

of Pep-2 in pH 7.5 phosphate buffer with 0% TFE revealed 13% α -helicity, identical with Pep-1. However, Pep-2 had an even greater helical potential than Pep-1, as the α -helicity increased to 81% in 80% TFE.

DNA binding was further characterized by assessing the efficacy of the peptides in protecting DNA from digestion by the restriction endonucleases *Hind*III and *Eco*RI. Linearized plasmid PBR322 DNA was digested and analyzed by methods similar to those reported by others.¹⁹ Preincubation of peptide with DNA (30 min at 37 °C) prior to the initiation of digestion caused a decrease in subsequent DNA cleavage. Greater protection was seen with Pep-2 than with Pep-1, presumably because of the glutamine-mediated hydrogen bonds. Thus, Pep-2 at 20 μ M caused a 50% reduction in *Hind*III DNA cleavage; 20 μ M Pep-1 did not inhibit *Hind*III cleavage. Pep-2 at 120 μ M caused a 50% reduction in *Eco*RI DNA cleavage; 120 μ M Pep-1 caused a 20% reduction in *Eco*RI cleavage.

We have shown that a suitably designed peptide may adopt a predominantly α -helical conformation when bound to DNA, in spite of having minimal regular secondary structure in solution. Furthermore, hydrogen-bonding residues appear to increase the affinity of the helical peptides for binding to DNA, as has been postulated for helical regions of DNA-binding proteins. These results provide a necessary base for the rational design of sequence-specific DNA-binding peptides and demonstrate the potential utility of peptides in modeling the interactions between DNA and helical regions of endogenous proteins.

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Reactions of Coordinated Ligands: Coupling of Two Diphosphenes (P=P) at a Metal Center To Give a Coordinated Phosphametallo-cyclopentane. Synthesis and X-ray Structure of $(t\text{-BuPP-}t\text{-Bu})\text{Ni}(t\text{-BuP-}t\text{-BuP-}t\text{-BuP-}t\text{-BuP})$: A Square-Planar Ni(II) Geometry Imparted by Sterically Demanding Ligands

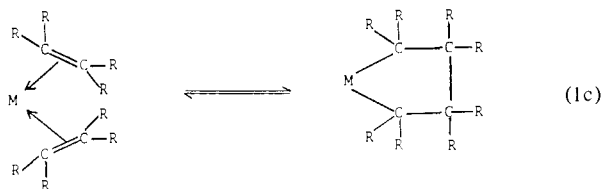
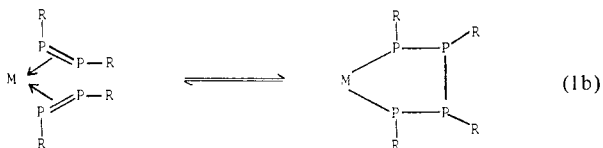
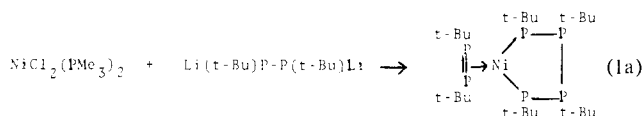
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There has been much recent interest in multiple bonding among the heavier main group 5 elements.¹ Structural details have been reported for unsupported P=P,^{1,2} P=As,³ and As=As⁴ double

bonds and some transition-metal complexes.⁵ Some initial reactivity studies have also been reported.^{5,6} We report here the synthesis and X-ray crystal structure of the unusual complex $(t\text{-BuPP-}t\text{-Bu})\text{Ni}(t\text{-BuP})_4$ (**1**) (eq 1a) which is unique for the



following reasons: (a) **1** contains the phosphametallo-cyclopentane unit $\text{Ni-}t\text{-BuP-}t\text{-BuP-}t\text{-BuP-}t\text{-BuP}$ which demonstrates the first example of a coupling reaction between two diphosphenes (P=P) units at a metal center (eq 1b).⁷ Such a reaction would be analogous to metallacyclopentane formation for alkenes (eq 1c).⁸ (b) **1** is the first example of a mononuclear η^2 -bonded diphosphene transition-metal complex that does not have Cp, CO, or PR₃ as supporting ligands.⁹ Mononuclear η^2 -bonded P=P systems are

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(7) A few other examples of R₄P₄ units coordinated to transition metals are known. They have generally been prepared by direct reaction of metal carbonyls with cyclic phosphines (RP)_n, e.g., Fe₂(CO)₉(PC₆F₅)₄: (a) Elmes, P. S.; Leverett, P.; West, B. O. *J. Chem. Soc., Chem. Commun.* 1971, 747. (b) Ang, H. G.; West, B. O. *Aust. J. Chem.* 1967, 20, 1120.

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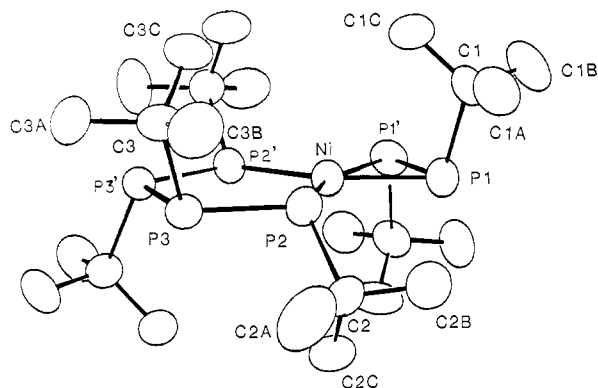


Figure 1. General view of **1**. Key bond lengths and angles are given in ref 13 and the text.

rare; so far only one other for Ni has been reported.⁹ (c) **1** contains the shortest P–P distance so far reported for mononuclear η^2 -bonded diphosphene complexes (2.110 (5) Å).⁹ (d) The coordination geometry around the Ni atom in **1** also bears a curious twist. Four-coordinate mononuclear Ni(II) complexes generally prefer a planar geometry.¹⁰ However, the presence of bulky substituents on ligands can frequently cause a pseudotetrahedral geometry to be stabilized due to the relief of steric strain.¹⁰ In **1** despite the presence of bulky *t*-Bu groups attached to each phosphorus atom the coordination geometry about Ni is virtually planar. In fact the configuration of ligands does give the best relief from steric strain (see below).

We have prepared **1** via the interaction of $\text{NiCl}_2(\text{PMe}_3)_2$ with $\text{Li}_2(t\text{-BuP-P-}t\text{-Bu})$ (1:1) in THF at -78°C .¹¹ The complex is air-sensitive both in the solid state and in solution. The formation of a coordinated diphosphene via salt elimination from Pt(PPh_3)₂Cl₂ and $\text{Li}_2(\text{PhPPPPh})$ has been recently reported.⁹ In this case the PPh_3 groups remain bound to Pt and $(\text{PPh}_3)_2\text{Pt}(\text{PhPPPPh})$ is the product. However, in the formation of **1** both PMe_3 groups initially attached to Ni are lost and replaced by phosphorus atoms of the metallacycle, each of which acts as a one-electron donor.

The ¹H NMR spectrum of **1** shows a complex multiplet at δ 1.0–1.6 (relative to Me_4Si , in C_6D_6 , ambient temperature). The ³¹P{¹H} NMR shows a second-order six-spin AA'BB'XX' pattern which we have successfully simulated.¹¹ The large value of $^1J_{\text{P}(1)\text{-P}(1')} = 275\text{ Hz}$ ¹¹ is consistent with the strong P=P coupling observed in $[\text{Pd}(\text{PhP}=\text{PPh})\text{dppe}]$ and related complexes⁹ and also with the strong phosphorus couplings found in the free diphosphene systems.¹

(9) P=P distances for mononuclear η^2 -coordinated diphosphenes are as follows: $(\text{PPh}_3)_2\text{Pt}(\text{PC}_6\text{F}_5)_2$, 2.156 (7) Å (Reference 7a). (Elmes, P. S.; Scudder, M. L.; West, B. O. *J. Organomet. Chem.* **1976**, *122*, 281); $\text{Cp}_2\text{Mo}(\text{PH})_2$, 2.146 (3) Å (Green, J. C.; Green, M. L. H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1974**, 212. Cannillo, E.; Coda, A.; Prout, K.; Doran, J.-C. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2608); $(\text{PEt}_3)_2\text{Ni}(\text{PSiMe}_3)_2$, 2.149 (2) Å (Schafer, H. Z. *Naturforsch., B* **1979**, *34B*, 1358. Deppisch, B.; Schafer, H. *Acta Crystallogr., B* **1983**, *38B*, 748); $(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)\text{Pd}(\text{PPh}_2)_2$, 2.121 (4) Å (Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932). See also, for related complexes: Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2237.

(10) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 21, p 790.

(11) **1** may be isolated as orange crystals following evaporation to dryness of the reaction mixture and recrystallization of the residue from hexane: yield 30%, mp 183–184 °C dec; IR (Nujol mull, KBr plates) 1470 s, 1450 s, 1390 m, 1350 s, 1260 w, 1165 s, 1130 w, 1100 br w, 1020 m, 1010 m, 935 br w, 840 m, 805 s, 755 cm^{-1} ; ¹H NMR (C_6D_6 ; ambient temperature) δ 1.0–1.6 (multiplet); ³¹P{¹H} NMR δ 53.6 m [appears as ddt (P(2) and P(2)')], δ 45.03 m, [appears as t (P(1) and P(1)')], δ 29.21 m [appears as dd (P(3) and P(3)')]. The six-spin AA'BB'XX' system has been successfully simulated by using the following coupling constants: $^1J_{\text{P}(1)\text{-P}(1')} = 275\text{ Hz}$; $^2J_{\text{P}(1)\text{-P}(2)} = 22\text{ Hz}$; $^2J_{\text{P}(1)\text{-P}(2')} = 1\text{ Hz}$; $^3J_{\text{P}(2)\text{-P}(3)} = 225\text{ Hz}$; $^1J_{\text{P}(3)\text{-P}(3')} = 325\text{ Hz}$ (The numbering scheme is the same as in Figure 1). Larger values of $^1J_{\text{P}(1)\text{-P}(1')}$ cause no apparent variation in the simulated spectrum so the value above can be taken as a minimum coupling constant. Observed and simulated spectra are deposited with the supplementary material. Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{NiP}_6$: C, 49.09%; H, 9.27%; P, 31.65%. Found: C, 49.01%; H, 9.25%; P, 30.94%.

The structure of **1** was determined by a single-crystal X-ray diffraction study (Figure 1).¹² There are several interesting features. The four phosphorus atoms of the phosphametallocycle, P(2), P(3), P(3)', P(2)', the two of the diphosphene, P(1), P(1)', and the Ni atom are all virtually coplanar.¹³ There is a crystallographically imposed twofold axis which passes through the midpoint of the diphosphene unit (P(1) and P(1)'), the Ni atom and the two phosphorus atoms of the phosphametallocycle which are not bound to Ni (P(3) and P(3)'). The *t*-Bu groups of the diphosphene are in the trans configuration as found in most other cases of diphosphene coordination to transition metals.¹⁴ The P(1)–P(1)' distance of this unit of 2.110 (5) Å is the shortest so far reported for a mononuclear η^2 -diphosphene unit.⁹ The distance falls almost exactly half-way between the values normally expected for a single P–P bond (ca. 2.2 Å) and those observed for uncoordinated P=P double bonds (ca. 2.0 Å).¹⁵

The six *t*-Bu groups occupy alternate positions above and below the plane containing six P atoms and the Ni. Although the coordination of Ni by P atoms is planar the four closest *t*-Bu groups actually occupy pseudotetrahedral sites about this atom. This configuration thus minimizes steric repulsion between ligands. The two unique P–P distances of the five-membered ring are both in the range expected for P–P single bonds¹⁵ (P(2)–P(3) = 2.237 (5) Å; P(3)–P(3)' = 2.196 (4) Å). All the phosphorus atoms of the five-membered ring have noncoordinated lone pairs. Those attached to the nickel atom (P(2) and P(2)') are presumed to be one-electron rather than three-electron donors because of their pyramidal geometry (Ni–P(2)–P(3) = 114.8 (2)°, Ni–P(2)–C(2) = 121.2 (4)°, P(3)–P(2)–C(2) = 104.2 (4)°).

Stable uncoordinated *t*-BuP=P-*t*-Bu has never been isolated, presumably because the *t*-Bu groups are not sufficiently bulky to prevent oligomerization to the tetramer (*t*-BuP)₄.¹⁶ We have failed to detect any free (*t*-BuP)₄ or (*t*-Bu)₄P₄²⁻ in the reaction mixture (³¹P NMR). Although the precise mechanism of formation of **1** is not known at least the involvement of the Ni center in the coupling of the diphosphene units is clearly indicated. One possibility for the mechanism could be a concerted rearrangement. The isolation and characterization of **1** therefore supports the model of an η^2 -coordinated diphosphene as an alkene analogue.⁹

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Supplementary Material Available: Observed and simulated

(12) CAD-4 crystal data: $\text{NiP}_6\text{C}_{24}\text{H}_{34}$, *M*, 587.25, monoclinic, space group *C2/c* (No. 15), *a* = 10.392 (2) Å, *b* = 20.360 (8) Å, *c* = 15.538 (3) Å, β = 90.577 (18)°, *U* = 3287.6 (2.6) Å³, *D_c* = 1.186 g cm⁻³, *Z* = 4, $\lambda(\text{Mo K}\alpha)$ = 0.71069 Å (graphite monochromator), $\mu(\text{Mo K}\alpha)$ = 8.909 cm⁻¹. Methods: Patterson, difference Fourier, full-matrix least squares. Refinement of 1540 observed reflections (*I* > 3 σ (*I*) (2984 unique measured) (4° < 2 θ < 50°) gives current *R* and *R_w* values of 0.0797 and 0.0965, respectively. Data/parameter ratio = 10.62. All non-hydrogen atoms anisotropic, hydrogen atoms not located. There was no disorder in the *t*-Bu groups and the crystal decayed by 8.9% during data collection. The relatively high *R* factor is probably due to poor crystal quality.

(13) Deviation (Å) from the least-squares plane through Ni and the three unique P atoms are as follows: Ni –0.008 (1); P(1) 0.088 (4); P(2) –0.246 (3); P(3) 0.166 (3). Key bond lengths (Å) and angles (deg) are as follows: Ni–P(1) 2.257 (4); Ni–P(2) 2.149 (4); P(3)–P(3') 2.196 (4); P(2)–P(3) 2.237 (5); P(2)–Ni–P(2') 101.2 (2); P(2)–Ni–P(1) 101.5 (1); P(2)–Ni–P(1') 157.2 (2); Ni–P(1)–P(1') 82.1 (1); P(1)–Ni–P(1') 55.7 (1); Ni–P(2)–P(3) 114.8 (2); P(2)–P(3)–P(3') 104.6 (2). A complete listing is provided as supplementary material.

(14) Examples of cis configurations for diphosphenes coordinated to transition metals. $\text{Fe}_2(\text{CO})_6(t\text{-BuP})_2$; Vahrenkamp, H.; Wolters, D. *Angew. Chem.* **1983**, *95*, 152; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154. $\text{Ni}_5(\text{CO})_6[(\text{Me}_3\text{Si})_2\text{CHP}=\text{PCH}(\text{SiMe}_3)_2]\text{Cl}$; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1495.

(15) P–P single bonds are generally ca. 2.2 Å; e.g.: Baudler, M. *Angew. Chem.* **1982**, *94*, 520; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 492. Uncoordinated P=P double bonds are generally ca. 2.0 Å; see ref 1 and 2.

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$^{31}\text{P}\{^1\text{H}\}$ NMR spectra and listings of atomic coordinates, thermal parameters, bond lengths and angles, and structure factors (21 pages). Ordering information is given on any current masthead page.

On the Mechanism of Thermal Rearrangement of (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum

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Much effort has been devoted to changing the reactivity patterns of hydrocarbons by complexing them to transition metals.¹ Generally, this change is believed to occur by selective acceleration of one pathway through direct involvement of the metal in bond-cleaving and/or bond-forming processes. It has not been widely recognized that reactivity patterns can also be changed by selective inhibition of one or more pathways. The rearrangement of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum (**1**) is, we believe, an example of such a phenomenon.

Thermal rearrangement of **1** to (bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum was first reported by Grimme² and depicted as shown in Figure 1. However, our X-ray crystallographic analysis³ shows that the starting material has a syn cyclopropane ring rather than the anti stereochemistry proposed by Grimme (Figure 2).⁴ If migration occurred from this geometry, the product complex would have an exo- η^4 coordination of the hydrocarbon. However, it could presumably attain the final structure by intermolecular exchange, a process that can be shown to be very facile in the η^2, η^4 -bicyclo[4.2.1]nonatriene)tricarbonylmolybdenum under the reaction conditions.

The following data were gathered for the rearrangement. The reaction rate was found to be cleanly first order³ with activation parameters $\Delta H^\ddagger = 27.69 \pm 0.02$ kcal/mol and $\Delta S^\ddagger = -7.8 \pm 0.4$ cal/(mol K) between 72.9 and 125.6 °C in cyclohexane solution. Deuterated reactant³ **1-d₂** gave the product with the label distribution shown in Figure 3. The amount of deuterium (the total being defined as 200%) at each of the minor sites (C3 + C4 and C7 + C8) varied from 4.6% at 125 °C to 8.3% at 185.7 °C but was always equal at the two chemically distinct positions, within experimental error. Starting material recovered from a partial reaction (105.0 min at 125.9 °C) had 168.3% of the deuterium at C1 + C8, 28.9% at C2 + C7 and 2.8% at C3 + C6. Resubmission of the product to the reaction conditions did not cause further isomerization. Stereospecific labeling at C9 showed that there was concentration-dependent epimerization of the starting material, presumably caused by exchange of the ligand with traces of free hydrocarbon, which is known to epimerize very rapidly under these conditions.⁵ This process could be prevented from interfering seriously by running the reaction at low concentration. It could then be determined that the bicyclo[4.2.1]nonatriene complex was formed with essentially complete retention of configuration⁶—the small amount of apparently inverted product (Figure 3) really being due to epimerization of the reactant. In contrast, the process that shifted the labels around the ring in the reactant could be shown to occur with complete inversion of configuration at the migrating methylene.

(1) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980.

(2) Grimme, W. *Chem. Ber.* 1967, 100, 113-118.

(3) The details of the crystallography, the syntheses of the labeled compounds, and the kinetics will be given in a forthcoming full paper.

(4) The tungsten tricarbonyl complex has been shown to have a similar structure (Darensbourg, D., J. personal communication).

(5) Lewis, C. P.; Brookhart, M. *J. Am. Chem. Soc.* 1975, 97, 651-653.

(6) A similar conclusion has already been reached by Brookhart and Lewis (Lewis, C. P. Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1976).

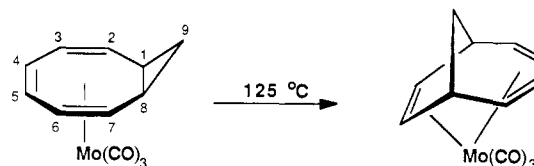


Figure 1. Original proposal for the rearrangement of (bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum.

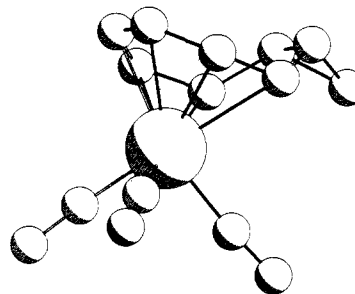


Figure 2. Computer-generated perspective drawing of (bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum from the X-ray crystal structure. Hydrogens are omitted for clarity.

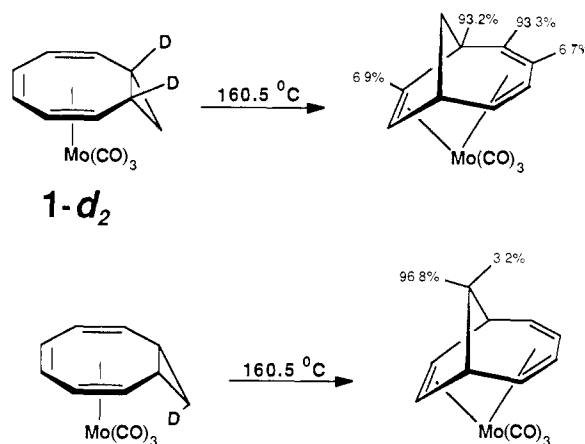


Figure 3. Deuterium distribution in the product from rearrangement of labeled (bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum.

The following conclusions can be drawn from these data. (1) The rearrangement occurs within the coordination sphere of the metal since the free hydrocarbon undergoes only epimerization⁵ and conversion to *cis*- and *trans*-8,9-dihydroindenes.^{7,8} (2) Both epimerization and conversion to the dihydroindenes are inhibited by complexation to the metal since the activation enthalpy for rearrangement of the hydrocarbon² is lower than that for the rearrangement of the complex. (3) The negative activation entropy rules out the possibility of CO dissociation in the rate-determining step.

The migration of label around the eight-membered ring could be explained by a mechanism like that in A of Figure 4 with the mechanistic rate constants having relative magnitudes $k_3 \gg k_0 \approx k_5 > k_1$ (exact values depending on the temperature, of course), but microscopic reversibility prohibits inversion of configuration at C9 in this mechanism. This problem could be avoided if the methylene group became completely disconnected from the eight-membered ring as in B of Figure 4, but the label distribution in recovered **1-d₂** eliminates such a mechanism. Since the degenerate rearrangement does occur with inversion at C9, it apparently must be a single-step [1,7] shift that does not involve the metal in direct C-C cleavage. Such a reaction is known for substituted bicyclo[6.1.0]nonatrienes.⁹

(7) Vogel, E. *Angew. Chem.* 1961, 73, 548-549.

(8) Baldwin, J. E.; Andrist, A. H.; Pinschmidt, R. K. *J. Am. Chem. Soc.* 1972, 94, 5845-5851.