J. Am. Chem. Soc. **1983**, *105*, 3737-3738

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Registry No. Semibulvalene, 6909-37-1.

Supplementary Material Available: Comparison of experimental and simulated spectra (2 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of an η^2-Phosphaalkene Nickel Complex

A. H. Cowley,* R. A. Jones,* C. A. Stewart, and
A. L Stuart

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

J. L. Atwood,* W. E. Hunter, and H.-M. Zhang

Department of Chemistry, University of Alabama
Tuscaloosa, Alabama 35486

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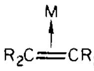
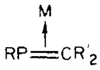
In principle, phosphaalkenes, RP=CR'$_2$, can function as η^1 (P donor) or η^2 (P=C π-donor) ligands toward transition metals. However, to date only η^1 behavior has been demonstrated, both for phosphaalkenes[1,2] and also for the isoelectronic molecules RP=NR' and RP=O.[3,4] We now report the synthesis and structure and the first example of an η^2-bonded phosphaalkene complex (**2**), thus completing the series of complexes **1**-**3**.



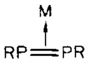
$\overset{\overset{M}{\uparrow}}{R_2C{=}CR_2}$

1[5]



$\overset{\overset{M}{\uparrow}}{RP{=}CR'_2}$

2



$\overset{\overset{M}{\uparrow}}{RP{=}PR}$

3[6]

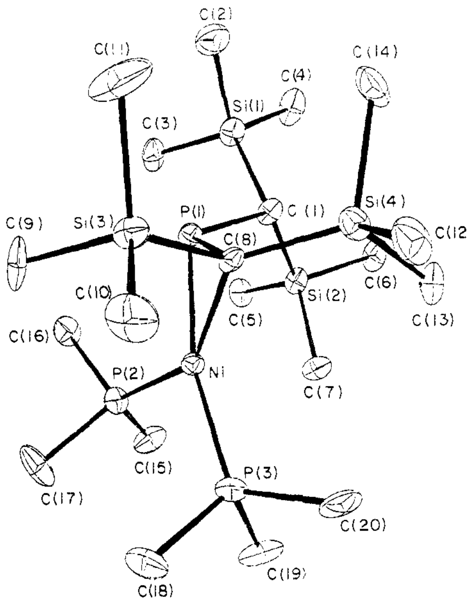


Figure 1. ORTEP view of $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**4**) showing the atom numbering scheme.

Table I. Pertinent Bond Lengths (Å) and Bond Angles (deg) for $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (4)

	Bond Lengths		
Ni-P(1)	2.239 (2)	P(1)-C(8)	1.773 (8)
Ni-P(2)	2.195 (3)	P(1)-C(1)	1.912 (8)
Ni-P(3)	2.202 (3)	C(8)-Si(3)	1.894 (8)
Ni-C(8)	2.020 (8)	C(8)-Si(4)	1.879 (8)
	Bond Angles		
P(1)-Ni-P(2)	99.9 (1)	C(1)-P(1)-C(8)	110.3 (4)
P(2)-Ni-P(3)	102.1 (1)	Ni-P(1)-C(8)	59.1 (3)
P(1)-Ni-C(8)	48.9 (2)	Ni-C(8)-P(1)	72.0 (3)
P(3)-Ni-C(8)	109.9 (2)	Si(3)-C(8)-Si(4)	113.8 (4)

In a typical reaction, 0.314 g (1.1 mmol) of $(Me_3P)_2NiCl_2$[7] in 50 mL of *n*-hexane was treated with 16.5 mL of a 0.14 M ethereal solution of $\{[(Me_3Si)_2CH]_2P\}Na$.[8] Evacuation of the solvent from the resulting cobalt blue solution produced an oil of the same color. ^{31}P NMR assay of the crude product revealed the presence of $[(Me_3Si)_2CH]_2PH$ (s, δ 72.2)[10] together with a complex set of peaks between +23 and −19 ppm. The blue oil was dissolved in 5 mL of *n*-hexane, and the resulting solution was allowed to stand for 2 days at −20 °C. During this time the color of the solution changed gradually from blue to dark brown, and red-brown crystals were deposited. Two recrystallizations from *n*-hexane afforded pure $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**4**) as orange-red crystals suitable for X-ray diffraction studies.

The structure of **1** has been solved by single-crystal X-ray methods[11] and is illustrated in Figure 1 along with the atom numbering protocol. A summary of pertinent metric parameters appears in Table I. The solid state of **4** consists of isolated neutral molecules with no short intermolecular contacts. The geometry at nickel is square planar, deviation (angstroms) from planarity

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(6) For η^2-diphosphene complexes, see: (a) Elmes, P. S.; Scudder, M. L.; West, B. O. *J. Organomet. Chem.* **1976**. *122*, 281. (b) Camillo, E.; Coda, A.; Prout, K.; Daran, J. C. *Acta Crystallogr. Sect. B.* **1977**, *B33*, 2608. (c) Deppisch, B.; Schäfer, H. *Ibid.* **1982**, *38*, 748. (d) Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, P. W.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932.

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(8) This solution can be made by treatment of a mixture of the phosphinyl radical $\{[(Me_3Si)_2CH]_2P\}\cdot$ and the corresponding dimer $[(Me_3Si)_2CH]_4P_2$ with an equimolar quantity of Na in *n*-hexane at 65 °C for 14 h.[9] However, recently we have learned from Professor Philip P. Power (personal communication) that the phosphide anion $\{[(Me_3Si)_2CH]_2P\}^-$ can be prepared more readily by treatment of $[(Me_3Si)_2CH]_2PCl$ with Li powder in Et_2O at 25 °C for 24 h. It is not possible to prepare the phosphide anion by deprotonation of $[(Me_3Si)_2CH]_2PH$, presumably because of steric effects.[10]

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(11) A single crystal of **4** with dimensions 0.35 × 0.35 × 0.10 mm was grown from *n*-hexane solution at −20 °C and sealed under dry nitrogen in a Lindemann capillary. Some crystal data for **4** are as follows: $C_{20}H_{55}NiP_3Si_4$, monoclinic, space group $P2_1/c$, $a = 8.742$ (6) Å, $b = 19.225$ (6) Å, $c = 20.111$ (8) Å, $\beta = 99.21$ (9)°, $U = 3336.5$ Å^3, $Z = 4$, and $D_c = 1.11$ g cm^{-3}. The final lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 38°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer. A total of 3523 symmetry-independent reflections was recorded (ω–2θ scans) to $2\theta_{max} = 40°$ by using graphite-monochromated Mo K$\bar{\alpha}$ X-radiation with $\bar{\lambda}$ 0.71069 Å. Standard reflections fluctuated within a range ±2% during data collection. The structure was solved by using direct methods (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368). Full-matrix least-squares refinement using the SHELX system (Sheldrick, G. M. SHELX76) and 1492 reflections with $F_o \geq 2.0\sigma(F_o)$ led to a final $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.031$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.030$. For further details of the diffraction experiment, see: Holton, E.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, *45*.

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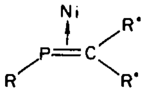
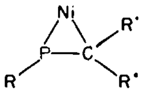
being Ni (−0.08), P(1) (−0.17), P(2) (0.12), P(3) (−0.07), and C(8) (0.21). The P–C bond length of 1.773 (8) Å in **4** is approximately midway between the P–C single-bond length of 1.85 Å and the P═C bond length of 1.67 Å which has been reported for uncoordinated phosphaalkenes.[13,14] Alkenes and diphosphenes undergo comparable increases of C═C or P═P bond length upon η^2 ligation.[5,6] The sum of bond angles at C(8) in **4** is 343.5°, indicating that the hybridization of the phosphaalkene carbon is approximately halfway between sp^2 and sp^3. The Si(3)–C(8)–Si(4) and C(1)–P(1)–C(8) bond angles in **4** are very similar to those exhibited by uncoordinated phosphaalkenes.[13,14] In valence bond terminology the bonding in **4** can be described as a resonance hybrid of π-bonded (I) or metallacyclic (II)[15] canonical forms.



I



II

From a molecular orbital standpoint the bonding in **4** is probably best represented as a dative π interaction. For example, MO calculations[16] on the model complex $Ni(PH_3)_2(C_2H_4)$ have revealed that the major contributor to ethene bonding is back-donation from a filled Ni 3d AO to the vacant olefinic π^* MO. Since MO calculations on $HP{=}CH_2$[17] and $HP{=}PH$[18] indicate the existence of low-lying π^* MO's, it is reasonable to suggest retro π-bonding as the primary bonding interaction in η^2 phosphaalkene (**2**) and diphosphene (**3**) complexes.

The square-planar geometry for **4** evidently persists in solution since the 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum comprises an ABX pattern. Computer simulation by routine methods afforded the parameters $\delta_{P(A)}$ −18.2, $\delta_{P(B)}$ −19.7, $\delta_{P(X)}$ +23.4, $J_{P(A)P(X)} = 45.8$, $J_{P(B)P(X)} = 28.6$, $J_{P(A)P(B)} = 27.0$ Hz. We have recently prepared the uncoordinated phosphaakene $(Me_3Si)_2C{=}PC(H)(SiMe_3)_2$ (**5**), for which $\delta_P = +404$.[9] In contrast to the η^1 (P bonded) phosphaalkene complexes,[1,2] a pronounced (>380 ppm) upfield coordination chemical shift thus accompanies η^2 complexations of **5**. This observation is consistent with back-donation from Ni 3d AO's to the phosphaalkene π^* MO.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

Note Added in Proof. Evidence has been presented recently for η^2-bonding of a phosphaalkene to Pt in solution. However, in the crystalline state the phosphaalkene was η^1-bonded.[19]

Registry No. 4, 85650-29-9.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors (13 pages). Ordering information is given on any current masthead page.

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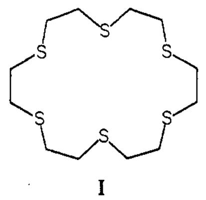
Crown Thioether Chemistry. The Nickel(II) Complex of 1,4,7,10,13,16-Hexathiacyclooctadecane, the Hexathia Analogue of 18-Crown-6

Eric J. Hintsa, JudithAnn R. Hartman, and
Stephen R. Cooper*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received January 31, 1983

The discovery of thioether coordination to Cu(II) in plastocyanin[1] has spurred development of thioether coordination chemistry, but there is a paucity of structural data on thioether complexes in general and homoleptic thioether complexes in particular.[2] We have recently begun to examine the chemistry of crown thioethers such as 1,4,7,10,13,16-hexathiacyclooctadecane[3] (I) (hereafter hexathia-18-crown-6) as a first step toward using them as ligands and were particularly intrigued by the early report of Black and McLean[4,5] that hexathia-18-crown-6 forms 1:1 complexes with Ni(II) picrate (as indicated by elemental analysis). We have examined this latter compound by diffraction methods and found it to be a unique octahedral complex with the *crown thioether wrapped around the metal ion.* This compound represents to our knowledge the first structurally characterized example of an octahedral transition-metal complex bound solely by thioether ligands.[6]



I

Hexathia-18-crown-6 (10 mg, 0.03 mmol; prepared as described previously[3,7]) was dissolved in 5 mL of acetone; upon addition of a refluxing solution of nickel picrate (15 mg, 0.03 mmol) in 5 mL of acetone the light yellow-green solution became bright yellow. After refluxing for 20 min, the solution was allowed to cool. The orange crystalline product was collected by filtration and dried in vacuo overnight, yield 0.019 g (80%). Anal. Calcd (Galbraith Laboratories, Knoxville, TN) for $C_{24}H_{28}N_6O_{14}S_6Ni$: C, 32.92; H, 3.23; N, 9.60; S, 21.97. Found: C, 32.74; H, 3.46; N, 9.36; S, 21.91. Recrystallization from hot CH_3CN afforded beautiful orange monoclinic prisms suitable for X-ray diffraction studies. Crystal data: space group *C2/c*, $a = 21.079$ (6) Å, $b = 8.685$ (2) Å, $c = 18.399$ (5) Å, $\beta = 93.63$ (2)°; d_{calcd}, 1.73 g/cm³, $Z = 4$; 2889 unique reflections with $F > 3\sigma(F)$ were collected with a Syntex R3 diffractometer with use of Mo Kα (0.71069 Å) radiation. The structure was solved by heavy atom methods and refined by cascade block-diagonal least-squares methods (with anisotropic thermal parameters for all non-hydrogen atoms). At the present stage of refinement $R = 6.2\%$ and $R_w = 5.8\%$.[8,9]

In $[Ni(II){\cdot}hexathia\text{-}18\text{-}crown\text{-}6]^{2+}$ the nickel(II) ion is on a center of symmetry and is neatly encapsulated within the hexathia-18-crown-6 ligand (Figure 1). Hexathia-18-crown-6 wraps

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(8) $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and $w = 1/\sigma^2F + 0.001F^2$.

(9) Tables of positional and thermal parameters are available as supplementary material.

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