somewhat longer, averaging 2.69 Å (cf. ref 6). The diphosphene ligands interact most closely with Ni(3) and Ni(5) as exemplified by the short Ni–P distances, average ca. 2.18 Å.[8] The P–Ni(1),

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(1) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589.

(2) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4045–4046.

(3) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R. *J. Chem. Soc., Chem. Commun.* **1983**, 881–882.

(4) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506–5507.

(5) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085–2086. Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Ibid.* **1983**, *105*, 7460–1. Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Ibid.* **1983**, *105*, 7750–1. Cowley, A.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Ibid.* **1983**, *105*, 7751–2.

(6) Longoni, G.; Chini, P.; Cavalieri, A. *Inorg. Chem.* **1975**, *15*, 3025–3029. Calabrese, J. C.; Dahl, L. F.; Cavalieri, A.; Chini, P.; Longoni, G.; Martinego, S. *J. Am. Chem. Soc.* **1974**, *96*, 2616–2618.

(7) A red-brown crystal of **1** of dimensions 0.10 × 0.12 × 0.14 mm was mounted on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. With Mo Kα ($\lambda = 0.71069$ Å) and crystal cooled to 140 K, crystal data were as follows: monoclinic $P2_1/c$; $a = 19.853$ (4) Å, $b = 13.686$ (3) Å, $c = 23.298$ (4) Å; $\beta = 113.13$ (1)°; $Z = 4$; $\mu = 19.5$ cm^{-1} (range of absorption correction factors 1.2–1.36). Data were collected to $2\theta_{max}$ of 45° with a ω scan technique. A total of 7592 unique data were collected of which 5484 had $I > 2\sigma(I)$. Scattering factors and corrections for anomalous scattering were from Vol. IV of the International Tables. The structures were solved by direct methods. Computer programs were those of SHELXTL, version 3, July 1981 package. The refinement was marred by a disorder of all four Si's on one of the diphosphene groups that exhibited 50–50 disorder with another set of four Si's. Two of the three methyl groups were shared by these disordered Si's. Occupancy factors were initially refined to 0.51–0.49 and subsequently fixed at 0.50. With an absorption correction and anisotropic thermal parameters for atoms other than methyl carbons and hydrogens $R = 0.07$ and $R_w = 0.074$.

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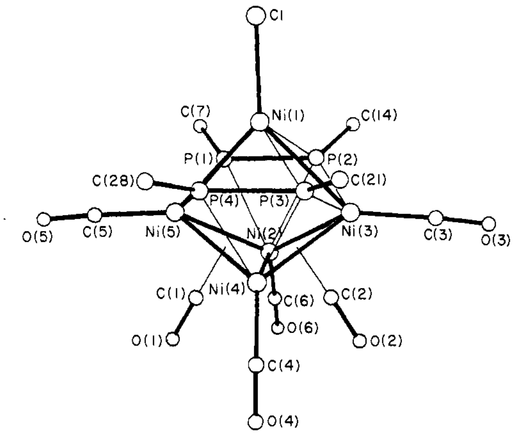

Figure 1. Computer-generated diagram of **1** showing numbering scheme. The SiMe$_3$ groups are not shown for clarity. Some important bond distances (Å) and angles (deg): P(1)–P(2) = 2.085 (4), P(3)–P(4) = 2.098 (4), Ni(2)–Ni(4) = 2.528 (2); Ni(3)–Ni(2), –Ni(4) = 2.556 (2), 2.560 (2); Ni(5)–Ni(2), –Ni(4) = 2.583 (2), 2.559 (2); Ni(1)–Ni(3), –Ni(5) = 2.706 (2), 2.682 (2); C(1)–Ni(5), –Ni(2), –Ni(4) = 1.955 (13), 2.088 (9), 2.050 (12); similarly for C(2); Ni–C distances for terminal carbonyls average 1.795 (3); Ni–Cl = 2.229 (7); Ni(2)–Ni(5)–Ni(4) = 58.9 (1); P(2)–Ni(1)–P(3) = 100.7 (1); P(2)–Ni(1)–P(4) = 125.4 (1); Ni(1)–P(3)–Ni(3) = 72.3 (1); Ni(3)–P(3)–Ni(4) = 68.3 (1); P(3)–Ni(4)–P(4) = 52.4 (1).

P–Ni(2), and P–Ni(3) distances are almost 0.2 Å longer, averaging ca. 2.37 Å. The P(1)–P(2) and P(3)–P(4) distances are 2.085 (4) and 2.098 (4) Å. These lengths are quite close to the average distances for a P–P double bond, 2.02–2.06 Å, and very much shorter than the 2.2–2.5 Å average for a P–P single bond. The P···P distances between each of the diphosphene moieties are long, P(2)–P(3) = 3.672 and P(1)–P(4) = 3.680 Å precluding any P–P bonding between diphosphene units.

We believe the structure of **1** is unique for several reasons: (i) it is the first example of a metal cluster that involves essentially unsupported heavier main-group element double bonds as an integral part of the framework;[9] (ii) the diphosphene ligands are also interesting since they are in the cis configuration, and with one exception[9] all published structural data have dealt with trans diphosphenes only; (iii) so far as we are aware there are no other transition-metal clusters involving nine-atom frameworks in a geometry resembling **1**.

Several other aspects of the structure of **1** are also worthy of comment. Each of the diphosphene ligands behaves as a σ-donor toward Ni(3) and Ni(5), which results in fairly short Ni–P distances. The Ni–P distances involving Ni(1), Ni(2), and Ni(4) are among the longest reported.[8,10] These bond lengths suggest that the diphosphenes are behaving as very weak π-bonding ligands toward these three nickel atoms. Another feature of interest of **1** is that it has an odd number of electrons. Ni(1) is in the formal oxidation state of 1+ while the other nickel atoms are neutral.

The synthetic route to **1** again demonstrates the powerful effect of steric factors on the product obtained. Dahl and Lower have reported that a very similar reaction between PCl$_2$Ph and [Ni$_6$(CO)$_{12}$]$^{2-}$ gave the species Ni$_8$(CO)$_8$(μ_4-PPh)$_6$ involving a cubic arrangement of nickel atoms with each face capped by a μ_4-phenylphosphido group.[11] Substituting the phenyl group with CH(SiMe$_3$)$_2$ results in a drastic change in the nature of the product. Studies using a variety of bulky substituents at the phosphorus atom are now under way in this laboratory.

Acknowledgment. We are grateful to the Research Corporation and NSF (CHE-8116355) for financial support.

Registry No. 1, 88703-05-3; Na$_2$[Ni$_6$(CO)$_{12}$], 88669-39-0; P[CH(SiMe$_3$)$_2$]Cl$_2$, 76505-20-9.

Supplementary Material Available: Listing of atom coordinates, temperature factors, and bond distances and angles and structure factor tables for **1** (39 pages). Ordering information is given on any current masthead page.

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(8) McAuliffe, C. A. "Phosphine, Arsine and Stibine Complexes of the Transition Elements"; Elsevier: Amsterdam, 1973; p 129–144.

(9) Vahrenkamp, H.; Wolters, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154. This paper describes the structure and preparation of the compound [[Fe(CO)$_3$]$_2$(P-*t*-Bu)$_2$], which has two Fe and two P atoms in a tetrahedral array. The complex has the cis diphosphene moiety *t*-BuP=P-*t*-Bu bonded to (CO)$_3$Fe–Fe(CO)$_3$ with mutually perpindicular PP and FeFe axes. In this sense the PP double bond is "supported" by iron carbonyl although the PP distance is 2.059 (3) Å, consistent with a PP double bond formulation.

(10) Hope, H.; Olmstead, M. M.; Power, P. P.; Viggiano, M. *Inorg. Chem.*, in press. The complex [Ni(CN)$_2$[P(CH$_2$OH)Ph$_2$]$_3$] has an Ni–P bond length of 2.400 (3) Å.

(11) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046–5047.

Intramolecular Alkoxypalladation/Carbonylation of Alkenes

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Furan and pyran rings occur frequently in current synthesis targets such as the ionophore antibiotics,[1] and new synthesis methods are increasingly important. Hydroxyalkenes of appropriate length can be activated by Pd(II) toward addition of the hydroxy group to the double bond. The product would be an alkylpalladium(II) complex which might be usefully cleaved by CO or other agents.[2] In this paper, we consider the selectivity parameters in general aliphatic cases, including a short stereoselective synthesis of a glandular secretion from the civet cat, compound **1a**.[7,8]

Our simplest test case is compound **1a** from the civet cat. Initial studies were carried out with the racemic alcohol **2**.[9] The Pd(II)-catalyzed cyclizations are operationally simple. A mixture

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(1) For example, the ionophore antibiotics: ApSimon, J. "The Total Synthesis of Natural Products"; Wiley-Interscience: New York, 1976; Vol. 4, p 263.

(2) The intermolecular addition of nucleophiles to alkenepalladium(II) complexes is very general,[3] but catalytic addition/CO trapping is usually not efficient. (a) For general examples of 1-alkenes in catalytic alkoxycarbonylation (50–60% yields) and studies with disubstituted alkenes (low yields), see: James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810. (b) For examples of stoichiometric addition of secondary amines to 1-alkenes followed by CO insertion and full characterization of the intermediate acylpalladium(II) complex, see: Hegedus, L. S.; Siirala-Hansen, K. *Ibid.* **1974**, *97*, 1184. (c) For examples of stoichiometric addition of carbon nucleophiles followed by CO trapping ("carboacylation"), see: Hegedus, L. S.; Darlington, W. H. *Ibid.* **1980**, *102*, 4980. The intramolecular version is also well-known,[4-6] but trapping with CO is successful only in special cases.[5,6]

(3) For a general discussion, see: (a) Collman, J. P.; Hegedus, L. S., "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 585–590. (b) Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: Oxford, 1982; pp 157–162. (c) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: Berlin, 1980; pp 5–35. Many examples with oxygen nucleophiles are known. For discussion and leading references, see: Trost, B. M. *Tetrahedron* **1977**, *33*, 2615–2649.

(4) Hegedus, L. S.; McKearing, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444 and references therein.

(5) For an example involving amines, amides, and carboxylate, with CO trapping, see: Hegedus, L. S.; Allen, G. F.; Olsen, D. J. *J. Am. Chem Soc.* **1980**, *102*, 3583.

(6) (a) Semmelhack, M. F.; Zask, A. *J. Am. Chem. Soc.* **1983**, *105*, 2034. (b) Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W.; Spiess, E.; Zask, A. *Ibid.* **1982**, *104*, 5850.

(7) For isolation, structure determination, and the first synthesis, see: Mauer, B.; Grieder, A.; Thommen, W. *Helv. Chim. Acta* **1979**, *62*, 44.

(8) For previous syntheses of the racemic product, see: (a) Kim, Y.; Mundy, B. P. *J. Org. Chem.* **1982**, *47*, 3556. (b) Ley, S. V.; Lygo, B.; Molines, H.; Morton, J. K. *J. Chem. Soc., Chem. Commun.* **1982**, 1251. For a synthesis of the natural optical isomer, see: (c) Seebach, D.; Pohmakotr, M. *Helv. Chim. Acta* **1979**, *62*, 843. **Note Added in Proof**: A synthesis of racemic **1a** was reported after this manuscript was submitted: Bates, H. A.; Deng, P.-N. *J. Org. Chem.* **1983**, *48*, 4479.

(9) For typical procedures, structure elucidation, and complete characterization data, see the supplementary material.

0002-7863/84/1506-1496$01.50/0