Synthesis of $Cp^*Fe(CO)_2CH_2SiMe(SiMe_3)_2$. To an ice-cooled solution of $[Cp^*Fe(CO)_2]^-Na^+$ prepared from Hg (4 mL), Na (0.3 g, 13 mmol), and $[Cp^*Fe(CO)_2]_2$ (1.5 g, 3.0 mmol) in THF (50 mL) was added $ClCH_2SiMe(SiMe_3)_2$ (1.35 g, 5.7 mmol). The reaction mixture was stirred at room temperature overnight. THF was removed in vacuo, and subsequent to extraction into 50 mL of hexane, the residue was purified by silica gel column chromatography. Elution with hexane gave pure $Cp^*Fe(CO)_2CH_2SiMe(SiMe_3)_2$ (30%) as a yellow orange oil.

Photolysis of $Cp^*Fe(CO)_2CH_2SiMe(SiMe_3)_2$. A solution of $Cp^*Fe(CO)_2CH_2SiMe(SiMe_3)_2$ in C_6D_6 in a NMR tube was photolyzed, and the reaction was monitored by ^{29}Si NMR spectroscopy. After 1 h of irradiation, ^{29}Si NMR spectroscopy showed a complex mixture, composed of starting material $Cp^*Fe(CO)_2CH_2SiMe(SiMe_3)_2$ (δ −33.65, −16.72), final products $Cp^*Fe(CO)_2SiMe_3$ (δ 40.13) and $Cp^*Fe(CO)_2SiMe_2CH_2SiMe_3$ (δ 0.37, 42.0),[6b] and reactive intermediates and/or unstable byproducts with resonances at δ −13.17 (or −11.30), 1.50 (or 0.52), and 14.95 that were tentatively assignable to intermediate $Cp^*Fe(CO)_2SiMe(SiMe_3)CH_2SiMe_3$, which could be degraded to each of the two final products. After 8.5 h of irradiation only the two final products were found besides broad signals at $\delta \simeq -16$, and $\simeq 0$ assignable to polymeric materials.

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Phosphinomethyl Complexes of Niobocene

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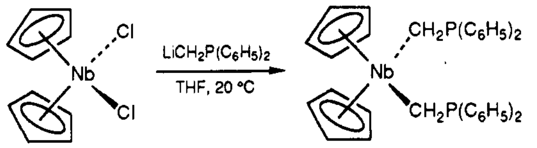
Reaction of $LiCH_2P(C_6H_5)_2$ with Cp_2NbCl_2 gives paramagnetic $Cp_2Nb[CH_2P(C_6H_5)_2]_2$ (1); $Cp_2Nb(Cl)CH_2P(C_6H_5)_2$ (4) is observed only as an unstable intermediate. Oxidation of 1 by $AgBF_4$ gives $Cp_2Nb[CH_2P(C_6H_4)_2]_2{}^+BF_4{}^-$ (6); reduction by $Na/C_{10}H_8$ gives $Na^+\{Cp_2Nb[CH_2P(C_6H_4)_2]_2\}^-$ (5), both isolable in analytically pure form as stable, diamagnetic solids. The anion of the latter crystallizes as its $Na(18\text{-crown-}6)(THF)_2{}^+$ salt in the monoclinic space group $C2/c$ with cell parameters a = 27.088 (15) Å, b = 9.560 (5) Å, c = 25.903 (14), β = 126.19 (3)°, and Z = 4. The structure was refined to R = 0.044 and R_w = 0.046 using 3493 uniquely observed reflections. Reaction of 1 with $(C_7H_8)Mo(CO)_4$ gives $Cp_2Nb[\mu\text{-}CH_2P(C_6H_5)_2]_2Mo(CO)_4$ (7), which crystallizes in the monoclinic space group $P2_1/n$ with cell parameters a = 13.401 (5) Å, b = 17.188 (5) Å, c = 19.768 (6), β = 99.25 (3)°, and Z = 4. The structure was refined to R = 0.081 and R_w = 0.085 using 1851 uniquely observed reflections. Both 5^- and 7 possess pseudotetrahedral Nb atoms, the latter octahedral Mo. Both Nb and Na in 5 lie on crystallographic 2-fold axes; no interaction between Nb and P is evident. The C–Nb–C angles to the phosphinomethyl groups are found to be 74.2 (2)° in 5^- (d^2 Nb), ca. 80–85° in 1 (d^1 Nb, estimated from ESR data), and 90.4° in 7 (d^1 Nb).

Introduction

The phosphinomethyl ligand, R_2PCH-, has proved to be a source of interesting and, in several cases, quite unusual chemistry, especially upon attachment to early transition metals. We and others have explored both mono- and dinuclear complexes of this ligand with group 4 metals,[1-3] as well as with metals in groups 8–10.[4] We anticipated that attachment of R_2PCH_2- to a group 5 metal such as niobium might lead in several directions unavailable to the group 4 analogues due in part to the availability of three rather than two readily accessible oxidation states. We herein describe the preparation and properties of the first such systems, phosphinomethyl derivatives of niobocene, including the structural characterization of a cyclic niobium-containing heterobimetallic lacking a metal–metal bond.

Results and Discussion

Phosphinomethyl Nb(IV) Derivatives. Addition of 2 equiv of either $LiCH_2P(C_6H_4)_2$ or its TMEDA complex to Cp_2NbCl_2 (Cp = η^5-C_5H_5) at 20 °C leads to ca. 65% isolated yields of analytically pure $Cp_2Nb[CH_2P(C_6H_5)_2]_2$ (1) as a thermally stable but air-sensitive tan solid (eq 1).



1

(1)

Spectroscopic characterization is limited to ESR analysis at ambient temperature: the paramagnetic Nb(IV) center gives rise to a 10-line pattern (^{93}Nb, $I = {}^9/_2$, 100%) centered about g = 1.99 with $a(^{93}Nb)$ = 90.0 G. In toluene, further (poorly resolved) splitting is observed for the four equivalent methylene hydrogens with $a(^1H) \approx 7$ G. These values compare well with other dialkylniobocenes, e.g. for $Cp_2Nb(CH_3)_2$, g = 1.998, $a(^{93}Nb)$ = 88.8 G, and $a(^1H)$ =

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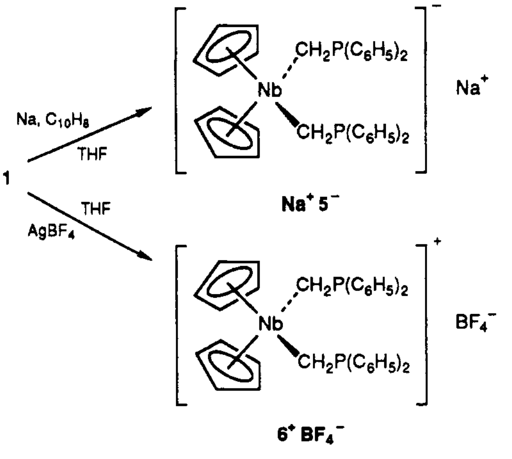
6.3 G.[5] The lack of observable hyperfine splitting by phosphorus implies the absence of any significant Nb–P interaction.

Although addition of $LiCH_2P(C_6H_5)_2$ to Cp_2ZrCl_2 is readily controlled to give either $Cp_2Zr(Cl)CH_2P(C_6H_5)_2$ (**2**) or $Cp_2Zr[CH_2P(C_6H_5)_2]_2$ (**3**) as the major product,[1] the niobium analogue to **2**, $Cp_2Nb(Cl)CH_2P(C_6H_5)_2$ (**4**), proved to be inaccessible. All attempts to add 1 equiv of $LiCH_2P(C_6H_5)_2$ to Cp_2NbCl_2 led to isolation of 1:1 mixtures of Cp_2NbCl_2 and **1**. Monitoring of the addition by ESR showed initial loss in intensity of the signal due to Cp_2NbCl_2 [$a(^{93}Nb) = 116.6$ G] and the appearance of a new signal with $a(^{93}Nb) \approx 105$ G. The species responsible for this signal rapidly decayed into the final mixture of Cp_2NbCl_2 and **1**, however. Similarly, attempts to selectively replace one phosphinomethyl group in **1** by halide were unsuccessful. Reactions of **1** with equimolar HCl, CH_3I, NBS, CH_3COCl, or $C_6H_5ICl_2$ all gave rise to the same transient signal with $a(^{93}Nb) \approx 105$ G seen above, and in each case rapid decay to niobocene dihalide was again observed. We suggest that **4** is indeed being formed but is unstable with respect to redistribution in solution. Stable monoalkylniobocene halides, though uncommon, are known and display ESR characteristics similar to the transient species in the above experiments, e.g. $Cp_2Nb(Cl)CH_2Si(CH_3)_3$ shows $a(^{93}Nb) = 106.6$ G.[6] On the other hand, other monoalkyls such as $Cp_2Nb(Cl)CH_2C_6H_5$ are indeed unstable with respect to redistribution to dialkyl and dihalide.[7]

Reactions of $Cp_2Nb(CH_2PPh_2)_2$ (1). Carbonylation reactions of **2** and **3** give unexpected products due to secondary reactions of the insertion products associated with the presence of the phosphinomethyl moieties.[1c,3] Hoping that such processes might serve to trap an otherwise unisolable CO insertion product from **1**, carbonylation was attempted (20–50 °C, 1–2 atm of CO) but led to no reaction. However, attempts at one-electron oxidation and reduction of **1** proved to be more productive.

Reduction of **1** is achieved by treatment of a THF solution of **1** with Na/naphthalene reagent at room temperature, forming the simple sodium salt $Na^+[Cp_2Nb[CH_2P(C_6H_5)_2]_2]^-$ (**5**) as a thermally stable brown solid in 60% yield. Oxidation of **1** with $AgBF_4$ in THF at room temperature similarly affords the simple salt $Cp_2Nb[CH_2P(C_6H_5)_2]_2{}^+BF_4{}^-$ (**6**) as a stable greenish-black solid in 81% yield (eq 2). Both d^2 $\mathbf{5}^-$ and d^0 $\mathbf{6}^+$ are ESR silent, as expected. Comparisons of their ^1H NMR spectra show



(2)

the expected differences: signals for $\mathbf{5}^-$ appear to high field (Cp at δ 4.65; CH_2 at δ −0.03; ^{31}P at δ 2.5) compared with signals for $\mathbf{6}^+$ (Cp at δ 5.55; CH_2 at δ 1.96 in CD_3NO_2; ^{31}P at δ 5.3). In neither system is evidence for direct Nb–P interaction seen, consistent with expectations based upon the 18-electron nature of the Nb in $\mathbf{5}^-$, and the similar lack of Zr–P interaction in **3**,[1] which is isoelectronic with $\mathbf{6}^+$. Very few examples of oxidized or reduced niobocene dialkyls have been reported to date,[8] and the series $\mathbf{6}^+$, **1**, and $\mathbf{5}^-$ is the second to have been prepared and the first for which the three contiguous oxidation states have all been characterized spectroscopically and isolated in pure form.[9]

X-ray Crystal Structure of $Cp_2Nb(CH_2PPh_2)_2{}^-$ ($\mathbf{5}^-$). It did not prove possible to obtain X-ray-quality crystals from the simple salt $Na^+\mathbf{5}^-$. However, reduction of **1** in the presence of 18-crown-6 afforded red crystalline $Na(18\text{-crown-}6)(THF)_2{}^+Cp_2Nb(CH_2PPh_2)_2{}^-$. Platelike crystals

Table I. Crystal Data for $[(C_5H_5)_2Nb(CH_2PPh_2)_2]^-[Na(18\text{-crown-}6)(THF)_2]^+$ (5) and $(C_5H_5)_2Nb(CH_2PPh_2)_2Mo(CO)_4 \bullet 0.5THF$ (7)

	$\mathbf{5}^-$	7
mol formula	$C_{56}H_{74}NaNbO_8P_2$	$C_{42}H_{39}MoNbO_{4.5}P_2$
mol wt	1053.05	866.57
color and habit	red plates	brown-purple needles
cryst syst	monoclinic	monoclinic
d(calcd), g cm^{-3}	1.29	1.28
cryst dimens, mm	0.07 × 0.62 × 1.10	0.032 × 0.075 × 0.35
space group	$C2/c$	$P2_1/n$
molecules/unit cell	4	4
cell constants[a]		
a, Å	27.088 (15)	13.401 (5)
b, Å	9.560 (5)	17.188 (5)
c, Å	25.903 (14)	19.768 (6)
β, deg	126.19 93)	99.25 (3)
V, A^3	5414 (4)	4494 (3)
T, K	130	293
abs coeff (μ), cm^{-1}	3.29	6.2

[a] Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator.

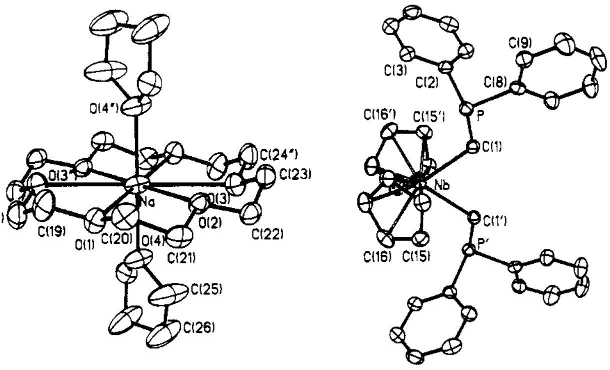


Figure 1. Computer-generated representation of (left) cation and (right) anion of $Na(18\text{-crown-}6)(THF)_2{}^+Cp_2Nb(CH_2PPh_2)_2{}^-$ (**5**).

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[8] See ref 7 for electrochemical formation of the dibenzylniobocene anion and cation (in solution only). See also: (a) Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 893 (reduction). (b) Bristow, G. S.; Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1984**, 399 (oxidation). (c) Lappert, M. F.; Milne, C. R. C. *J. Chem. Soc., Chem. Commun.* **1978**, 925 (oxidation products isolated). (d) Gowik, P.; Klapötke, T. *J. Organomet. Chem.* **1989**, *375*, C20 (oxidation products isolated).

[9] In an elegant and comprehensive study the three members of the analogous series derived from the metallocycle $Cp_2Nb(2\text{-}CH_2C_6H_4C_6H_4\text{-}2\text{-}CH_2)$ were structurally characterized; however, the anion could not be obtained pure enough for NMR analysis: Bailey, S. I.; Engelhardt, L. M.; Leung, W.-P.; Raston, C. L.; Ritchie, I. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1747. $\mathbf{5}^-$ is the first such anion to be characterized spectroscopically.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $(THF)_2(18\text{-crown-}6)Na[Cp_2Nb(CH_2PPh_2)_2]$

	x	*y*	*z*	U^a
Nb	0	4777 (1)	7500	20 (1)*
P	1434 (1)	3024 (1)	8610 (1)	23 (1)*
C(1)	649 (2)	2814 (3)	7914 (2)	22 (2)*
C(2)	1804 (2)	3751 (4)	8255 (2)	25 (2)*
C(3)	2046 (2)	5088 (4)	8423 (2)	33 (2)*
C(4)	2290 (2)	5720 (4)	8136 (2)	42 (3)*
C(5)	2305 (2)	5008 (4)	7687 (2)	41 (2)*
C(6)	2081 (2)	3653 (4)	7523 (2)	37 (2)*
C(7)	1833 (2)	3032 (4)	7804 (2)	29 (2)*
C(8)	1776 (2)	1247 (4)	8813 (2)	24 (2)*
C(9)	2353 (2)	1058 (4)	9396 (2)	30 (2)*
C(10)	2607 (2)	−255 (4)	9607 (2)	45 (2)*
C(11)	2291 (2)	−1426 (4)	9248 (2)	45 (2)*
C(12)	1722 (2)	−1270 (4)	8673 (2)	40 (2)*
C(13)	1466 (2)	50 (4)	8459 (2)	30 (2)*
C(14)	289 (2)	4564 (4)	8580 (2)	29 (2)*
C(15)	−349 (2)	4681 (4)	8187 (2)	31 (2)*
C(16)	−509 (2)	5973 (4)	7867 (2)	35 (2)*
C(17)	48 (2)	6666 (4)	8080 (2)	35 (2)*
C(18)	549 (2)	5780 (4)	8523 (2)	32 (2)*
Na	0	10000	0	39 (1)*
O(1)	−748 (1)	8985 (3)	281 (1)	36 (1)*
O(2)	298 (1)	10462 (3)	1195 (1)	33 (1)*
O(3)	1153 (1)	11051 (3)	987 (1)	37 (1)*
O(4)	475 (2)	7837 (3)	195 (1)	52 (2)*
C(19)	−1373 (2)	8888 (6)	−230 (2)	51 (2)*
C(20)	−675 (2)	9599 (5)	824 (2)	40 (2)*
C(21)	−10 (2)	9592 (4)	1367 (2)	38 (2)*
C(22)	919 (2)	10717 (4)	1717 (2)	39 (2)*
C(23)	1181 (2)	11712 (4)	1497 (2)	39 (2)*
C(24)	−1430 (2)	8131 (5)	−769 (2)	48 (2)*
C(25)	842 (4)	7296 (6)	817 (2)	101 (5)*
C(26)	1119 (4)	5962 (7)	806 (2)	103 (4)*
C(27)	823 (3)	5673 (7)	115 (2)	89 (4)*
C(28A)	659 (5)	7040 (9)	−153 (4)	44 (2)
C(28B)	333 (4)	6741 (8)	−240 (4)	35 (2)

[a] Values marked with an asterisk refer to the equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of sufficient quality for diffraction were obtained from THF by layering with hexane. The structure determination was uneventful (Tables I and II). Anion 5^- exhibits a simple monomeric structure (Figure 1), lacking close contacts with the counterion complex. The Nb–C bond distances to the phosphinomethyl ligands were found to be 2.353 (3) Å, similar to the 2.30 (2)–2.34 (3) Å range in $Cp_2Nb(2\text{-}CH_2C_6H_4C_6H_4\text{-}2\text{-}CH_2)^-$.[9] Of note is the small ∠C–Nb–C of 74.2 (2)° subtended by the phosphinomethyl ligands in 5^-, consistent with the predicted diminution of the L–M–L angle in $CpML_2$ along the series $M(d^0) > M(d^1) > M(d^2)$.[10] For comparison, the value in $Cp_2Nb(2\text{-}CH_2C_6H_4C_6H_4\text{-}2\text{-}CH_2)^-$ is 80 (1)°.[9] The closest Nb–P distance in 5^- is about 4.0 Å, well outside the range expected for electronic interaction and consistent with expectations based on the d^2, 18-electron nature of the metal. The 2-fold axis in 5^- contrasts with the structure 3, which shows quite dissimilar conformations for the two $(C_6H_5)_2PCH_2^-$ ligands about the d^0, 16-electron Zr in the solid state, and Zr–P distances of 3.64 and 3.70 Å.[1b] The structure of the cation is virtually superimposable with that previously reported.[9] Other structural data for 5^- compare well with those expected from $Cp_2Nb(2\text{-}CH_2C_6H_4C_6H_4\text{-}2\text{-}CH_2)^-$ (Table III).

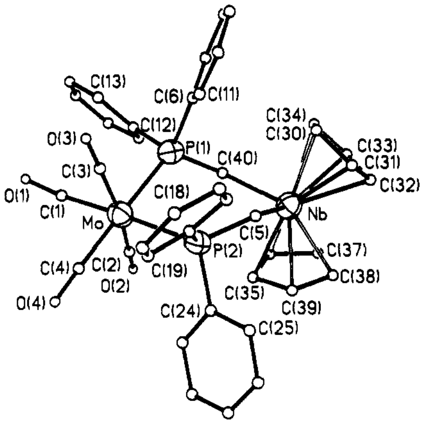

Figure 2. Computer-generated representation of $Cp_2Nb[\mu\text{-}CH_2P(C_6H_5)_2]_2Mo(CO)_4$ (7).

Synthesis of the Nb(IV)–Mo Heterobimetallic 7. Complexation of 1 to a second transition-metal fragment has been achieved. Reaction of (norbornadiene)$Mo(CO)_4$ with 1 at 25 °C gives rise to ≥60% yields of analytically pure $Cp_2Nb[\mu\text{-}CH_2P(C_6H_5)_2]_2Mo(CO)_4$ (7) as an extremely air- and water-sensitive red-brown powder, exhibiting IR bands at 2009, 1913, and 1880 (br) cm^{-1}, indicative of a *cis*-$Mo(CO)_4(PR_3)_2$ complex. Like 1, 7 displays a 10-line pattern in the ESR, but with $a(^{93}Nb) = 95.5$ G, and no observable splitting by hydrogen. It is known that a correlation exists between $a(^{93}Nb)$ values and C–Nb–C bond angles in dialkylniobocenes.[11] Although the extremely high solubility of 1 in vituraily all organic solvents foiled all attempts at obtaining crystals, the value of $a(^{93}Nb) = 90.0$ G implies that ∠C–Nb–C ≈ 80–85°, comparable to the 83° mean value in $Cp_2Nb(2\text{-}CH_2C_6H_4C_6H_4\text{-}2\text{-}CH_2)$[9] and considerably smaller than the 100.2° C–Zr–C bond angle in 3.[1b] The increase in $a(^{93}Nb)$ for 7 relative to 1 strongly suggests that the C–Nb–C angle has opened up upon complexation; in contrast, the corresponding angle in 3 closes to 93.5° upon complexation to $Cr(CO)_4$.[1b] In order to establish a more definitive basis for comparison the effort was undertaken to obtain X-ray-quality crystals of 7.

X-ray Crystal Structure of Heterobimetallic 7. Layering of a concentrated THF solution of 7 with hexane afforded after diffusional mixing large, brownish-purple needles which had to be maintained in contact with solvent until mounting to prevent collapse. After numerous tries, during which cooling was also found to shatter the crystals, a single crystal was successfully mounted and analyzed at room temperature. Refinement to *R* = 0.081 was achieved after the identification of two molecules of THF per molecule of 7, with an occupancy estimated at 25% from the electron density difference map. These molecules occupy vacancies in the lattice and do not interact significantly with any part of the Nb/Mo bimetallic (Tables I and IV).

Complex 7 is monomeric and isostructural with $Cp_2Zr[\mu\text{-}CH_2P(C_6H_5)_2]_2Cr(CO)_4$ (8).[12] Both compounds relieve severe steric crowding by adopting distorted twist-boat conformations (Figure 2; see also Figures 10 and 11 in ref 1b). Comparisons of bond lengths and angles for the most part reveal only small differences of an expected nature (Table III). As implied by the ESR data, the observed

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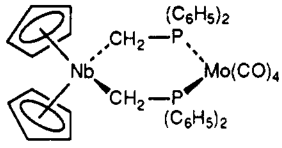
(12) Atom coordinates for selected atoms of 7 and 8 (those of the latter appropriately transformed from the original data in ref 1b) are given in Table XV of the supplementary material.

Table III. Selected Bond Lengths (Å) and Angles (deg)

	$[Cp_2Nb(CH_2PPh_2)_2]^-$ (5^-)	$Cp_2Zr(CH_2PPh_2)_2$[a]	$Cp_2Nb(CH_2PPh_2)_2Mo(CO)_4$ (7)	$Cp_2Zr(CH_2PPh_2)_2Cr(CO)_4$[a]
$d_{M^b-CH_2}$	2.353 (3)	2.284 (8), 2.340 (9)	2.274 (23), 2.309 (23)	2.292 (9), 2.329 (9)
∠CH_2–M–CH_2	74.2 (2)	100.2 (3)	90.4 (9)	93.5 (3)
$d_{M-C(Cp)}$(range)	2.304–2.459 (6)	2.460–2.560 (14)	2.387–2.480 (22)	2.504–2.570 (10)
d_{P-CH_2}	1.813 (3)	1.808 (9), 1.813 (9)	1.776 (23), 1.832 (24)	1.816 (9), 1.817 (9)
$d_{P-C(Ph)}$(range)	1.848 95), 1.856 (4)	1.848–1.868 (10)	1.834–1.857 (27)	1.838–1.862 (10)
∠M–CH_2–P	119.1 (2)	122.2 (5), 129.0 (5)	128.2 (13), 131.4 (13)	122.4 (4), 128.1 (5)
$d_{P-M'}$[c]			2.549 (7), 2.552 (6)	2.404 (3), 2.412 (3)
∠CH_2–P–M′			116.5 (8), 119.8 (8)	117.8 (3), 120.5 (3)
∠C(Ph)–P–M′(range)			106.8–119.1 (8)	108.2–120.0 (3)
$d_{M'-CO(\text{trans to P})}$			1.962 (30), 1.996 (29)	1.848 (10), 1.854 (9)
$d_{M'-CO(\text{cis to P})}$			2.031 (31), 2.032 (32)	1.873 (11), 1.883 (11)
d_{CO}(range)			1.135–1.175 (40)	1.146–1.160 (14)
∠P–M′–CO(trans)			175.1 (10), 176.6 (8)	172.1 (3), 176.7 (3)
∠P–M′–CO(cis)(range)			86.2–100.0 (8)	85.1–98.7 (3)
∠P–M′–P			89.2 (2)	92.4 (1)

[a] Reference 1b. [b] M = Nb or Zr. [c] M′ = Mo or Cr.

∠C–Nb–C of 90.4 (9)° is larger than that inferred for 1, although still smaller than the 93.5 (3)° ∠C–Zr–C in 8. This is in spite of the larger size of the $Mo(CO)_4$ fragment being spanned in 7 relative to the $Cr(CO)_4$ in 8: the average *d*(P–Cr) in 8 is 2.408 Å while *d*(P–Mo) in 7 is 2.550 Å. The effect of the d^1 configuration of Nb(IV) in 7 vs the d^0 Zr(IV) in 8 still predominates (vide supra). As a consequence, the P–Mo–P angle in 7 is also smaller than the P–Cr–P angle in 8 [89.2 (2) vs 92.4 (1)°]. Although more than 4 Å separates the Nb from any atom in the $Mo(CO)_4$ fragment, 7 is a very compact structure, with very little conformational freedom available to it.



7

Unfortunately, efforts to crystallize the cationic Nb(V) system 6^+ were unsuccessful. Although apparently stable indefinitely in the solid state, 6^+ decomposed in solution, frustrating our efforts to explore this material further.

Concluding Remarks. One of the hoped-for goals in this work was to generate intramolecular Nb–P bonding of the sort seen in $Cp_2Zr[\eta^2\text{-}CH_2P(C_6H_5)_2]$,[1] but in a diamagnetic system such as $Cp_2Nb[\eta^2\text{-}CH_2P(C_6H_5)_2]$, which might be accessible through reduction of 4. The availability of such systems would be of potential value in further exploring the puzzling behavior of the Zr(III) analog.[13] Due to the inaccessibility of 4, however, alternative approaches were briefly explored, such as deprotonation of $Cp_2Nb(Cl)P(C_6H_5)_2CH_3$,[14] but without success. Nevertheless, through attachment of the heterodifunctional phosphinomethyl ligand we have demonstrated the first niobocene-based system in which three contiguous oxidation states *and* subsequent construction of a heterodimetallic are all feasible.[14]

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of prepurified nitrogen using vacuum or Schlenk techniques or a Vacuum Atmospheres drilab Model HE-553-2. Common organic solvents were first distilled from sodium benzophenone ketyl or dianion under nitrogen and then bulb-to-bulb transferred under high vacuum to assure water- and oxygen-free conditions. Niobium(V) chloride (Fluka), diphenylphosphine and *n*-Bu_3SnCl (Aldrich), and methyldiphenylphosphine and $Mo(CO)_6$ (Strem) were used without further purification. All solid reagents were brought into the drybox after being held at high vacuum for a minimum of 12 h. The reagents *n*-$Bu_3Sn(\sigma\text{-}C_5H_5)$,[15] Cp_2NbCl_2,[16] $Cp_2Nb(Cl)CO$,[17] $LiCH_2PPh_2$,[18] $LiCH_2PPh_2{\cdot}TMEDA$.[19] and $(C_7H_8)Mo(CO)_4$[20] were prepared according to literature methods.

Spectroscopic measurements were obtained using the following instrumentation: IR, Perkin-Elmer IR-8 grating and IBM IR32 FT spectrometers; ESR, Varian E-4 (X-band) spectrometer; NMR, Varian EM-390, Nicolet NT-360, and GE QE-300 spectrometers. Benzene-d_6 and chloroform-d_1 were dried with and vacuum-transferred from P_2O_5 and stored over 3-Å molecular sieves. Elemental analysis was performed by Dornis and Kolbe Microanalytical Laboratory (West Germany).

Bis(η^5-cyclopentadienyl)bis[(diphenylphosphino)methyl]niobium(IV) (1). To a suspension of 1.18 g (4.0 mmol) of dichlorobis(η^5-cyclopentadienyl)niobium in 400 mL of benzene was added dropwise, with stirring, a solution of 1.29 g (4.0 mmol) of [(diphenylphosphino)methyl]lithium-*N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane complex in 100 mL of benzene (admixed with 5–10 mL of THF) at 25 °C under N_2. The dark brown solution was stirred at 25 °C for an additional 5 h. Removal of solvent under high vacuum left a dark brown oily residue which was stirred with two 50-mL portions of benzene. The benzene extracts were filtered to remove LiCl and then concentrated in vacuo to yield a dark brown oil. The oil was stirred with 60 mL of *n*-hexane until a free flowing brown solid was obtained. This suspension was cooled to −20 °C for 12 h and filtered, and the isolated tan solid was washed with 2 × 15 mL of cold *n*-hexane to remove any residual TMEDA/$PMePh_2$. After drying, 1 was isolated as a tan microcrystalline solid (2.48 g; 65%). Mp: 91–94 °C dec. ESR (THF): 10 lines (Nb, $I = {}^9/_2$), $a(^{93}Nb) = 90.0$ G. Anal. Calcd for $C_{36}H_{34}NbP_2$: C, 69.58; H, 5.47. Found: C, 69.48; H, 5.50.

Bis(η^5-cyclopentadienyl)bis[(diphenylphosphino)methyl]niobium(III) Anion, (18-Crown-6)bis(tetrahydrofuran)sodium Salt ($Na(18\text{-crown-}6)(THF)_2{}^+5^-$). To a solution containing 500 mg (0.81 mmol) of 1 in THF (15 mL), cooled to −78 °C, was added dropwise a THF solution containing $Na[C_{10}H_8]$ (15 mL; 110 mg of $C_{10}H_8$; 20 mg of Na metal; 0.86 mmol) and 227 mg (0.86 mmol) of 18-crown-6. The brown solution was stirred at −78 °C for 2 h, warmed to room temperature, and stirred for 3 h. Solvent removal in vacuo gave a brown oil. The oil was stirred

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[14] Cf.: Serrano, R.; Royo, P. *J. Organomet. Chem.* **1983**, *247*, 33.

[15] Darensbourg et al. successfully prepared two oxidation states and both a heterobimetallic neutral and a cation based on the $Cp_2Nb(SC_6H_5)_2$ system: Darensbourg, M. Y.; Silva, R.; Reibenspies, J.; Prout, C. K. *Organometallics* **1989**, *8*, 1315.

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Table IV. Atomic Coordinates ($\times10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for $Cp_2Nb(\mu\text{-}CH_2PPh_2)_2Mo(CO)_4\bullet0.5THF$ (7)

	x	*y*	*z*	U^a
Mo	3940 (2)	6572 (1)	7075 (1)	55 (1)*
Nb	2713 (2)	8951 (1)	5860 (1)	57 (1)*
P(1)	2776 (5)	6801 (4)	5939 (3)	52 (2)*
P(2)	3374 (5)	7871 (4)	7507 (3)	48 (2)*
O(1)	4492 (17)	4886 (12)	6713 (11)	104 (7)
O(2)	5690 (18)	7109 (13)	6280 (11)	106 (7)
O(3)	2232 (18)	5650 (13)	7713 (11)	113 (7)
O(4)	5486 (19)	6322 (14)	8447 (13)	126 (8)
C(1)	4397 (23)	5552 (17)	6800 (15)	84 (9)
C(2)	5078 (23)	6939 (15)	6588 (14)	70 (8)
C(3)	2860 (23)	6009 (17)	7500 (15)	86 (9)
C(4)	4949 (25)	6398 (19)	7921 (16)	91 (9)
C(5)	2578 (18)	8493 (14)	6940 (11)	55 (6)
C(6)	1403 (18)	6738 (13)	5910 (11)	56 (7)
C(7)	771 (23)	6616 (18)	5292 (16)	96 (9)
C(8)	−277 (22)	6588 (16)	5219 (14)	77 (8)
C(9)	−663 (24)	6687 (17)	5814 (14)	86 (9)
C(10)	−61 (23)	6821 (15)	6437 (15)	82 (9)
C(11)	941 (21)	6837 (13)	6460 (12)	58 (7)
C(12)	3019 (20)	6013 (15)	5361 (12)	64 (7)
C(13)	2710 (20)	5277 (15)	5458 (12)	66 (7)
C(14)	2939 (21)	4671 (17)	5055 (13)	77 (8)
C(15)	3477 (24)	4788 (19)	4582 (15)	98 (10)
C(16)	3800 (27)	5496 (20)	4454 (18)	114 (12)
C(17)	3537 (22)	6132 (18)	4840 (14)	82 (9)
C(18)	2692 (18)	7682 (12)	8238 (11)	52 (6)
C(19)	3186 (22)	7301 (15)	8809 (13)	73 (8)
C(20)	2640 (24)	7203 (18)	9374 (16)	95 (10)
C(21)	1681 (23)	7387 (16)	9350 (15)	86 (9)
C(22)	1170 (29)	7782 (20)	8799 (17)	114 (12)
C(23)	1686 (24)	7945 (19)	8221 (16)	101 (10)
C(24)	4345 (18)	8540 (13)	7959 (11)	51 (6)
C(25)	4063 (20)	9180 (13)	8309 (11)	58 (7)
C(26)	4827 923)	9652 (18)	8621 (13)	83 (9)
C(27)	5790 (23)	9488 (15)	8667 (13)	72 (8)
C(28)	6114 (22)	8891 (15)	8333 (13)	76 (8)
C(29)	5350 (22)	8387 (18)	7998 (13)	78 (8)
C(30)	860 (16)	8742 (11)	5725 (10)	86 (9)
C(31)	1082	9506	5981	85 (9)
C(32)	1475	9937	5470	111 (11)
C(33)	1496	9440	4899	120 (12)
C(34)	1117	8702	5056	98 (10)
C(35)	4506 (15)	8974 (10)	6191 (10)	85 (9)
C(36)	4304	9088	5471	88 (9)
C(37)	3796	9811	5342	81 (9)
C(38)	3685	10144	5983	79 (8)
C(39)	4123	9626	6508	76 (8)
C(40)	2946 (20)	7718 (13)	5499 (12)	60 (7)
O(5)	2174	3445	2362	124 (31)
O(6)	2470	6178	1163	124 (32)
C(41)	2212	3078	1911	72 (32)
C(42)	1346	3446	1351	66 (28)
C(43)	826	3674	1735	47 (25)
C(44)	1268	4053	1932	116 (47)
C(45)	2415	6442	1663	84 (35)
C(46)	3340	5949	2159	91 (38)
C(47)	3808	6171	2008	135 (55)
C(48)	3508	5779	1573	184 (77)

[a] Values marked with an asterisk refer to the equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

with several portions of *n*-hexane followed by filtration to remove any residual naphthalene. The isolated brown solid was dried under high vacuum to obtain 450 mg (64%) of impure salt. Purification was achieved by stirring the crude product with benzene (4 × 20 mL) followed by filtration to remove insoluble impurities. Solvent removal from the combined filtrates gave a brown solid which was dried in vacuo to obtain 317 mg (45%) of Na(18-crown-6)(THF)$_2^+$**5**$^-$, judged as being >95% pure by ^{1}H NMR spectroscopy. The complex was ESR silent. ^{1}H NMR (C_6D_6): δ -0.03 (d, J_{PCH} = 5.44 Hz, 4 H), 3.20 (br s, 24 H), 4.65 (s, 10 H), 6.90–7.40 (br m, 12 H), 7.80–8.10 (br m, 8 H). ^{31}P NMR (C_6D_6): δ 5.3.

A red platelike crystal of Na(18-crown-6)(THF)$_2^+$**5**$^-$, suitable for X-ray structure determination, was obtained by the slow diffusional mixing of an *n*-hexane solvent layer into a saturated THF solution at ambient temperature. The crystal was extremely air sensitive, rapidly discoloring and losing crystallinity upon removal from an inert-nitrogen atmosphere. In order to retard decomposition, the crystal was coated with a hydrocarbon oil before it was mounted on the diffractometer. Data collection was performed at 130 K (N_2 stream) since the crystal did not shatter upon cooling.

X-ray Crystal Structure Determination for the Salt of the Bis(η^5-cyclopentadienyl)bis[(diphenylphosphino)methyl]niobium(III) Anion (Na(18-crown-6)(THF)$_2^+$5$^-$). The oil-coated crystal was mounted and placed in the cold stream of a Syntex P2$_1$ diffractometer fitted with a graphite monochromator. Computer programs used were those of SHELXTL, Version 5, installed on a Data General Eclipse computer. Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources.[21] The final lattice parameters were determined by a least squares fit of 14 centered reflections in the range 35° < 2θ < 50°. Data for 4799 reflections, using a ω scan method with a 2.3° range and a 1.5° offset for background at a speed of 18.0 deg min^{-1}, was obtained. No decay in the intensities of two standard reflections was observed during the course of data collection. However, the crystal immediately decomposed when it was reexamined under the microscope.

The crystal data are presented in Table I. The structure was solved by Patterson methods. Although the systematic absences are consistent with either space group *C*2/*c* or *Cc*, inspection of the structure clearly shows the presence of a 2-fold axis parallel to *b*, thus favoring the *C*2/*c* space group. There is half a molecule of the formula unit in the asymmetric unit. Both Nb and Na lie on crystallographic 2-fold axes. One of the carbon atoms of the THF molecule has two alternative positions, each assigned one-half occupancy. An absorption correction was applied.[22] Non-hydrogen atoms were assigned anisotropic thermal parameters in the final cycles of refinement, except for the disordered carbon atom of the THF molecule. Hydrogen atoms (except for the disordered carbon and its neighbor) were included at calculated positions using a riding model, with a C–H of 0.96 Å and U_H = $1.2U_C$. Refinement of 3493 reflections with $I > 2\sigma(I)$ gave final R = 0.044 and R_w = 0.048 (308 parameters, $w = (\sigma^2(F_o)^{-1})$. The largest feature on a final difference map was 0.74 e Å^{-3} in height and probably corresponds to a hydrogen atom that is common to the two disordered carbons. The largest shift in the final cycle of refinement was 0.037 for *y* of C(6).

Sodium Salt of Bis(η^5-cyclopentadienyl)bis[(diphenylphosphino)methyl]niobium(III) (Na$^+$5$^-$). To a solution containing 530 mg (0.85 mmol) of **1** in 25 mL of THF at ambient temperature was added dropwise a THF solution of Na[$C_{10}H_8$] (15 mL; 112 mg of $C_{10}H_8$; 20 mg of Na metal; 0.87 mmol) over a 30-min interval. The brown solution was stirred at 27 °C for 5 h. Solvent removal in vacuo gave a brown oil. The crude oil was extracted with several portions of *n*-hexane followed by filtration to remove residual naphthalene. The isolated brown solid exhibited no ESR signal. No additional purification was required as the product was found to be analytically pure (yield: 328 mg; 60%). NMR (C_6D_6): δ -0.03 (d, J = 5.44 Hz, 2 H), 4.65 (s, 10 H), 6.90–7.40 (br m, 12 H), 7.60–7.80 (br m, 8 H). Anal. Calcd for $C_{26}H_{34}NaNbP_2$: C, 66.99; H, 5.27. Found: C, 66.92; H, 5.30.

Bis(η^5-cyclopentadienyl)bis[(diphenylphosphino)methyl]niobium(V) Tetrafluoroborate (6$^+$BF$_4^-$). To a mixture containing 621 mg (1.00 mmol) of **1** and 195 mg (1.00 mmol) of $AgBF_4$ was added 25 mL of THF. The mixture was stirred at ambient temperature for 2 h. The suspension was filtered to remove insoluble AgCl (99 mg; 90% of theoretical). The dark brown THF filtrate was concentrated in vacuo to obtain a waxy brown solid. The solid was washed with several portions of ether to remove any unreacted **1** and/or other nonionic impurities. The resulting brown solid, which could not be redissolved in THF,

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(21) *Organometallic Syntheses*; King, R. B., Ed.; Academic Press: New York, 1965; Vol. 1, p 125.

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

was extracted with 2 × 30 mL CD_3NO_2. The black solution was concentrated in vacuo to obtain $6^+BF_4^-$ as an analytically pure black solid (yield: 573 mg; 81%). Complex $6^+BF_4^-$ was found to be ESR silent. NMR: (CD_3CN) δ 5.44 (s, 10 H), 7.10–8.10 (br m, 20 H); (CD_3NO_2) δ 1.96 (d, J = 14 Hz, 4 H), 5.55 (s, 10 H), 7.10–8.10 (br m, 20 H). ^{31}P NMR (CD_3NO_2): δ 2.5. Anal. Calcd for $C_{36}H_{34}BF_4NbP_2$: C, 61.05; H, 4.80. Found: C, 60.99; H, 4.82.

Bis(η^5-cyclopentadienyl)bis[μ-(diphenylphosphino)methyl-*C,P*](*cis*-tetracarbonylmolybdenum)niobium(IV) (7). A solution of 36.0 mg (0.12 mmol) of (norbornadiene)tetracarbonylmolybdenum in 15 mL of THF was added dropwise to a rapidly stirred solution of 68.3 mg (0.11 mmol) of 1 in 15 mL of THF at 27 °C under N_2. The reaction mixture was stirred for 3 h at 25 °C, heated to 50 °C, and stirred for an additional 2 h. The tan solution was filtered to remove any precipitated solid and the solvent removed in vacuo to give a brown solid. Crude 7 was stirred with 15 mL of ethyl ether, filtered out, and washed with 15 mL n-hexane to remove excess $(C_7H_8)Mo(CO)_4$. Pure 7 was obtained as a brown microcrystalline powder (55.6 mg; 61%): ESR (THF): 10 lines (Nb, $I = {}^9/_2$), $a(^{93}Nb)$ = 96.5 G; IR (THF): 1881 (vs), 1914 (sh), 2009 cm^{-1} (s). Anal. Calcd for $C_{40}H_{34}MoNbO_4P_2$: C, 57.91; H, 4.10. Found: C, 57.78; H, 4.14.

Large brown-purple needles, suitable for X-ray crystal structure determination, were obtained from the slow diffusional mixing of an n-hexane solvent layer into a concentrated THF solution of 7 at ambient temperature. The crystals must be kept in the mother liquor to prevent cracking and loss of crystallinity. The needles are very air and moisture sensitive, rapidly discoloring and collapsing to a yellow-white powder upon exposure to air. To prevent decomposition during data collection, the needles were coated with an epoxy resin immediately after removal from the mother liquor prior to mounting. The crystals were also observed to shatter when cooled to 130 K in a stream of N_2. Hence, room-temperature data collection was required to obtain the structural data for crystalline 7.

X-ray Crystal Structure Determination for Bis[(diphenylphosphino)methyl]niobocene–Molybdenum Tetracarbonyl Complex 7. A small needle of 7 was coated with epoxy and mounted on a glass fiber for room-temperature data collection. A Syntex $P2_1$ diffractometer fitted with a graphite monochromator was used for data collection. Data for 6337 reflections using a ω scan method at a speed of 8 deg min^{-1} in the range $2\theta < 45°$ were obtained. Three check reflections were monitored during the course of data collection and showed no loss in intensity.

Crystal data are summarized in Table I. The structure was solved by Patterson and Fourier methods in the space group $P2_1/n$. Due to the rather low number of observed data, the cyclopentadiene groups were treated as rigid bodies, with C–C bond lengths of 1.420 Å. Hydrogen atoms were included at calculated positions on the cyclopentadiene groups using a C–H bond length of 0.96 Å and U_H = 0.09 Å^2. The remaining hydrogen atoms were included using a riding model, with a C–H bond length of 0.96 Å and U_{iso} equal to 1.2 times that of the bonded carbon. An absorption correction was made using program XABS 22. After applying the correction, the ten largest peaks on a difference map were used to assemble two THF molecules. An examination of packing diagrams shows that the THF molecules occupy vacancies in the crystal structure and do not interact strongly with any portion of the Nb–Mo heterobimetallic species. The THF molecules did not refine, so their positional parameters were fixed at those determined from the difference map. With an occupancy fixed at 0.25, the isotropic thermal parameters of the atoms of the THF molecules converged at values between 0.047 and 0.184 Å^2. Final refinement was carried out with anisotropic thermal parameters for Mo, Nb, and the two phosphorus atoms. Block-cascade least-squares refinement of 1851 reflections with $I > 2.5\sigma(I)$, gave final R = 0.081 and R_w = 0.085 (205 parameters, $w = 1/[\sigma^2(F_o) + 0.014F_o]$). The largest feature on a final difference map was 0.99 e Å^{-3} near the THF molecules.

Chlorobis(η^5-cyclopentadienyl)(methyldiphenylphosphine)niobium(III). To a suspension of 1.18 g (4.0 mmol) of dichlorobis(η^5-cyclopentadienyl)niobium in 60 mL of THF was added at once 880 mg (0.83 mL; 4.4 mmol) of methyldiphenylphosphine. The suspension was treated with 7.20 g (4.6 mmol Na) of 1.47% w/w Na/Hg and rapidly stirred for 14 h at 27 °C under N_2. The resulting dark green slurry was filtered and the solvent removed in vacuo to give a green oil. The oil was stirred with 3 × 30 mL of toluene, and the extracts were filtered and concentrated in vacuo to ca. 10 mL. Addition of 50 mL of n-hexane and cooling to −20 °C for 6 h afforded dark green microcrystalline material which was isolated by filtration, washed with 3 × 10 mL of n-hexane, and dried in vacuo. The yield was 1.01 g (55%) of a dark green powder, which was used in the experiments described below without further purification.[23] ^1H NMR (C_6D_6): δ 1.90 (d, J = 7.2 Hz, 3 H), 4.67 (d, J = 1.8 Hz, 10 H), 6.97–7.05 (m, 6 H), 7.34–7.38 (m, 4 H). ^{31}P NMR (C_6D_6): δ 41.5.

Sodium naphthalide may also be used as the reducing reagent. The product is then purified as above except for several n-hexane washes which must be performed to remove residual naphthalene. The yield is comparable to above (ca. 55–60%).

Attempted Preparation of Chlorobis(η^5-cyclopentadienyl)[(diphenylphosphino)methyl]niobium(IV) (4). (A) By Nucleophilic Displacement of Cl^- in Cp_2NbCl_2 (1). A rapidly stirred suspension of niobocene dichloride in an appropriate solvent was treated with exactly 1 equiv of a nucleophilic source of the (diphenylphosphino)methyl group. The addition(s) was(were) performed at temperatures ranging between +30 and −78 °C. Both polar (i.e. THF, DME) and nonpolar (i.e. benzene, toluene, Et_2O) solvents were used. Strong (i.e. $LiCH_2PPh_2$), mild (i.e. $ClMnCH_2PPh_2$), and weak (i.e. $Me_3SnCH_2PPh_2$) nucleophilic reagents were selected. During the course of the addition, samples were withdrawn by syringe, placed in a 5-mm quartz tube, and analyzed by ESR spectroscopy. All intermediate and final product ratios were estimated from ESR signal intensity data. In all cases, except for $Me_3SnCH_2PPh_2$ which is too poor of a nucleophile to give any reaction, an intermediate, exhibiting a niobium hyperfine coupling [$a(^{93}Nb)$] of ca. 105 G, was observed by ESR spectroscopy. This unstable species was assumed to be $Cp_2Nb(Cl)CH_2P(C_6H_5)_2$ (4). In an attempt to isolate the monosubstituted product, the reaction mixture was filtered to remove any insoluble material and the dark brown filtrate concentrated in vacuo to give a brown oil. The oil was taken up in benzene, and the solution was filtered to remove LiCl if necessary and concentrated again to give a brown oily solid. The solid was stirred with n-hexane, filtered out, washed with n-hexane, and dried to yield a brown powder. ESR data in all cases showed a predominance of 1 and trace amounts of niobocene dichloride. The desired 4 was never isolated.

(B) By Nucleophilic Displacement of Cl^- in $Cp_2Nb(Cl)R$. To a stirred solution of $Cp_2Nb(Cl)PMePh_2$ or $Cp_2Nb(Cl)CO$ in an appropriate solvent was added dropwise a solution containing a stoichiometric amount of $LiCH_2PPh_2$·TMEDA or $LiCH_2PPh_2$. The lithium reagent was added dropwise to the Nb(III) complex at either 0 or 25 °C. The addition was monitored by ^1H NMR spectroscopy to observe any changes associated with Cl^- substitution. Each Nb(III) species was observed to be inert with respect to $^-CH_2PPh_2$ attack at ambient temperature. Hence, the reaction mixture was heated to and held at an elevated temperature to promote Cl^- displacement. Samples were removed and monitored by ^1H NMR spectroscopy for each successive temperature plateau. In general, the Nb(III) complexes were inert toward nucleophilic substitution at temperatures <50 °C. Higher temperatures led only to the thermal decomposition of the complexes. Again, no phosphinomethyl derivatives were isolated.

(C) By Niobium–Carbon Bond Cleavage in 1. A rapidly stirred solution in 1 in either THF or benzene was treated with an appropriate source of X^- (where X = Cl, Br, or I) at either 0 or 25 °C. The halogen reagent, prepared as 1 M solution in THF or benzene, was added dropwise via a syringe to 1. The reaction was monitored by ESR spectroscopy with time. A rapid loss of the ESR signal for 1 coupled with the appearance of one for Cp_2NbCl_2 was observed. Several electrophilic halide-containing reagents lead to poorly resolved ESR spectra and extensive decomposition. Both HCl and $C_6H_5ICl_2$ exhibited a transient signal

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(23) The absorption correction is made using Program XABS, H. Hope and B. Moezzi, University of California, Davis. The program obtains an absorption tensor from $F_o - F_c$ differences.

(24) Although repeated washings afford material that is >95% pure by ^1H NMR spectroscopy, several attempts to obtain acceptable analytical data on this compound were unsuccessful.

exhibiting an $a(^{93}Nb)$ value of ca. 103-106 G. These data agree with those of the intermediate species observed by method A and were thus attributed to 4. Like methods A and B, this route did not lead to isolable 4.

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Supplementary Material Available: Listings of bond lengths, bond angles, temperature factors, and derived hydrogen coordinates for 7 and 5 and a table giving a comparison of atom coordinates for 7 and 8 (10 pages). Ordering information is given on any current masthead page.

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"Genuine Heterocycles" from the Acid-Induced Cyclization of (Silylamino)(imino)(chalcogeno)phosphoranes and as a Result of Chloride Ion Abstraction from Bis[bis(trimethylsilyl)amino]thiophosphoryl Chloride

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The thio and seleno derivatives of the tricoordinate phosphorane $\mathrm{P[N^tBu(SiMe_3)](N^tBu)E}$ 1 (E = S, Se) undergo a novel cyclization upon reaction with Lewis acids. A number of derivatives of the $\overline{\mathrm{NSiEP}}$ framework have been isolated and characterized, including X-ray crystal structures of three derivatives, the neutral complexes $\overline{\mathrm{N^tBuSiMe_2SP}}\mathrm{(Me)N^tBu{\cdot}AlCl_3}$ (2a) and $\overline{\mathrm{N^tBuSiMe_2SeP}}\mathrm{(Me)N^tBu{\cdot}GaCl_3}$ (3), and the triflate salt of the protonated complex $[\overline{\mathrm{N^tBuSiMe_2SP}}\mathrm{(Me)N^tBu{\cdot}H^+}]$ (2c). The new compounds are rare examples of ring systems which contain only one atom of each element in the heterocyclic framework, systems for which we introduce the terminology "genuine heterocycles". A similar cyclization process is observed for the new thiophosphoryl chloride $\mathrm{P[N(SiMe_3)_2]_2(S)Cl}$ (4) in the presence of chloride ion acceptors to give salts of the cation $[\overline{\mathrm{N(SiMe_3)SiMe_2SP}}\mathrm{(Me)N(SiMe_3)_2}]^+$ (5), a direct analog of genuine heterocycles 2. Two salts of 5 have been structurally characterized. Both cyclization reactions have been examined by variable-temperature ^{31}P and ^1H NMR spectroscopy, and speculations are made as to the nature of the observed intermediates. The $\overline{\mathrm{NSiSP}}\mathrm{(N)}$ genuine heterocyclic unit is shown to be thermodynamically unstable with respect to the isomeric $\overline{\mathrm{NSiNP}}\mathrm{(S)}$ 1,3-diazasilaphosphetidine framework 6. The isomerization process is initiated by reaction with a base and can also be promoted thermally for salts of 5.

Introduction

We have recently introduced the term "genuine heterocycles"[1] to describe ring systems which contain only one atom of each element in the cyclic skeleton and to distinguish them from multielement heterocycles which are derivatives of a homocyclic, or heterocatenate form.[2-5] Considering the 12 elements most commonly observed in cyclic environments (B, C, N, O, Al, Si, P, S, Ga, Ge, As, Se), one can envisage as many as 220 different three-membered *genuine heterocycles* and 1485 possible four-membered systems.[6] Interestingly, fewer than 40 examples of genuine heterocyclic frameworks (containing these elements) have been isolated and spectroscopically identified,[7-11] and only 10 examples have been characterized by X-ray crystallography.[10-12] Most recently, the first example of a five-membered genuine heterocycle con-

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(1) Preliminary communication: Burford, N.; Spence, R. E. v. H; Whalen, J. M.; Rogers, R. D.; Richardson, J. F. *Organometallics* 1990, *9*, 2854.

(2) See, for example: Gilchrist, T. L. *Heterocyclic Chemistry*; Pitman Publishing: London, 1985. Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, U.K., 1985.

(3) See, for example: Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press: New York, 1987; Vol. 1 and 2.

(4) See also, for example: Woollins, J. D. *Non-Metal Rings, Cages and Clusters*; Wiley: Chichester, U.K., 1988. Power, P. P. *Angew. Chem., Int. Ed. Engl.* 1990, *29*, 449. Power, P. P. *J. Organomet. Chem.* 1990, *400*, 49. Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 1209.

(5) See, for example: *Rings, Clusters, and Polymers of Main Group and Transition Elements*; Roesky, H. W., Ed.; Elsevier: Amsterdam, 1989.

(6) $n!/2m(n-m)!$, where n is the number of different elements (12) and m is the number of atoms in the ring (3 or 4).