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Oxidative Addition of a Dinuclear and Divalent Vanadium Hydride to an Olefin C−H Bond, Leading to Catalytic Hydrogenation

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Summary: The dinuclear and divalent hydride complex $\{[(Me_3Si)N{=}P(Ph)_2C(H)P(Ph)_2{=}N(SiMe_3)]V\}_2(\mu\text{-}H)_2$ (**1**) *performs oxidative addition to the styrene* β*-C−H bond, affording the novel dinuclear trivalent vanadium complex* $\{[(Me_3Si)N{=}P(Ph)_2C(H)P(Ph)_2{=}N(SiMe_3)]V\}_2(H)(\mu\text{-}H)_2(\mu,\eta^1{:}\eta^2\text{-}CHCHPh)$ (**2**). *Room-temperature hydrogenolysis re-formed* **1** *and ethylbenzene in catalytic fashion. Reaction of* **1** *with ethylene afforded instead the mixed-valence* $\{[(Me_3Si)N{=}P(Ph)_2C(H)P(Ph)_2{=}N(SiMe_3)]V\}_2(\mu\text{-}H)_3$ (**3**) *and a mixture of 2-butene and 3-methyl-1,4-pentadiene.*

In the manufacture of synthetic rubber based on vanadium catalyst technology, the control of the elastomer molecular weight is achieved by introducing small amounts of hydrogen gas into the feed.[1] However, the hydrogenolysis of the V−C bond not only terminates the chain growth but also reduces vanadium toward the inactive divalent state with consequent catalyst deactivation.[2] Poor stability of vanadium hydrides and the resulting reduction of the metal center toward the divalent state[3] are generally linked to the modest performance of vanadium complexes as Ziegler−Natta catalysts.[4] Thus, to improve the activity of vanadium catalysts, it is important to understand the stability of vanadium hydrides and their ability to perform olefin insertion reactions.

Molecular vanadium hydrides are rare species and are exclusively limited to derivatives containing the metal in either medium or low oxidation states.[5,6] The insertion of ethylene into the V−H bond, which may in principle lead to polymerization, has so far only been achieved upon photolysis of $VH(CO)_5$.[7] Even the simple coordination of an olefin to vanadium is not a straightforward process.[8,9] Evidence for labile ethylene coordination was obtained in the case of a cationic pentavalent complex.[10]

In this paper, we describe the oxidative addition of a dinuclear divalent vanadium hydride to the styrene β-C−H bond to form the corresponding trivalent vinyl hydride derivative precursor to either catalytic hydrogenation or ethylene di- and trimerization.

We have recently described the preparation of the extremely air-sensitive, *divalent and dinuclear* hydride complex $\{[(Me_3Si)N{=}P(Ph)_2C(H)P(Ph)_2{=}N(SiMe_3)]V\}_2(\mu\text{-}H)_2$ (**1**) via mild-condition reductive hydrogenolysis of the *trivalent and mononuclear* dialkylvanadium complex $[CH(PPh_2NSiMe_3)_2]V(CH_3)_2$.[11] Treatment of a red-brown toluene solution of **1** with styrene results in a rapid color change to brown-green from which dark

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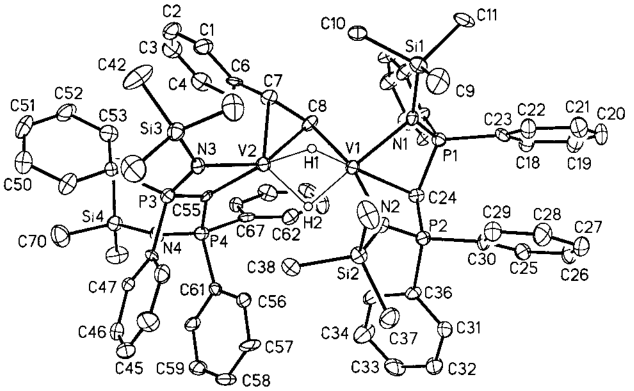

Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level. Relevant bond distances (Å) and angles (deg): V(1)−C(24) = 2.362(6), V(1)−N(1) = 2.157(5), V(1)−N(2) = 2.082(5), V(1)−C(24)−P(1) = 84.6(2), V(1)−C(24)−P(2) = 84.3(2), V(2)−C(55) = 2.332(5), V(2)−N(3) = 2.101(5), V(2)···N(4) = 5.168(5), V(2)−C(8) = 2.214(6), V(2)−C(7) = 2.149(6), C(8)−C(7)−C(6) = 125.0(6), V(1)−C(8) = 2.296(6), C(7)−C(8) = 1.433(8), V(1)−H(1) = 1.68(5), V(1)−H(2) = 1.75(5), V(2)−H(1) = 1.78(5), V(2)−H(2) = 1.78(5), V(1)−H(1)−V(2) = 89.0(2), V(1)−H(2)−V(2) = 90.0(3), V(1)−V(2) = 2.5074(16), C(7)−V(2)−C(8) = 38.4(2), C(7)−V(2)−N(3) = 107.5(3), C(7)−V(2)−C(55) = 98.7(2), C(7)−V(2)−H(1) = 92.0(2), C(7)−V(2)−H(2) = 117.4(3).

brown crystals of the new paramagnetic complex $\{[(Me_3Si)N{=}P(Ph)_2C(H)P(Ph)_2{=}N(SiMe_3)]V\}_2(H)(\mu\text{-}H)_2(\mu,\eta^1{:}\eta^2\text{-}CHCHPh)$ (**2**) were isolated.[12]

The formula of **2** was elucidated by an X-ray crystal structure[13] and by a quantitative Toepler pump degradation experiment.[12] The complex contains two vanadium atoms, each differently bonded to a phosphinimide $(Me_3Si)N{=}P(Ph)_2C(H)P(Ph)_2{=}N(SiMe_3)$ anion (Figure 1). The first vanadium is surrounded by the ligand which uses the central bridgehead carbon and the two nitrogen as donors. The ligand in this case adopts the usual tridentate type of geometry[10] with the VN_2P_2C plane folded along the V−C vector. The second vanadium uses instead the carbon atom for bonding and only one of the two nitrogen atoms. The second nitrogen atom remains uncoordinated and points away from the vanadium atom. This particular vanadium atom is also side-on coordinated to a bridging styryl unit, forming two comparable V−C distances. The styryl group adopts the same bridging side-on/end-on bonding mode previously observed in another late-metal complex, $[FeCo(CO)_7(\mu\text{-}CH{=}CPhH)]$.[14] The difference Fourier map also yielded the positions of the two bridging hydrides. The V−V distance is rather short and possibly falls in the so-called V−V bonding range. The low value of the magnetic moment ($\mu_{eff} = 1.30\ \mu_B$) is also in agreement with the presence of a strong magnetic coupling between the two vanadium atoms.

The hexacoordination of the vanadium π-bonded to the styryl moiety is severely flattened and strongly suggests that another hydride, probably terminally bonded, might be present in what otherwise appears to be an empty coordination site. Also, the strange partial dissociation of one of the two nitrogen atoms of the pincer ligand substantiates this proposal. Regrettably, the even moderate paramagnetism did not allow a conclusive assignment of the hydride resonances, whereas, consistent with the solid-state structure, the ^{51}V NMR spectrum showed two magnetically distinct vanadium atoms (2003.7 and −290.3 ppm). However, the IR spectrum showed the presence of one medium-intensity resonance at 1786 cm^{-1}, which is likely due to the terminally bonded hydride. Finally, a chemical degradation experiment carried out in toluene with gaseous HCl in a sealed vessel connected to a Toepler pump yielded the expected 3 equiv of H_2 (91%), thus supporting the proposed formulation.

The long C−C bond distance of the styryl moiety indicates that a substantial reduction of the C−C double bond has occurred. Since **1** was readily formed by reductive hydrogenolysis of a trivalent alkyl under pressure and at room temperature, it is conceivable to expect that **2** could also undergo hydrogenolysis, forming ethylbenzene and a vanadium hydride ready for another cycle of hydrogenation. Accordingly, the catalytic hydrogenation of styrene (Scheme 1) proceeds slowly at room temperature and atmospheric pressure but considerably faster under H_2 pressure. In a standard experiment under H_2 pressure (60 atm), a solution of **1** (10 mg) in toluene (100 mL) completed the conversion of 1 g of styrene to ethylbenzene in 15 h, corresponding to about 10 turnovers/min. Although the overall catalytic activity is rather modest, compared to that of the well-established late-metal hydrogenation catalysts, this is nevertheless the first time that catalytic styrene hydrogenation has been observed for vanadium.[15]

Complex **1** also reacts with ethylene under atmospheric pressure and at room temperature to form the dinuclear, mixed-valence V(II)/V(III) trihydride derivative $\{[(Me_3Si)N{=}P(Ph)_2C(H)P(Ph)_2{=}N(SiMe_3)]V\}_2(\mu\text{-}H)_3\cdot(ether)$ (**3**). The molecular connectivity was elucidated by an X-ray crystal structure and by a Toepler

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(12) **2**: neat styrene (0.18 mL, 1.6 mmol) was added to a brown-red solution of **1** (1.0 g, 0.8 mmol) in toluene (80 mL). The initial brown color changed immediately to dark green. After the mixture was stirred for 24 h, the solvent was removed in vacuo and the solid residue redissolved in ether (80 mL). Concentration of the resulting brown-green ether solution to a small volume (20 mL) and standing for 24 h at room temperature afforded dark brown crystals of **2** (0.7 g, 0.5 mmol, 68%). Anal. Calcd (found) for $C_{70}H_{89}N_4P_4Si_4V_2$: C, 63.47 (63.68); H, 6.77 (6.81); N, 4.23 (4.15). IR (Nujol mull, cm^{-1}): ν 1956 (w), 1898 (w), 1786 (w), 1585 (w), 1480 (m), 1435 (m), 1338 (w), 1262 (m), 1245 (m), 1162 (m), 1114 (s, br), 1064 (w), 1027 (s), 1000 (m), 936 (s), 915 (s), 833 (s, br), 800 (m), 746 (w), 697 (m), 660 (m, sh), 640 (m), 602 (m, sh). $\mu_{eff} = 1.30\ \mu_B$. **3**: a brown-red solution of **1** (0.26 g, 0.2 mmol) in toluene (60 mL) was saturated with ethylene gas. The color changed immediately to brown-green. After 24 h, the solvent was removed in vacuo and the solid residue redissolved in ether (40 mL). Concentration of the resulting brown-green ether solution (10 mL) and standing for 72 h at room temperature afforded orange-yellow crystals of **3** (0.12 g, 0.095 mmol, 47%). Anal. Calcd (found) for $C_{66}H_{91}N_4OP_4Si_4V_2$: C, 61.23 (61.68); H, 7.09 (6.81); N, 4.33 (4.25). IR (Nujol mull, cm^{-1}): ν 1561 (w), 1304 (w), 1261 (m), 1245 (m), 1111 (s), 1088 (m), 1047 (w), 1027 (w), 836 (s), 803 (m), 771 (w), 741 (m), 722 (m), 694 (s), 668 (m), 639 (w), 602 (w). $\mu_{eff} = 2.18\ \mu_B$. For details on Toepler pump degradation experiments see the Supporting Information.

(13) Crystal data for **2**: $C_{70}H_{89}N_4P_4Si_4V_2$, $M_r = 1324.56$, monoclinic, $P2_1/c$, $a = 12.2471(16)$ Å, $b = 25.845(4)$ Å, $c = 22.596(3)$ Å, $\beta = 96.628(2)°$, $V = 7104.5(16)$ Å^3, $Z = 4$, $D_{calcd} = 1.237$ g cm^{-3}, absorption coefficient 0.463 mm^{-1}, $F(000) = 2792$, 55 195 (7447) collected (unique) reflections, R1 = 0.0535, wR2 = 0.0863, GOF = 1.016. **3**: $C_{66}H_{91}N_4P_4Si_4V_2O$, $M_r = 1294.55$, orthorhombic, $P2_12_12_1$, $a = 12.2689(16)$ Å, $b = 15.472(2)$ Å, $c = 37.491(6)$ Å, $V = 7116.7(19)$ Å^3, $Z = 4$, $D_{calcd} = 1.208$ g cm^{-3}, absorption coefficient 0.461 mm^{-1}, $F(000) = 2740$, 17 037 (7455) collected (unique) reflections, R1 = 0.0722, wR2 = 0.1452, GOF = 1.032. Phenyl groups were refined as idealized and rigid hexagons to keep a favorable data/parameter ratio.

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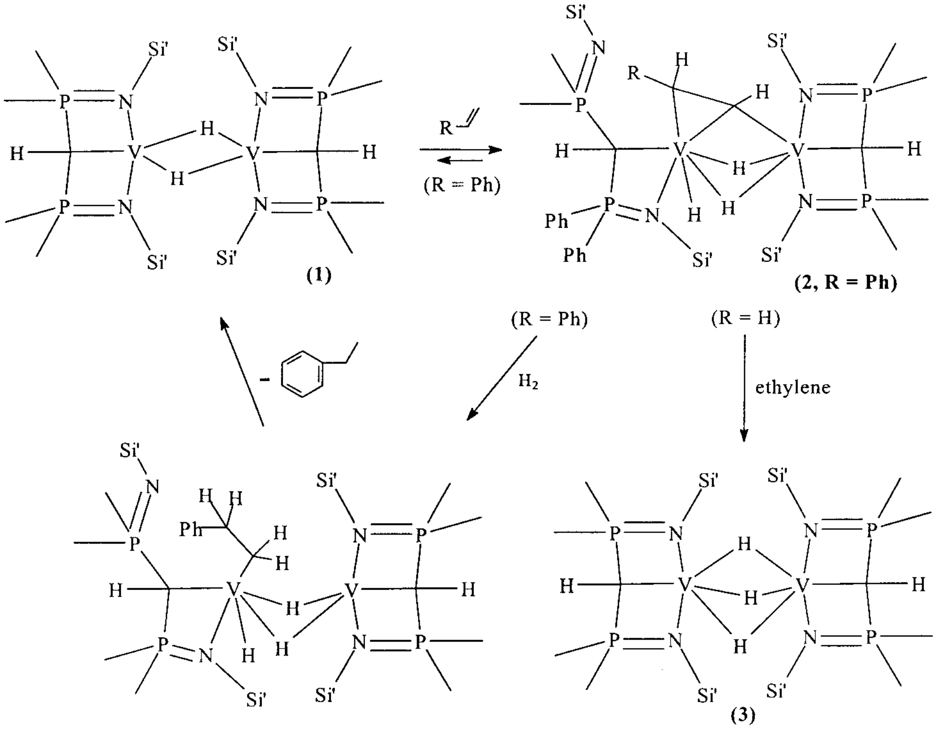
Scheme 1



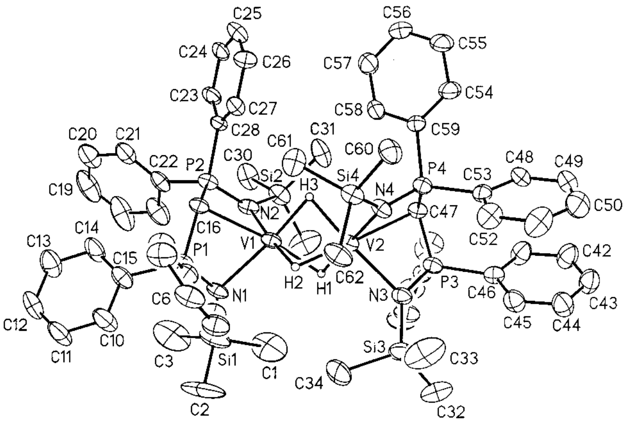


Figure 2. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level. Relevant bond distances (Å) and angles (deg): V(1)–N(1) = 2.173(9), V(1)–C(16) = 2.421(11), V(1)–N(2) = 2.118(9), V(1)–H(1) = 1.98(9), V(1)–H(2) = 1.91(9), V(1)–H(3) = 1.82(9), V(1)···V(2) = 2.421(3), H(1)–V(1)–C(16) = 168(4), H(2)–V(1)–N(2) = 174(4), N(1)–V(1)–H(3) = 159(4), N(1)–V(1)–N(2) = 94.3(4), N(1)–V(1)–C(16) = 70.2(3).

pump degradation experiment, showing the complex to basically possess a structure rather similar to that of the mixed-valence hydride/chloride derivatives[11] previously reported. Other than the presence of the three bridging hydrides, complex **3** does not display any particular feature (Figure 2). The GC-MS of the reaction mother liquor clearly showed the presence of larger than stoichiometric amounts of 2-butene and a smaller amount of 3-methyl-1,4-pentadiene. No other products were detected in the chromatogram. The presence of these two products indicates that **1** promotes ethylene di- and trimerization. However, while the dimerization of ethylene to 2-butene does not require acquisition or loss of hydrogen atoms and therefore can be achieved in a catalytic fashion, the formation of the diene does require the formal elimination of one molecule of hydrogen. At this stage, we are unsure whether 2-butene is formed as such or if it stems from the isomerization of initially formed 1-butene. Since no H_2 gas was detected in the reaction mixture, the formation of the mixed-valence trihydride **3** most likely results from the formation of the pentadiene. Given that **3** is unreactive toward olefins, its formation may well poison the catalytic formation of 2-butene.

The partial oxidation of the metal and the acquisition of one additional hydride are in line with the initial formation of a vinyl/hydride species similar to **2**, followed by insertion of either one or two molecules of ethylene. The formation of the 3-methylpentadiene has some implications for the regiochemistry of the olefin insertion, which is currently under study.

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Supporting Information Available: Complete listings of structural parameters and crystal data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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