Control experiments using preformed complexes **7** gave results which were essentially identical with those employing in situ generation.

In most cases the products could be identified in the reaction mixture by ^{1}H NMR (see Table IV), directly or after filtration of precipitate. Approximate total yields were determined by integration of the NMR signals of the crude reaction product and the relative yields by integration of the signals from the isolated amine fraction. In order to determine the yields more accurately, most reactions were repeated on a 0.1-mmol scale. After the appropriate reaction time (see Table III), the solvent and excess amine were evaporated. In the case of methyl-, dimethyl-, and diisopropylamines, 1 mL of water and a few drops of concentrated hydrochloric acid were added to the residue and the mixture was extracted three times with 1.5 mL of hexane, in order to remove the hydrocarbon byproducts, if any. The resulting mixture was then treated with a small amount of solid NaOH and extracted three times with 1.5 mL of hexane. Evaporations of the solvent gave the amine products, the relative amounts of which were determined by ^{1}H NMR.

In the reactions with trimethylamine, the crude, dried reaction products were extracted with water (2 × 1 mL) to give, after evaporation, the essentially pure quarternary ammonium salts.

Isolation of Linalyldimethylamine (14c). The nerylpalladium complex **5b** containing 10% of the isomer **5a** (0.049 g, 0.1 mmol) was dissolved in dichloromethane and cooled to –78 °C, and triphenylphosphine (0.052 g, 0.02 mmol) was added. When all had dissolved, dimethylamine (0.3 mmol) in ca. 100 μL of benzene was added, immediately followed by excess triphenylphosphine (0.100 g, 0.38 mmol). The solution was stirred for 5 min at –78 °C and then warmed to –30 °C. After a few minutes a heavy yellow precipitate of tetrakis(triphenylphosphine)palladium(0) was formed. After addition of hexane (3 mL) the precipitate was removed by filtration and the solvent was evaporated at –20 °C. The amine product was isolated as described above. The yield was essentially quantitative, and the product contained mainly linalyldimethylamine **14c** (80%) but also some neryldimethylamine **14b** (12%) and geranyldimethylamine **14a** (8%).

Using the same procedure but reacting instead the geranyl complex **7a** gave a mixture of geranyldimethylamine **14a** (84%) and linalyldimethylamine **14c** (16%).

Acknowledgment. We thank the Swedish Natural Science Research Council for a grant to A. V. from the Visiting Scientists Program and Professor B. Trost for valuable discussions and a copy of T. R. Verhoeven's thesis.

Registry No. **1a**, 89302-63-6; **1b**, 89362-81-2; **2a**, 96328-66-4; **3a**, 96328-68-6; **3b**, 96392-64-2; **4a**, 96328-70-0; **4b**, 96392-66-4; **5a**, 96328-72-2; **5b**, 96392-68-6; **6a**, 96328-74-4; **6b**, 96392-70-0; **7a**, 96328-76-6; **7b**, 96392-72-2; **8a**, 96328-78-8; **8b**, 96392-74-4; **9a**, 96328-80-2; **9b**, 96392-76-6; **12a**, 96348-40-2; **12b**, 96328-59-5; **13**, 96328-60-8; **14a**, 51768-88-8; **14b**, 53652-01-0; **14c**, 96328-61-9; **15a**, 96328-62-0; **15b**, 96328-63-1; **16**, 76027-07-1; **19**, 123-35-3; Pd(PPh$_3$)$_4$, 14221-01-3; GerNerNH, 96328-64-2; GerNHMe, 63343-64-6; MeNH$_2$, 74-89-5; Me$_2$NH, 124-40-3; Me$_3$N, 75-50-3; *i*-Pr$_2$NH, 108-18-9; (η^3-geranyl)triphenylphosphine)(acetonitrile)palladium tetrafluoroborate, 96328-82-4; tetrakis(acetonitrile)silver tetrafluoroborate, 93556-88-8; ocimene, 13877-91-3.

Synthesis of Methyl and Hydride Derivatives of Permethylvanadocene and Their Reactions with Carbon Monoxide

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Oxidation of permethylvanadocene with 1 equiv of HCl yields the paramagnetic chlorovanadium(III) complex (η^5-C$_5$Me$_5$)$_2$VCl, **2**. This complex can be alkylated with methyllithium to yield the paramagnetic methyl complex (η^5-C$_5$Me$_5$)$_2$VCH$_3$, **3**. Complex **3** undergoes hydrogenolysis under hydrogen pressures of 17–25 atm to yield a paramagnetic monohydride complex (η^5-C$_5$Me$_5$)$_2$VH, **4**, which exchanges with a deuterium atmosphere to yield the monodeuteride. Treatment of **4** with carbon monoxide at 1 atm produces the diamagnetic carbonyl hydride complex (η^5-C$_5$Me$_5$)$_2$V(H)CO, **6**. Treatment of **3** with excess carbon monoxide at room temperture and 1 atm pressure yields the diamagnetic acetyl carbonyl complex (η^5-C$_5$Me$_5$)$_2$V[C(O)CH$_3$](CO), **5**. Two intermediates in the conversion were observed spectroscopically by varying the reaction conditions. These were tentatively identified as the diamagnetic methyl carbonyl complex (η^5-C$_5$Me$_5$)$_2$V(CH$_3$)CO, which was observed at low temperature by ^{1}H NMR, and the paramagnetic acetyl complex (η^5-C$_5$Me$_5$)$_2$VC(O)CH$_3$, which was observed by infrared spectroscopy under a deficiency of CO at room temperature.

Introduction

Bis(cyclopentaidenyl)vanadium, or vanadocene, exhibits a rich chemistry which includes coordination of two-electron ligands,[1a] oxidation to V(III) followed by coordination of additional ligands,[1a–c] synthesis of V(III) alkyl complexes,[1d–g] and insertion of CO into the vanadium–alkyl bond of these complexes to form acyl complexes.[1h,i] However, no hydride derivative of vanadocene has ever been prepared.

We have reported the synthesis of permethylvanadocene and its oxidation with ferrocenium ion to yield acetonitrile and carbonyl adducts of vanadium(III).[2] In light of the

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increased stability of pentamethylcyclopentadienyl complexes when compared to their unsubstituted analogues,[3] and the ability of early transition-metal hydride complexes containing this ligand to reduce carbon monoxide,[4,5] we undertook the synthesis of alkyl and hydride derivatives of permethylvanadocene. We report here the synthesis of methyl and hydride derivatives and their reactions with carbon monoxide.

An alternate synthesis of permethylvanadocene, its reaction chemistry with carbon monoxide and alkyl isocyanides, and its oxidation to cyano-, halo-, and thiolatovanadium(III) complexes have recently been reported.[6] Reactions with elemental sulfur to yield a persulfido complex[7] and with phenyl azide to yield a phenylimido complex[8] have also been reported.

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF) was predried over CaH_2. Pentane, hexane, THF, and toluene were purified by distillation from sodium–benzophenone ketyl and stored under nitrogen or argon. Toluene-d_8 was vacuum distilled from CaH_2 and stored in an inert-atmosphere glovebox. Solutions of HCl in toluene were prepared by bubbling gaseous HCl into dry, distilled toluene for 15–20 min and were standardized by adding an aliquot to 50 mL of water and titrating with standard base immediately before use. Decamethylvanadocene was prepared by the published procedure.[2] Solutions of methyllithium in diethyl ether were purchased from Aldrich Chemical Co. Other chemicals and gases were reagent grade and were used without further purification.

Air-sensitive solids were stored and manipulated in a Vacuum Atmospheres inert-atmosphere box equipped with a freezer. Air-sensitive solutions and dry, deoxygenated solvents were transferred through 18-gauge stainless-steel cannulae. All reactions were carried out in dry, deoxygenated solvents under an atmosphere of nitrogen using standard inert-atmosphere and Schlenk-tube techniques. Fischer-Porter bottles and attendant stainless-steel fittings were obtained from Fischer & Porter Co., Lab-crest Scientific Division, Warminster, PA.

Infrared spectra were obtained with a Perkin-Elmer Model 599B spectrophotometer as Nujol or halocarbon mulls and calibrated with polystyrene. Proton NMR spectra at 89.55 MHz were obtained with a JEOL FX90Q Fourier-transform spectrometer. Chemical shifts are reported in parts per million (δ) with reference to internal tetramethylsilane. Variable-temperature bulk magnetic susceptibility measurements were made on a PAR Model 155 vibrating sample magnetometer calibrated with $HgCo(SCN)_4$. Field strength was monitored with a rotating coil gaussmeter, and the temperature was measured with a calibrated GaAs diode. Mass spectra were obtained with an AEI MS 12 mass spectrometer equipped with a direct-inlet system using an ionization voltage of 70 eV. Selected ions with relative abundance greater than 1% are reported. Elemental analyses were performed by the microanalytical laboratory of the University of California, Berkeley, CA, and Spang Microanalytical Laboratory, Eagle Harbor, MI. Many of the compounds reported here are thermally sensitive. Correct elemental analyses were obtained on many of these 2–3 h after submitting them to the laboratory at Berkeley. Samples sent through the mail gave poor analyses.

Bis(pentamethylcyclopentadienyl)chlorovanadium(III). $(\eta^5\text{-}C_5Me_5)_2VCl$. A dark red solution of decamethylvanadocene (4.0 g, 12.4 mmol) in hexane (125 mL) was treated with HCl in toluene (42.0 mL of 0.32 M solution, 13.4 mmol, 8% excess). The color of the solution changed immediately to yellow-brown and then to dark blue over a period of 15 min. This solution was stirred at room temperature for an additional 2 h. The flask was sealed and placed in a freezer at −30 °C for 12 h and then moved to another at −70 °C for 6 h, causing large blue crystals to precipitate. The solvent was decanted from these crystals at low temperature via cannula, and then they were washed with hexane (20 mL) at −78 °C in a similar manner and dried under vacuum to yield 3.2 g (72%) of product. An analytical sample was obtained by sublimation (90° C/10^{-4} torr).

Anal. Calcd for $C_{20}H_{30}ClV$: C, 67.32; H, 8.47; Cl, 9.93. Found: C, 67.48; H, 8.24; Cl, 10.18.

Infrared: 2990 sh (m), 2950 sh (m), 2905 (s), 2860 sh (m), 2720 (w), 1503 sh (m), 1483 (m), 1455 sh (m), 1440 (m), 1425 sh (m), 1376 (s), 1158 (w), 1065 (w), 1020 (s), 950 (w), 800 (w), 738 sh (w), 721 (w), 621 (w) cm^{-1}.

Mass spectrum [*m*/*e* (relative abundance)]: 356 (100), M^+; 375 (22); 358 (34); 359 (7); 321 (91), M − Cl; 221 (47), M − C_5Me_5; 135 (93), $C_5Me_5^+$.

Bis(pentamethylcyclopentadienyl)methylvanadium(III). $(\eta^5\text{-}C_5Me_5)_2VCH_3$. A dark blue suspension of $(C_5Me_5)_2VCl$ (2.00 g, 5.60 mmol) in hexane (60 mL) was treated with methyllithium solution (4.00 mL of 1.55 M solution in diethyl ether, 6.20 mmol, 10% excess) added dropwise from a syringe. The solution was stirred at room temperature for 3 h, during which time the blue color faded and a white precipitate was deposited. This was removed by filtration, and the volume of the pale blue filtrate was reduced to 20 mL under vacuum. The flask was then refilled with nitrogen, sealed with a glass stopper, and placed in a freezer at −70 °C for 16 h. The large crystals that formed were separated by decanting the solvent at low temperature via cannula and dried under vacuum. This yielded 1.51 g (80%) of very air-sensitive black crystals. Purer samples for analysis and magnetic studies were obtained by recrystallization from pentane at −78 °C.

Anal. Calcd for $C_{21}H_{33}V$: C, 74.97; H, 9.89. Found: C, 75.06; H, 9.61.

Infrared: 2980 (m), 2900 (s), 2860 sh (m), 2720 (w), 1489 (m), 1436 (m), 1377 (s), 1159 (w), 1125 (w), 1066 (w), 1023 (s), 803 (w), 724 (w) cm^{-1}.

Mass spectra [*m*/*e* (relative abundance)]: 336 (1.6), M^+; 321 (100), M − CH_3.

Bis(pentamethylcyclopentadienyl)hydridovanadium(III). $(\eta^5\text{-}C_5Me_5)_2VH$. A solution of $(C_5Me_5)_2VCH_3$ (0.97 g, 2.88 mmol) in hexane (30 mL) in a 6-oz Fischer-Porter bottle was flushed with hydrogen by pressurizing to 200 psi and venting and was then maintained at 375 psi for 12 days. During this time the color changed from pale blue to green. The hydrogen was then vented, the solution was transferred to a Schlenk flask via cannula, and the flask was sealed with a glass stopper. The volume of the solution was then reduced to 20 mL under vacuum, and the flask was refilled with nitrogen and placed in the freezer at −70 °C. The crystals that formed were separated by decanting the solvent at low temperature via cannula and dried under vacuum to yield 0.82 g (88%) of dark green product. Samples for analysis and magnetic studies were recrystallized from pentane at −78 °C and were obtained as dark brown crystals.

Anal. Calcd for $C_{20}H_{31}V$: C, 74.51; H, 9.69. Found: C, 74.53; H, 9.69.

Infrared: 2719 (w), 1625 (s) (same in hexane solution), 1483 (m), 1432 (m), 1374 (s), 1062 (w), 1022 (s), 797 (w), 468 (m), 426 (w) cm^{-1}.

Mass spectrum [*m*/*e* (relative abundance)]: 323 (2.6); 322 (25); 321 (100), $(C_5Me_2)V^+$.

Bis(pentamethylcyclopentadienyl)deuteridovanadium(III). $(\eta^5\text{-}C_5Me_5)_2VD$. A solution of $(C_5Me_5)_2VH$ (0.35 g, 1.08 mmol) in hexane (10 mL) in a 6-oz Fischer-Porter bottle was stirred under 300 psi of D_2 for 24 h. The pressure was then vented, and the solution was transferred to a 25-mL Schlenk flask via cannula. The flask was then sealed with a glass stopper and placed in a freezer at −70 °C for 16 h. The crystals that formed were separated by decanting the solvent at low temperature and dried under vacuum to yield 0.28 g (80%) of black crystalline product.

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Infrared: the spectrum is the same as $(C_5Me_5)_2VH$ except the band at 1625 cm^{-1} (ν_{V-H}) is very weak and a new, strong band appears at 1177 cm^{-1} (ν_{V-D}).

Mass spectrum [m/e (relative abundance)]: 323 (<1); 322 (6.4); 321 (26), $(C_5Me_5)_2V^+$; 41 (100).

Bis(pentamethylcyclopentadienyl)acetylcarbonylvanadium(III). $(\eta^5\text{-}C_5Me_5)_2V(COCH_3)CO$. Carbon monoxide was bubbled into a solution of $(C_5Me_5)_2VCH_3$ (0.50 g, 1.49 mmol) in hexane (20 mL) through a needle for 15 min at room temperature. During this time, the color of the solution changed from blue to dark green. The flask was then sealed with a glass stopper and cooled to −70 °C for 16 h. The green crystals that formed were separated by decanting the solvent at low temperature via cannula and dried under vacuum to yield 0.35 g (60%) of dark green needles. This complex is thermally sensitive and decomposes, even when stored at −40 °C, in a few weeks. Analysis could not be obtained due to this instability.

^{1}H NMR (toluene-d_8): δ 1.53 (s, 30 H, $C_5(CH_3)_5$); 2.43 (s, 3 H, $-COCH_3$).

Infrared: 2720 (w), 1864 (s), 1849 (s), 1590 br (s) [1867 (s), 1596 (m) in hexane solution], 1379 (s), 1312 (m), 1259 (w), 1043 (m), 1023 (m), 878 (w), 860 (w), 722 (w) cm^{-1}.

Bis(pentamethylcyclopentadienyl)hydridocarbonylvanadium(III). $(\eta^5\text{-}C_5Me_5)_2V(H)CO$. Carbon monoxide was bubbled into a solution of $(C_5Me_5)_2VH$ (0.35 g, 1.08 mmol) in hexane (25 mL) for 10 min. During this time the initial dark brown color of the solution changed to light green. The flask was then sealed with a glass stopper, and the volume of the solution was reduced to 15 mL under vacuum. The flask was then refilled with nitrogen and placed in a freezer at −70 °C for 16 h. The green crystals that formed were separated by decanting the solvent at low temperature and dried under vacuum to yield 0.27 g (71%) of product.

^{1}H NMR (toluene-d_8): δ 1.69 (s, 30 H, $C_5(CH_3)_5$); −7.34 (br, s, 1 H, VH).

Infrared: (reacts with halocarbon oil) 2720 (w), 1860 (s), 1819 sh (m), 1690 (s) [1874 (s), 1681 (m) in hexane solution], 1375 (s), 1067 (w), 1023 (s), 797 (w), 721 (w), 697 (m), 612 (w), 542 (m) cm^{-1}.

Results and Discussion

Permethylvanadocene (1) is readily oxidized by 1 equiv of HCl in hydrocarbon solvents to the "bent" chlorovanadium(III) derivative 2. This reaction proceeds through a yellow-brown intermediate which is probably the vanadium(IV) dichloride, and this then reacts further with 1 to yield the dark blue vanadium(III) product. A similar course is followed when 1 is oxidized with half an equivalent of Br_2 to yield the vanadium(III) bromide complex. This has been shown to occur also in the oxidation of bis(ethyltetramethylcyclopentadienyl)vanadium(II).[9] Complex 2 has also been prepared by the oxidation of 1 with benzyl chloride.[6]

While complex 2 is quite air sensitive, both as the solid and in solution, it is thermally stable and can be purified on a large scale by vacuum sublimation.

The mass spectrum of 2 shows an intense molecular ion peak at m/e 356 with weaker peaks at m/e 357, 358, and 359 in the proper ratios for the isotope distributions of ^{35}Cl, ^{37}Cl, ^{12}C, and ^{13}C in the molecule. Magnetic susceptibility measurements on solid samples of 2 between 6 and 56 K yield a temperature-independent effective magnetic moment of 2.78 ± 0.10 μ_B for the molecule. This is consistent with its formulation as a high-spin, 16-electron complex of vanadium(III) with two unpaired electrons.

Alkylation of 2 with methyllithium in hexane or diethyl ether yields the methyl complex $(\eta^5\text{-}C_5Me_5)_2VCH_3$ (3). This complex is extremely soluble in hydrocarbon and ether solvents and is best purified by recrystallization from pentane at low temperature. It is also very air-sensitive, both as a solid and in solution, and the vanadium–carbon bond is thermally labile. Attempted vacuum sublimations of 3 at 70 °C yielded mixtures of 3 and 1. The mass spectrum of 3 shows a weak molecular ion peak at m/e 336 and the largest peak in the spectrum is m/e 321, which represents loss of the methyl group to give $(C_5Me_5)_2V^+$. Alkyl group loss is the dominant feature of the mass spectra of vanadocene alkyls also.[1g] Magnetic susceptibility data for solid samples of 3 indicate simple Curie behavior in the temperature range of 5–50 K and yield an effective moment of 2.77 ± 0.10 μ_B. This value is consistent with the formulation of 3 as a high-spin, 16-electron bent metallocene with two unpaired electrons.

In an attempt to prepare a hydride derivative of permethylvanadocene, 2 was treated with 1 equiv of lithium triethylborohydride in diethyl ether. The crude product of this reaction was examined by infrared spectroscopy, and it showed a new absorption at 1625 cm^{-1} that appeared to be a metal–hydrogen stretch. However, the major product of this reaction was permethylvanadocene. A clean synthesis of the hydride 4 was achieved by hydrogenolysis of the methyl complex 3 under moderate hydrogen pressure (17–25 atm). Although this reaction is very slow, it does produce 4 cleanly and in high yield. This hydride complex is very air sensitive and has been obtained from reaction mixtures in various colors including green, dark blue, and black. However, repeated low-temperature recrystallizations of these materials from pentane or hexane have always yielded dark brown crystals.

The infrared spectrum of 4 shows a strong absorption at 1625 cm^{-1} which is assigned to the V–H stretching frequency. The deuterium-substituted analogue is prepared by stirring a hexane solution of the hydride under D_2 (20 atm) at room temperature. After this treatment, the band at 1625 cm^{-1} essentially disappears and is replaced by a new, strong band at 1177 cm^{-1}. There is no evidence for deuterium incorporation into the ring methyl groups of this complex under these conditions, as has been observed when $(C_5Me_5)_2ZrH_2$ is treated with D_2.[10]

Magnetic susceptibility data on solid samples of 4 show that the Curie law is obeyed between 5 and 50 K and yield a magnetic moment of 2.81 ± 0.10 μ_B, indicating that this is also a high-spin, 16-electron complex.

The mass spectrum of 4 shows a strong peak at m/e 321 corresponding to $(C_5Me_5)_2V^+$ and weaker peaks at m/e 322 and 323 with the correct intensities for ions containing one and two ^{13}C atoms, respectively. These ions must be formed by loss of the hydride hydrogen atom for the molecular ion. This is supported by the fact that the mass spectrum of the deuteride is essentially identical with that of the hydride.

Complex 4 does not react with ethylene at pressures up to 17 atm.

In order to evaluate the ability of these alkyl and hydride derivatives of permethylvanadocene to reduce carbon monoxide, reactions of 3 and 4 with CO were examined. When methyl complex 3 in hexane solution is exposed to excess CO at 1 atm, a green, diamagnetic complex (5) forms immediately. The infrared spectrum of this complex shows a strong absorption due to a terminal carbonyl ligand at 1867 cm^{-1} and a weaker absorption at 1596 cm^{-1} which we assign to the C=O stretch of a new acetyl ligand. The formulation of this complex as an acetylcarbonylvanadium(III) derivative is also supported by the proton NMR spectrum which shows, in addition to the ring methyl peak at δ 1.53, a single peak at δ 2.43 which is

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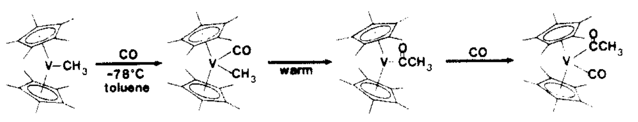

3

5

Figure 1. Reaction of methyl complex **3** with carbon monoxide.

assigned to the protons of the acetyl methyl group.

When complex **3** is treated with approximately 1 equiv of carbon monoxide at low temperature in an NMR tube, another diamagnetic complex is produced in addition to a small amount of **5**. This new complex also has a resonance in the proton NMR spectrum at δ 1.53 due to the ring methyl protons and a new peak at δ 0.26 which appears to be due to a methyl group on vanadium. When this sample is treated with more carbon monoxide, it is converted cleanly to **5**.

When complex **3** is titrated with carbon monoxide at room temperature and monitored by infrared spectroscopy, a slightly different result is obtained. After addition of 0.5 equiv of CO, the infrared spectrum shows a large absorption at 1596 cm^{-1} attributed to an acyl stretch and a very weak absorption at 1867 cm^{-1}. Addition of another 0.5 equiv aliquot of CO causes both of these bands to gain intensity. Addition of more CO increases the intensity of the band at 1867 cm^{-1}.

When this experiment is repeated and monitored by NMR, no signals are observed until 1 equiv of CO has been added and then only the signals due to acetyl carbonyl complex **5** are seen. These data can be reconciled as shown in Figure 1. Addition of CO to the methyl complex forms the methyl carbonyl complex which can be trapped and observed at low temperature. At room temperature, rapid CO insertion takes place to give an acetyl complex. This acetyl complex is paramagnetic, and so it is NMR silent and its acyl stretch occurs at 1596 cm^{-1}. Addition of more CO traps the acetyl complex as the diamagnetic acetyl carbonyl.

When the hydride complex **4** is exposed to carbon monoxide at 1 atm, a green, diamagnetic complex forms immediately. This complex is formulated as the simple carbonyl addition product bis(pentamethylcyclopentadienyl)vanadium carbonyl hydride **6**. The infrared spectrum of **6** shows a strong, terminal CO stretch at 1874 cm^{-1} and a medium-intensity metal–hydride stretch at 1681 cm^{-1}. The analogous complex prepared from **4**-d_1 and CO shows no absorption at 1681 cm^{-1} and a new band at 1221 cm^{-1}, confirming this assignment. The proton NMR spectrum shows a sharp resonance at δ 1.69 due to the ring methyl protons and a broad resonance at δ −7.34 due to the hydride ligand. The high-field chemical shift of this hydride resonance is in the same region as the hydride resonances of $Cp_2M(H)CO$ (M = Nb, δ −6.39; M = Ta, δ −6.80)[11] and is markedly different from the low-field shifts observed for the bis(pentamethylcyclopentadienyl)metal dihydrides of group 4[12] which reduce carbon monoxide.[4] No further reaction of **6** with CO is observed at pressures up to 25 atm.

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Registry No. 1, 74507-60-1; 2, 89710-27-0; 3, 96427-57-5; 4, 96427-58-6; 4-*d*, 96427-59-7; 5, 96427-60-0; 6, 96427-61-1; (η^5-$C_5Me_5)_2V(Me)CO$, 96427-62-2; (η^5-$C_5Me_5)_2V(COCH_3)$, 96427-63-3; CO, 630-08-0.

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Oxidation of Olefins by Palladium(II). 10.[1] Products of the Reaction of $PdCl_4^{2-}$ with Allyl Alcohol in Aqueous Solution

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The reaction of allyl alcohol **7** with aqueous $PdCl_4^{2-}$ gave β-hydroxypropanal, hydroxyacetone, acrolein, propanal, propene, and traces of acetone as products. By deuterium isotope distribution studies using $CH_2{=}CHCD_2OH$ and $CD_2{=}CHCH_2OH$ as substrates, it could be shown that β-hydroxypropanal and hydroxyacetone were formed by the hydroxypalladation–hydride shift mechanism found for other acyclic olefins while acrolein was formed by a direct hydride extraction from the alcohol carbon. Propanal is formed in a secondary reaction by reduction of the acrolein while propene is formed by decomposition of intermediate (π-allyl)palladium(II) species. The acetone probably results from oxidation of the propene by $PdCl_4^{2-}$. The isotope effect, k_H/k_D, for hydride shift in the formation of β-hydroxypropanal is 1.9. This value is in close agreement with earlier results using ethene-*1,2*-d_2.

Introduction

Allyl alcohol is a rather unique substrate in palladium(II) catalysis because both the olefin and alcohol functional groupings can participate in the reaction. It has been reported that allyl alcohol reacts with palladous chloride either without solvent or in 50% aqueous acetic acid solution to give, in addition to hydrofurfuryl alcohol derivatives obtained from addition of hydroxyl of one allyl alcohol to the double bond of another, propene, acrolein, propanal, and (π-allyl)palladium chloride plus other minor products.[3]

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(1) Part 9: Winstein, S.; McCaskie, J.; Lee, H.-B.; Henry, P. M. *J. Am. Chem. Soc.* 1976, *98*, 6913.

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