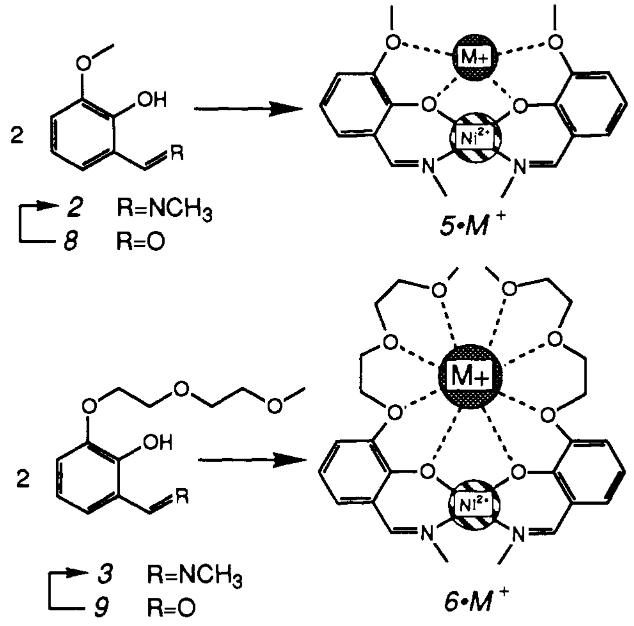

Figure 3.

that are dependent on both the structure of the polyether chain and on the structure of the Ni(II) chelate. *Most importantly, complex **4** extracts metal ions effectively even when generated in situ.*

The ability of Ni(II) complex **4** to transport alkali metal ions selectively into chloroform solution was tested with the picrate extraction technique.[12] As expected, imine **1** is unable to transport any alkali metal ion examined into chloroform solution.[13] However, nickel complex **4** functions as an ionophore and is able to transport almost 50% of the sodium ion present into chloroform.

Ionophores are typically characterized by their ability to select one metal ion over another. Cyclic ionophores exhibit significant preferences in their binding, whereas simple podands do not.[14] As can be seen in Figure 2, complex **4** displays substantial cation selectivity. Thus, the ability of complex **4** to extract Na^+ (44%) may be compared with its ability to extract Li^+ (30%), K^+ (14%), Rb^+ (13%), or Cs^+ (15%). Therefore, the rigid geometry of the transition-metal chelate has partially preorganized[15] the flexible ligand **1** and has generated a cation-selective ionophore.

We wondered if the selectivity of this ionophore would be sensitive to the structure of the polyethers on each salicylaldimine unit. It was anticipated that as the length of the polyether chain was shortened, the selectivity of the complex would shift toward smaller cations. Indeed, this is precisely what is observed. Complex **5**, with four oxygens available to bind an alkali metal ion, preferentially extracts Li^+ (63%), in comparison to Na^+ (40%), K^+ (16%), Rb^+ (15%), or Cs^+ (16%). It is interesting that this selectivity does not parallel the selectivity of 12-C-4, which prefers Na^+ in organic solvents.[16] This interesting result is presumably a reflection of the geometric constraints imposed by tetrahedral Ni(II).

The result of increasing the length of the polyether chain is more difficult to predict. A shift in selectivity toward larger cations might be anticipated, owing to the presence of eight potential ligand sites and the concomitant larger size of the receptor. Alternatively, a decrease in selectivity, caused by the increased flexibility of the ligand, might be observed. The latter of these two possibilities is realized. Although **6** does show some preference for Na^+, extraction of K^+ by this complex is almost as efficient.

To test whether these non-natural ionophores would self-assemble in situ, the following experiment was performed. A chloroform solution containing 25 mM Ni(II) bis(2-ethylhexanoate) and 50 mM imine **1** was prepared and layered below an aqueous solution of sodium picrate ($[M^+]$ = 7.5 mM). After the solution was stirred rapidly[12] for 3 min, 40% of the sodium ion in the aqueous phase had been extracted into the chloroform layer, whereas in the absence of imine **1**, 8% was extracted.[17] Importantly, even correcting for this 8%, the value of 40% is only slightly less than the value obtained when **4** is preformed in ethanol. *This indicates that the ionophore has self-assembled in situ.*

In this communication we have demonstrated that the predictable, organized geometries of transition-metal chelates can be utilized to control the orientation of two flexible polyether chains. In this way, a selective alkali metal ion binding site is generated. As is true for enzymes regulated by subunit dimerization, *this binding site may be generated in situ.* Because of the sensitivity of Ni(II) salicylaldimine complex geometry to the size of the substituent on nitrogen, it may be possible to fine-tune the selectivities of these molecules by simply altering the identity of this group. This strategy can in principle be used to control the assembly of receptors other than crown ethers, with implications for the regulation of artificial enzymes and as an approach toward protein design. The extension of this work toward the design of oriented, *peptide-based* receptors is in progress.

Supplementary Material Available: ^1H NMR and high-resolution MS data on compounds **1**, **2**, **3**, **7**, and **9** and combustion and UV–vis analysis of compounds **4**, **5**, and **6** (1 page). Ordering information is given on any current masthead page.

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(12) Pedersen, C. J. *Fed. Proc.* **1968**, *27*, 1305–1309. Typical procedure: A 50 mM chloroform solution of imine **1** or a 25 mM solution of **4** was prepared, and 0.4 mL of the respective solution was layered below 0.5 mL of the specified picrate salt solution ($[M^+]$ = 7.5 mM). The two-phase system was stirred with a VWR Brand Vortexer, set at speed 7, for 3 min, and the layers were separated by centrifugation. The extent of alkali metal ion transport was determined quantitatively by spectrophotometrically measuring the loss of picrate absorbance at 356 nm in the aqueous layer. The percent of cation extracted was calculated with the formula $100 \times \{1 - \{A_{356}(\text{host})/A_{356}(\text{CHCl}_3)\}\}$. Control experiments indicated that stirring for 9 min did not increase the amount of metal ion extracted.

(13) An additional control experiment excluded the possibility that picrate ion itself was the complexing agent. Twenty-five mM $NiSO_4$ was added to the basic, aqueous NaPicrate solution, and the extraction experiment was repeated in the presence and absence of 50 mM **1**. In neither case was any picrate anion transported into the chloroform solution.

(14) See ref 9. For a signficant exception, see: Iimori, T.; Still, W. C.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 3439–3441.

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(16) Massaux, J.; Desreux, J. F.; Duyckaerts, G. *J. Chem. Soc., Dalton Trans.* **1980**, 865–868.

(17) This value of 10% is likely due to the formation of $Ni^{II}(picrate)_2$.

An Alkylidene Complex of Vanadium: Synthesis and Structure of Cyclopentadienyl[bis(dimethylphosphino)ethane]-(neopentylidene)vanadium(III)

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Transition-metal alkylidene complexes of the nucleophilic ("Schrock") type have developed as an important class of compounds, displaying many interesting types of (catalytic) reactivity such as olefin metathesis[1] and ring-opening metathesis polymerization (ROMP).[2] These complexes have been intensively studied for the 4d/5d transition metals Nb, Ta, Mo, W, and Re[3] but are practically unknown for the 3d transition metals ($Cp_2Ti(CH_2)PMe_3$ has been described[4]). For vanadium, only

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(3) For some recent developments, see: (a) Horton, A. D.; Schrock, R. R.; Freudenberger, J. H. *Organometallics* **1987**, *6*, 893. (b) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1432. (c) Wallace, K. G.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

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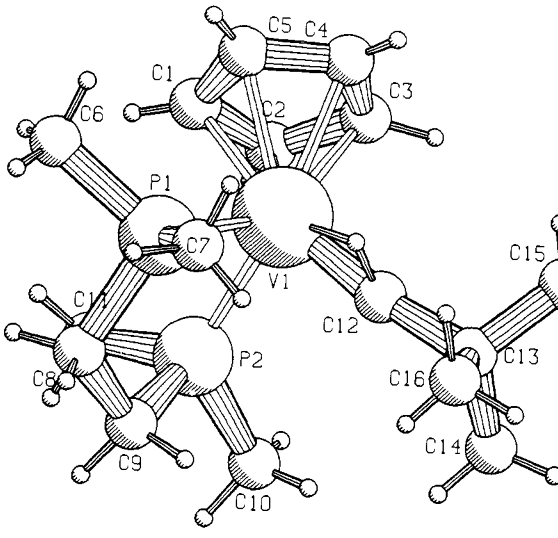

Figure 1. Molecular structure of $CpV(CHCMe_3)dmpe$ (**3**). Selected structural parameters are as follows: V(1)–C(12) = 1.809 (3) Å, V(1)–P(1) = 2.363 (1) Å, V(1)–P(2) = 2.331 (1) Å, C(12)–H(121) = 1.00 (5) Å, V(1)–H(121) = 1.66 (5) Å, ∠P(1)–V(1)–P(2) = 79.48 (5)°, ∠P(1)–V(1)–C(12) = 99.4 (1)°, ∠P(2)–V(1)–C(12) = 91.5 (1)°, ∠V(1)–C(12)–C(13) = 173.3 (3)°, ∠V(1)–C(12)–H(121) = 65 (3)°, ∠C(13)–C(12)–H(121) = 113 (3)°.

a few electrophilic ("Fischer") type carbenes are known,[5] together with the complex $(C_5Me_5)V[P_3C_3(t\text{-}Bu)_3]$ which also contains multiple VC bond character.[6] Here we wish to report the synthesis and X-ray structure of the first "Schrock"-type alkylidene of vanadium, $CpV(CHCMe_3)dmpe$ (dmpe = 1,2-bis(dimethylphosphino)ethane).

Earlier we reported that $CpVCl_2(PMe_3)_2$ is a convenient precursor for vanadium alkyls like the 16e complex $CpVMe_2(PMe_3)_2$.[7] It proved possible to make more strongly electron-deficient V(III) alkyl complexes by increasing the size of the alkyl groups, as the phosphines can be displaced through the increasing steric demand of the alkyl groups. In this way 14e $CpV(CH_2CMe_3)_2PMe_3$ (**1**) and 12e $CpV[CH(SiMe_3)_2]_2$ (**2**) can be prepared (eq 1) as well as the amido compound $CpV[N(SiMe_3)_2]_2$. Both alkyl complexes

$$CpVCl_2(PMe_3)_2 + 2Me_3CCH_2MgCl \rightarrow \underset{(\mathbf{1})}{CpV(CH_2CMe_3)_2PMe_3}$$

$$CpVCl_2(PMe_3)_2 + 2LiCH(SiMe_3)_2 \rightarrow \underset{(\mathbf{2})}{CpV[CH(SiMe_3)_2]_2} \tag{1}$$

are paramagnetic (by NMR[8]), extremely air sensitive, and fairly thermolabile. **1** decomposes in solution at 20 °C ($t_{1/2}$ = 5–6 h) by release of neopentane. When **1** is thermally decomposed in the presence of the chelating phosphine dmpe, the greenish-brown neopentylidene complex $CpV(CHCMe_3)dmpe$ (**3**) can be isolated, indicating that **1** probably decomposes through α-H abstraction from the neopentyl methylene group (eq 2).

$$\underset{(\mathbf{1})}{CpV(CH_2CMe_3)_2PMe_3} + dmpe \xrightarrow[-PMe_3]{-CMe_4} \underset{(\mathbf{3})}{CpV(CHCMe_3)dmpe} \tag{2}$$

Complex **3** is diamagnetic, and, although strongly broadened by unresolved coupling with the ^{51}V nucleus ($I = 7/2$) and quadrupolar relaxation, the alkylidene α-C and α-H resonances can be observed at δ 259.7 and −7.76 ppm, respectively[8] (the broadening does, however, preclude determination of the α-C–H coupling constant). The upfield shift of the α-H resonance appears to be characteristic for alkylidene complexes with a metal center that is not in its highest oxidation state (compare δ −8.49 ppm in $Ta(CHCMe_3)(dmpe)_2Cl$[9]). It apparently indicates a very strong interaction with the metal center, and a highly distorted configuration of the alkylidene α-carbon is expected.

An X-ray structure determination of **3**[10] (Figure 1) shows a very obtuse $V–C_\alpha–C_\beta$ angle (V(1)–C(12)–C(13) = 173.3 (3)°), and the compound contains the most distorted alkylidene group observed so far. The V–C(12) distance of 1.809 (3) Å is considerably shorter than the 2.102 (3) Å found in a "Fischer"-type carbene of V(I)[5c] and clearly indicative of VC multiple bonding. The alkylidene α-H is strongly bent back toward the metal center, and strong interaction with the metal is reflected in the V–H(121) distance of 1.66 (5) Å, comparable with V–H bonding distances in vanadium hydrides like $[CpV(\mu\text{-}H)dmpe]_2$ (V–H = 1.64 (4), 1.72 (4) Å).[11] This kind of structure can be thought of as a "frozen" intermediate for the α-H transfer process from an alkylidene V(III) to an alkylidyne hydride V(V) species (such an interconversion has been observed in the $Ta(CHCMe_3)(dmpe)_2Cl$ system on interaction with $AlMe_3$[9]).

The reactivity of the vanadium alkylidene complex is currently under investigation. In view of the general differences in behavior between 3d and 4d/5d congeners of transition-metal complexes, an interesting comparison with the Nb/Ta–alkylidene complexes may be anticipated.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Experimental details and spectral data (^1H NMR and IR) for all compounds, details of structure determination, crystal data, and lists of positional and thermal parameters for **3** (15 pages); listing of observed and calculated structure factors for **3** (16 pages). Ordering information is given on any current masthead page.

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(8) **1**: ^1H NMR (benzene-d_6, 20 °C) δ −2.70 ($\Delta\nu_{1/2}$ = 265 Hz, 18 H, CMe_3), −4.72 ($\Delta\nu_{1/2}$ = 377 Hz, 9 H, PMe_3), Cp resonance not observed; **2**: ^1H NMR (benzene-d_6, 20 °C) δ 167.7 ($\Delta\nu_{1/2}$ = 4750 Hz, 5 H, Cp), 8.78 ($\Delta\nu_{1/2}$ = 230 Hz, 36 H, $SiMe_3$); **3**: ^1H NMR (benzene-d_6, 20 °C) δ 4.48 (t, J_{PH} = 1.8 Hz, 5 H, Cp), 1.44 (m, 2 H, PCH_2), 1.41 (ps t, 6 H, PMe), 1.27 (m, 2 H, PCH_2), 1.20 (s, 9 H, CMe_3), 0.67 (ps t, 6 H, PMe), −7.76 (very br, $\Delta\nu_{1/2}$ = 318 Hz, 1 H, V=CH—); ^{13}C NMR δ 19.09 (q, 126.6 Hz, PMe), 27.26 (q, 126.0 Hz, PMe), 33.34 (t, 130.6 Hz, PCH_2), 33.57 (q, 125.5 Hz, $C(CH_3)_3$), 46.2 (br s, CMe_3), 89.06 (d, 170.3 Hz, Cp), 259.7 (very br, $\Delta\nu_{1/2}$ = 780 Hz, V=C).

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(10) **3** crystallizes in the monoclinic space group $P2_1/a$, a = 13.699 (2) Å, b = 8.966 (1) Å, c = 15.386 (2) Å, β = 101.87 (1)° (130 K), Z = 4. Reflections (2651) with 1.35° ≤ θ ≤ 27.0° were considered observed. Twenty-eight hydrogen atoms (including H(121)) were localized from the Fourier difference maps and refined isotropically. The three other hydrogen atoms were included in the refinement riding on their carrier atoms (C(8), C(9), and C(11)) with a C–H distance of 1.0 Å. $R = 0.053$, $R_w = 0.050$ ($w = 1/\sigma^2(F)$) for 276 parameters.

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