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# Communications

## Vanadium Tetrazene Complex: Synthesis of Chlorophosphine(1,4-diphenyltetrazenido)vanadium(III), $Cl(PR_3)V(1,4\text{-}Ph_2N_4)$, $PR_3=PMe_3$, $PEt_3$

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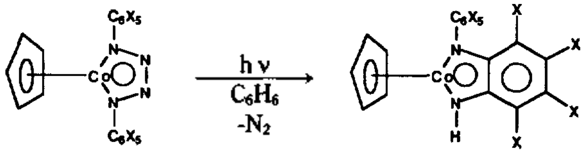
Cyclic transition metal tetrazene ($MN_4R_2$) complexes have been synthesized by coupling reactions between either an organic azide ($RN_3$; R=alkyl or aryl) or a diazonium salt ($RN_2^+$) and a metal complex in a low oxidation state, because the free tetrazene ligands were unavailable. Since 1967 several transition metal tetrazene complexes have been reported, including derivatives of Ni, Pt, Co, Rh, Ir, and Fe.[1] Recently we reported the preparation of a dianionic tetrazene **I** (Eq. 1), with which several transition metal tetrazene ($MN_4Ph_2$; M=Ni, Pd, Pt, Mo, W) and a main group element tetrazene ($Me_2SiN_4Ph_2$) complexes have been prepared.[2]

$$PhNHLi+PhN_3 \xrightarrow{THF} Ph(H)NN=NN(Ph)Li \xrightarrow[THF]{^nBuLi} [Li(THF)_x]_2[PhNN=NNPh],\ \mathbf{I} \qquad (1)$$

Cyclic metal tetrazene complexes have got attractions because of their novel bonding features. Attention has focused on the delocalization of $\pi$-electron in the metallacycles and the role of the d orbitals in bonding. For example, studies on the redox chemistry of $CpCo(1,4\text{-}R_2N_4)$($R=CH_3$, $C_6H_5$, $C_6H_5$, $2,4\text{-}F_2C_6H_3$, $2,6\text{-}(CH_3)_2C_6H_3$; $Cp=C_5H_5$) showed that tetrazene ligands are strong $\pi$-acceptor groups that can be used to stabilize electron-rich 19-electron complexes.[1k] Another interesting example is as follows: photolysis of cyclopetadienyl (1,4-diaryltetrazenido)cobalt, ($CpCoN_4Ar_2$; $Ar=C_6H_5$ or $C_6F_5$) underwent fragmentation involving concurrent bond breakages of C-H, C-F, and C-C to form a 1,4-diazabutadiene complex (Eq. 2).[3]



(2)

X=H or F

As described above, there have been no reports on the tetrazene complexes of Ti anf V group metals. In this communication, we report the synthesis of $V(1,4\text{-}Ph_2N_4)Cl(PR_3)$ ($PR_3=PMe_3$ and $PEt_3$).

In the beginning of this research, we tried to prepare a cyclic vanadium tetrazene complex by a metathetical reaction between a dianionic ligand $Li_2N_4Ph_2$, **I**, and a vanadium precursor $VCl_3(PR_3)_2$($PR_3=PMe_3$, $PEt_3$),[4] (Eq. 3). Small phosphine complexes of vanadium were employed to provide an electron density to the electron-deficient vanadium metal center and avoid the steric congestion around the small vanadium metal center.[5]

$$VCl_3(PR_3)_2+Li_2N_4Ph_2 \dashrightarrow (PR_3)_2Cl\overline{V[N(Ph)N=NN}Ph] + 2\,LiCl \qquad R=Et,\ Me \qquad (3)$$

When a yellow benzene slurry of the ligand **I** was added to a brown benzene slurry of $VCl_3(PEt_3)_2$ under argon at room temperature, there was an instantaneous color change from brown to dark-brown with a strong smell of phosphine. After 6 h, the resulting solution was filtered, concentrated, and layered by hexanes to give $(PEt_3)ClV[1,4\text{-}Ph_2N_4]$, **II**, in 32% yield. In the same way $(PMe_3)ClV[1,4\text{-}Ph_2N_4]$, **III**, was obtained in 67% yield. Complex **II** and **III** are air- and water-sensitive. $^1H$, $^{13}C$, $^{13}C\{H\}$ NMR and mass spectra studies of **II**[6] and **III**[7] revealed that unexpectedly cyclic vanadium tetrazene complexes containing only one phosphine group were produced by metathesis, together with liberation of one phosphine (Eq. 4). They are the first early-transition metal tetrazene complexes.

$$VCl_3(PR_3)_2+Li_2N_4Ph_2 \longrightarrow (PR_3)Cl\overline{V[N(Ph)N=NN}Ph] + 2\,LiCl+PR_3 \qquad R=Et,\ \mathbf{II};\ Me,\ \mathbf{III} \qquad (4)$$

The liberation of phosphine ligand during syntheses occurs probably due to the fact the volume of the ligand **I** is too big to be accommodated by the small vanadium. It is worth noting that the size of the phosphine ligand exerts an influence on the geometry around the vanadium metal center. NMR studies of **II** and **III**[6,7] indicate the difference in the symmetries around the vanadium metal. Complex **III**, which has $PMe_3$, shows four types of carbon atoms of the benzene ring on its $^{13}C$-NMR spectra and three types of hydrogen atoms on its $^1H$-NMR spectra, indicating that the two phenyl groups are in the same environment. Therefore the coordination sphere of vanadium in **III** can be described as a pseudotetrahedron. On the other hand, Complex **II** (a $PEt_3$ analog) exhibits complicated NMR peak-splittings. $^{13}C$-NMR spectra of **II** exhibit twelve different carbon peaks of the phenyl groups and $^1H$-NMR spectra also indicate the existence of two different benzene rings. One carbon atom of the benzene ring even appears as a doublet (δ 123.19) with a coupling constant $J_{C\text{-}P}=16.2$ Hz. Although at this time we cannot explain clearly why one carbon atom of the benzene ring on the tetrazene ligand backbone couples with the phosphorous atom, the results maybe imply that a larger phosphine ($PEt_3$) induces a more geometrically distorted tetrahedron. Reactivities and other chemistries of these complexes are under study.

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4. (a) J. Nieman and J. C. Huffman, *J. Organomet. Chem.*, **255**, 193 (1983); (b) Von K. Issleib and G. Bohn, *Anorg. Allgem. Chem.*, **301**, 188 (1959).
5. A radius of $V^{3+}$ with coordination number 6 is 0.78 Å. For additional informations, see; R. D. Shannon, *Acta Cryst.*, **A32**, 751 (1976).
6. Complex **II**. $^1H$-NMR ($C_6D_6$, 500 MHz): δ 7.32 (t, 2H, $C_6H_5$, $J=7.4$ Hz), 7.13 (t, 2H, $C_6H_5$, $J=7.1$ Hz), 7.06 (d, 2H, $C_6H_5$, $J=7.23$ Hz), 6.90 (t, 1H, $C_6H_5$, $J=7.1$ Hz), 6.77 (t, 1H, $C_6H_5$, $J=7.1$ Hz), 6.48 (d, 2H, $C_6H_5$, $J=7.23$ Hz), 1.35 (m, 6H, $P\underline{CH_2}CH_3$), 0.87 (m, 9H, $PCH_2\underline{CH_3}$); $^{13}C$-NMR ($C_6D_5$, 500 MHz): δ 153.78-114.42 ($C_6H_5$), 18.98 (td, $P\underline{CH_2}CH_3$, $J_{C\text{-}H}=128$, $J_{C\text{-}P}=63.2$ Hz), 6.18 (qd, $PCH_2\underline{CH_3}$, $J_{C\text{-}H}=128$, $^2J_{C\text{-}P}=4.2$ Hz); $^{13}C\{H\}$ NMR ($C_6D_6$, 500 MHz): δ 115.03, 116.71, 118.13, 129.13, 129.34, 147.31, 153.74 (s, $C_6H_5$), 123.19 (d, $C_6H_5$, $J_{C\text{-}P}=16.2$ Hz). MS (EI): 412.27 ($M^+$-2, 2), 379.49 ($M^+$-Cl, 11), 365.47 ($V(PEt^2)N_3Ph_2$, 8), 351.45 ($V(PEt_3)N_2Ph_2$, 6), 337.41 ($V(PEt_3)ClN_4Ph$, 5), 235.19 ($V(NHPh)_2$, 33), 225.17 ($VN_4(PEt_3)$, 67), 212.16 ($N_4H_2Ph_2$, 24), 119.06 ($PhN_3$, 20), 105.09 ($PhN_2$, 18) 93.09 ($NH_2Ph$, 100).
7. Complex **III**. $^1H$-NMR ($C_6D_6$, 500 MHz): δ 6.43 (d, 4H, $C_6H_5$, $J=7.5$ Hz), 6.78 (t, 4H, $C_6H_5$, $J=7.5$ Hz), 7.14 (t, 2H, $C_6H_5$, $J=7.5$ Hz), 0.925 (m, 9H, $CH_3$); $^{13}C$-NMR ($C_6D_6$, 500 MHz): δ 129.37 (dd, $C_6H_5$, $J_{C\text{-}H}=156$, $^3J_{C\text{-}H}=8.2$ Hz), 118.23 (dt, $C_6H_5$, $J_{C\text{-}H}=160$, $^3J_{C\text{-}H}=7.4$ Hz), 114.97 (dt, $C_6H_5$, $J_{C\text{-}H}=155$, $^3J_{C\text{-}H}=6.4$ Hz), 1.32 (q, $CH_3$, $J_{C\text{-}H}=118$ Hz); $^{13}C\{H\}$ NMR ($C_6D_6$, 500 MHz): 147.16 (s, $C_6H_5$), δ 129.37 (s, $C_6H_5$), 118.23 (s, $C_6H_5$), 114.97 (s, $C_6H_5$), 1.31 (s, $CH_3$). MS (EI): 372.22 ($M^+$, 4), 336.24 ($M^+$-Cl, 6), 323.32 ($V(PMe_3)$-$N_3Ph_2$, 15), 296.19 ($M^+$-$PMe_3$, 6), 212.11 ($N_4H_2Ph_2$, 5), 105.08 ($PhN_2$, 35), 93.09 ($NH_2Ph$, 100), 77.06 (Ph, 59).

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# Synthesis of Prostaglandins II[1]. Convenient Synthesis of Misoprostol

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It is well known that naturally occurring prostaglandins of E-series exhibit powerful gastric antisecretory activity and cytoprotection.[2] However, their numerous side effects, rapid metabolism, and chemical instability limit their application as a therapeutic agent for the treatment of peptic ulcer disease. Misoprostol **1**, the 15-deoxy-16-hydroxy-16-methylprostaglandin $E_1$ is a potent anti-ulcer agent which reduced the critical drawbacks of the natural prostaglandins.[3] Since its development, a number of synthetic methods for **1** have been reported. In most cases, the synthetic routes to **1** involve, for the introduction of ω-side chain, a 1,4-conjugate addition of an appropriate 16-hydroxy-16-methyl vinyl copper species to the cyclopentenone ring which already has the α-side chain.[4] Here we describe a new efficient synthetic approach to **1**.

Since the highly efficient method to construct the upper side chain had been available,[5] our attention was focused upon the introduction of the lower side chain bearing *trans-*