Contribution No. 2274 from the Central Research and Development Department,
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Preparation and Reactions of Triethylphosphine Complexes of Zerovalent Nickel, Palladium, and Platinum[1]

R. A. SCHUNN

Received June 23, 1975 AIC50441L

The triethylphosphine (L) complexes, PdL_4 and PtL_4, were prepared in high yield by reaction of the metal dichlorides, triethylphosphine, and potassium metal in tetrahydrofuran. The palladium complex was also obtained by thermal decomposition of $Pd(CH_3)_2L_2$ in excess triethylphosphine. Vacuum thermolysis of NiL_4 and PdL_4 gave NiL_3 and PdL_3, respectively. Protonation of ML_4 by ethanol gave HML_3^+ complexes which were isolated as the tetraphenylborate salts. The nickel hydride salts $[HNiL'_4][B(C_6H_5)_4]$ ($L' = P(CH_3)_3$ and $P(CH_3)_2(C_6H_5)$) were prepared from bis(1,5-cyclooctadiene)nickel(0), L', and $NaB(C_6H_5)_4$ in ethanol. PdL_3 reacted with C_6H_5CN to give $Pd(CN)(C_6H_5)L_2$ and with CH_3I to give $PdI(CH_3)L_2$; PdL_4 reacted with C_6H_5Br to give $PdBr(C_6H_5)L_2$.

Introduction

The triethylphosphine (L) complexes NiL_4,[2] PtL_4,[3,4] and PtL_3[3,4] are highly reactive, strong nucleophiles that undergo a variety of interesting and unusual reactions.[2,3,5-8] The purpose of the work described in this paper was to complete the above series of complexes by the synthesis of NiL_3, PdL_4, and PdL_3. Subsequent to the completion of this work, the synthesis of PdL_4 from bis(2-methallylpalladium chloride) and the phosphine in methanol was reported[9] along with its conversion to PdL_3. The PdL_4 complex has also been prepared in situ from $Pd(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)$ and the phosphine.[10] The complex PtL_4 was initially prepared from $Pt(B_3H_7)L_2$ and triethylphosphine[3,4] but a convenient preparation from K_2PtCl_4, triethylphosphine, and potassium hydroxide was recently described.[8] The NiL_4 complex was readily obtained from the reaction of bis(1,5-cyclooctadiene)nickel(0) with triethylphosphine[2] or, in lower yield, from the reduction of $NiBr_2L_2$ with sodium in *n*-heptane.[11]

In this paper, additional preparative routes to PdL_4 and PtL_4 and the conversion of NiL_4 and PdL_4 to NiL_3 and PdL_3, respectively, are described. Protonation of the zerovalent complexes to give cationic hydride complexes and reactions of PdL_4 and PdL_3 with some organic substrates are also described.

Experimental Section

Caution! Potassium metal reacts explosively with water and the lower alcohols. Insoluble residues from reactions using potassium metal are pyrophoric and should be disposed of by incineration or by careful treatment of a toluene or tetrahydrofuran suspension with n-butyl alcohol in a nitrogen atmosphere.

All experimental procedures including isolation and purification were performed either under vacuum or in an inert atmosphere of dry nitrogen or argon using conventional bench-top or glovebox techniques.[12] Low-temperature, bench-top filtrations were performed using an apparatus previously described.[13] Tetrahydrofuran was distilled from $LiAlH_4$. Other solvents were dried over 4A molecular sieves. All solvents were purged with nitrogen or argon.

Infrared spectra were recorded on a Perkin-Elmer 237 Grating Infracord spectrometer. ^1H NMR spectra were recorded on a Varian HR-220 or A-60 spectrometer. Phosphorus-31 NMR spectra were recorded on a Bruker HFX-90 (36.4 MHz) spectrometer.

Preparation of $Pd[P(C_2H_5)_3]_4$ from $Pd(CH_3)_2[P(C_2H_5)_3]_2$. The entire procedure was performed in a dry, nitrogen atmosphere. A 300-ml round-bottom flask, equipped with a magnetic stirring bar and a condenser topped with a vacuum line adapter with stopcock, was charged in a nitrogen-filled drybox with 20.0 g (0.054 mol) of $Pd(CH_3)_2[P(C_2H_5)_3]_2$[14] and 20.0 g (0.169 mol) of triethylphosphine. The flask was connected to two U-traps (in series) which were filled with dry nitrogen and cooled in liquid nitrogen; the second U-trap was connected through a tee to a source of dry nitrogen and a mineral oil bubbler. The reaction mixture was heated at 115° for a total of 40 hr during which it became bright yellow. The mixture was cooled in dry ice–acetone and the system was evacuated. All volatile products collected in the U-traps were combined and the gases which were not condensable at −78° were collected to give 0.051 mol (95%) of gas which was shown by mass spectroscopic analysis to be 99.5% C_2H_6.

The yellow reaction mixture was dissolved in ca. 175 ml of *n*-pentane and the filtered extract (no insolubles) was stored at −78° for 4 hr. The off-white, crystalline solid was collected at −78°, washed with several portions of cold *n*-pentane, and dried for 2 hr at −35° (0.1 μ) to give 28.4 g (91%) of $Pd[P(C_2H_5)_3]_4$: mp ca. 0°; ^1H NMR (C_6D_6, external $Si(CH_3)_4$) δ −0.8 (m, C_2H_5); ^{31}P NMR (toluene, external H_3PO_4, 25°) δ 1.98 (s). Anal. Calcd for $C_{24}H_{60}P_4Pd$: C, 49.8; H, 10.4; P, 21.4; Pd, 18.4; mol wt, 579. Found: C, 49.9; H, 10.5; P, 20.9; Pd, 18.6; mol wt (cryoscopically in C_6H_6), 297.

The compound is a yellow, pyrophoric liquid at room temperature which is very soluble in pentane, diethyl ether, and benzene and reacts with alcohols and chlorinated hydrocarbons. The molecular weight is consistent with dissociation in solution to $Pd[P(C_2H_5)_3]_3$ and triethylphosphine.

Preparation of $Pd[P(C_2H_5)_3]_4$ from $PdCl_2$. The entire procedure was performed in a dry, nitrogen atmosphere. A 1-l., three-necked flask, equipped with a magnetic stirrer, an addition funnel, and a condenser topped with a nitrogen inlet, was charged with 8.87 g (0.050 mol) of $PdCl_2$ and 300 ml of anhydrous tetrahydrofuran. A solution of 35.4 g (0.30 mol) of triethylphosphine in 25 ml of tetrahydrofuran was added over a 10-min period. An exothermic reaction occurred and the yellow solution was refluxed briefly and cooled to room temperature. A total of 7.8 g (0.20 g-atom) of potassium was added in three portions (cut into small pieces in a nitrogen box) and the mixture was refluxed with rapid stirring for ca. 2 hr during which the color changed from yellow to green and then brown. The solvent was removed under vacuum and the residue was extracted with 400 ml of *n*-pentane. The extract was concentrated to ca. 150 ml, and 6 ml of triethylphosphine was added. After cooling to −78° for 2 hr, a yellow, crystalline solid formed and was collected at −78°, washed with cold pentane, and dried at −30° (0.1 μ) for 2 hr to give 24.9 g of $Pd[P(C_2H_5)_3]_4$. An additional 1.4 g was obtained from the filtrate for a total yield of 26.3 g (91%). The complex was identical with that described above.

The Pd(0) complex may also be prepared by the reaction of $PdBr_2[P(C_2H_5)_3]_2$, triethylphosphine, and potassium in tetrahydrofuran.

Preparation of $Pt[P(C_2H_5)_3]_4$ from *cis*-$PtCl_2[P(C_2H_5)_3]_2$. The entire procedure was performed in a dry nitrogen atmosphere. A 1-l., three-necked flask was equipped with a magnetic stirring bar and a condenser attached to a source of dry nitrogen. The flask was filled with nitrogen and charged with 6.3 g (0.16 g-atom) of freshly cut potassium metal and 300 ml of anhydrous tetrahydrofuran and the mixture was refluxed with rapid stirring to disperse the potassium. After cooling to room temperature, 20.1 g (0.04 mol) of *cis*-$PtCl_2[P(C_2H_5)_3]_2$[15] and a solution of 18.9 g (0.16 mol) of triethylphosphine in 50 ml of tetrahydrofuran were added in rapid succession. The mixture was stirred at room temperature for 0.5 hr and refluxed for 2 hr to give a dark orange solution and a dark solid. After cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with a total of 300 ml of *n*-pentane in a nitrogen-filled drybox. The filtered, orange extract was treated with 2.36 g (0.02 mol) of triethylphosphine and cooled to −78° for 4 hr. The resulting white, crystalline solid was collected at −78°, washed with four, 20-ml portions of cold *n*-pentane, and dried for 1 hr at −35° (0.2 μ) to give 23.4 g (88%) of $Pt[P(C_2H_5)_3]_4$, mp 37–44°. Anal. Calcd for $C_{24}H_{60}P_4Pt$: C, 43.2; H, 9.1; P, 18.6; Pt, 29.2. Found: C, 43.1; H, 9.1; P, 17.8; Pt, 29.9.

Preparation of $Pt[P(C_2H_5)_3]_4$ from $PtCl_2$. The entire procedure was performed in a dry, nitrogen atmosphere. A 1-l. three-necked flask was equipped with a mechanical stirrer, a condenser topped with a nitrogen inlet, and an addition funnel. The flask was charged with 13.3 g (0.05 mol) of $PtCl_2$ and 300 ml of anhydrous tetrahydrofuran. A solution of 35.4 g (0.03 mol) of triethylphosphine in 30 ml of tetrahydrofuran was added over several minutes and the mixture was refluxed for 15 min. The clear, light yellow solution was cooled to 25° and 7.82 g (0.2 g-atom) of potassium metal (cut into small pieces) was added to the flask by removing the addition funnel. The mixture was slowly warmed to reflux; as the potassium melted, the heat was removed and the exothermic reaction was controlled with a cold bath. The mixture was refluxed for ca. 1.5 hr to give a black mixture and, after cooling, the solvent was removed under vacuum. The dark residue was extracted with ca. 300 ml of *n*-pentane in a nitrogen box. The orange extract was treated with 2.36 g (0.02 mol) of triethylphosphine and was cooled to −78° for 3–4 hr. The resulting white, crystalline solid was collected at −78°, washed with cold *n*-pentane, and dried at −25° (0.1 μ) for 1 hr to give 25.5 g (76%) of $Pt[P(C_2H_5)_3]_4$. The product was identical with that described above.

Preparation of $Ni[P(C_2H_5)_3]_4$ from Bis(1,5-cyclooctadiene)nickel(0). The procedure is similar to that previously described[2] except a larger scale is used.

In a nitrogen atmosphere, a solution of 50.0 g (0.42 mol) of triethylphosphine in 50 ml of *n*-pentane was added to a yellow slurry of 24.5 g (0.09 mol) of bis(1,5-cyclooctadiene)nickel[13] in 200 ml of *n*-pentane. The mixture became deep purple and, after stirring for ca. 30 min, was filtered to remove traces of nickel metal. The filtrate was cooled to −78° and after ca. 1 hr the pale yellow crystalline solid was collected at −78°, washed with cold *n*-pentane, and dried at −10° under vacuum to give 45.1 g (95%) of $Ni[P(C_2H_5)_3]_4$. Drying at higher temperatures results in slow loss of triethylphosphine. Anal. Calcd for $C_{24}H_{60}NiP_4$: C, 54.2; H, 11.4. Found: C, 54.3; H, 11.4. The product is a pale yellow, pyrophoric solid, mp ca. 40–45°, which gives deep purple or purple red solutions in ether, tetrahydrofuran, benzene, or pentane. It reacts with alcohols and chlorinated hydrocarbons.

Preparation of $Ni[P(C_2H_5)_3]_3$. A vacuum line flask was charged in a nitrogen box with 5.31 g (0.010 mol) of $Ni[P(C_2H_5)_3]_4$ and 50 g of copper shot. The flask was evacuated and heated in an oil bath at 46–47° (0.05 μ) for ca. 16 hr. The volatile materials were collected in a U-trap cooled in liquid nitrogen to give 1.16 g (98%) of triethylphosphine. The residual deep purple mass was extracted in an argon atmosphere with a total of 250 ml of *n*-pentane. The solvent was removed under vacuum, and the deep purple, waxy solid residue was dried at 25° (0.1 μ) for 16 hr and collected in an argon atmosphere to give 3.9 g (94%) of $Ni[P(C_2H_5)_3]_3$. Anal. Calcd for $C_{18}H_{45}NiP_3$: Ni, 14.2; P, 22.5; mol wt, 413. Found: Ni, 13.9; P, 21.1; mol wt, 412 (cryoscopically in C_6H_6, argon atmosphere).

The product is pyrophoric and is soluble in pentane, benzene, diethyl ether, and tetrahydrofuran; it reacts with ethanol and dichloromethane. The product also reacts with nitrogen to give a brown solid which exhibits an absorption assigned to $\nu_{N\equiv N}$ at 2075 cm^{-1} in the infrared spectrum.

Preparation of $Pd[P(C_2H_5)_3]_3$. The entire procedure was performed under vacuum or in a dry nitrogen atmosphere. A vacuum line flask was charged with 27.8 g (0.048 mol) of $Pd[P(C_2H_5)_3]_4$, evacuated, and heated at 70° (0.1 μ) for 2 hr. The volatile materials were collected in a trap cooled in liquid nitrogen and gave 5.6 g (97%) of triethylphosphine. The residue in the flask was pale-orange, liquid $Pd[P(C_2H_5)_3]_3$: 21.5 g (98%); ^1H NMR (C_6D_6, external ($Si(CH_3)_4$) δ −0.8 (m, C_2H_5); ^{31}P NMR (toluene, external H_3PO_4, 27°) δ 9.20 (s). Anal. Calcd for $C_{18}H_{45}P_3Pd$: C, 46.8; H, 9.9; P, 20.2; Pd, 23.1; mol wt, 460.9. Found: C, 47.1; H, 10.2; P, 19.2; Pd, 23.2; mol wt (cryoscopically in C_6H_6), 464.

The complex is a pyrophoric, orange liquid at 25°. It is very soluble in *n*-pentane, diethyl ether, benzene, and tetrahydrofuran and reacts with alcohols and chlorinated hydrocarbons. Concentrated solutions in *n*-pentane did not produce crystals after 4–6 hr at −78°.

Reaction of $Pd[P(C_2H_5)_3]_4$ with C_6H_5Br. The entire procedure was performed in a dry, nitrogen atmosphere. A solution of 1.7 g (0.0030 mol) of $Pd[P(C_2H_5)_3]_4$, 1.0 g (0.0064 mol) of bromobenzene, and 50 ml of *n*-hexane was refluxed for 3 hr and left at 25° for 16 hr. The solution was filtered free of a trace of insoluble solid and the colorless filtrate was stored at −78° for 3 hr. The white crystalline solid which formed was collected at −78°, washed with *n*-pentane, and dried for 1 hr at 25° (0.5 μ) to give 1.3 g (87%) of $PdBr(C_6H_5)[P(C_2H_5)_3]_2$: mp 96–98° (lit.[14] 89°); ^1H NMR (C_6D_6, external $(CH_3)_4Si$) δ −1.08, −1.65 (m, 30, C_2H_5), −7.28 (m, 5, C_6H_5). Anal. Calcd for $C_{18}H_{35}BrP_2Pd$: C, 43.3; H, 7.1. Found: C, 43.8; H, 7.4.

Reaction of $Pd[(C_2H_5)_3]_3$ with Benzonitrile. The entire procedure was performed in a dry, nitrogen atmosphere. A solution of 1.4 g (0.0030 mol) of $Pd[P(C_2H_5)_3]_3$ and 1.24 g (0.012 mol) of benzonitrile in 50 ml of toluene was refluxed for 1 hr to give a yellow solution. Toluene was removed under vacuum and the residual oil was washed with pentane to give 0.4 g of white solid. Pentane was vacuum evaporated from the filtrate and the residual yellow oil and the original white solid were combined and dissolved in *n*-hexane. The yellow hexane solution was cooled to −78° for 2 hr and the white crystalline solid was collected at −78°, washed with hexane, and dried for 1 hr at 25° (5 μ) to give 0.5 g (37%) of $Pd(CN)(C_6H_5)[P(C_2H_5)_3]_2$: mp 85–90°; ir (Nujol) 2140 (m) (ν_{CN}), 1580 (m) (C=C); ^1H NMR (C_6D_6, external $(CH_3)_4Si$) δ −0.33, −1.0 (m, 30, C_2H_5), −6.67 (m, 5, C_6H_5). Anal. Calcd for $C_{19}H_{35}NP_2Pd$: C, 51.2; H, 7.9; N, 3.1. Found: C, 51.4; H, 7.9; N, 3.4.

Vacuum evaporation of the yellow hexane filtrate gave a yellow oil which decomposed to platinum metal at 40° under vacuum.

Reaction of $Pd[P(C_2H_5)_3]_3$ with Allyl Bromide. The entire procedure was performed in a nitrogen-filled drybox. A solution of 1.4 g (0.0030 mol) of $Pd[P(C_2H_5)_3]_3$ in 50 ml of *n*-hexane was treated dropwise with 0.75 g (0.0062 mol) of allyl bromide. A white solid formed immediately and after stirring for 1 hr at 25° the solid was collected and dried briefly by suction (0.98 g). The filtrate was evaporated to dryness to give a white solid. The solids were combined and dissolved in ca. 50 ml of hot *n*-hexane. After 24 hr at 25° the white needle-like crystals were collected, washed with *n*-hexane, and dried for 2 hr at 25° (0.2 μ) to give 0.95 g (68%) of $PdBr(C_3H_5)[P(C_2H_5)_3]_2$, mp 67–69° dec. Anal. Calcd for $C_{15}H_{35}BrP_2Pd$: C, 38.9; H, 7.16; Br, 17.2; P, 13.4. Found: C, 39.1; H, 7.6; Br, 17.8; P, 13.6.

Reaction of $Pd[P(C_2H_5)_3]_3$ with Methyl Iodide. In a nitrogen-filled drybox, a solution of 1.38 g (0.0030 mol) of $Pd[P(C_2H_5)_3]_3$ and 2.05 g (0.0060 mol) of sodium tetraphenylborate in 50 ml of tetrahydrofuran was treated with 0.57 g (0.004 mol) of methyl iodide. The orange-yellow solution became yellow and a white precipitate formed. After stirring for 1 hr, the mixture was filtered, the filtrate was evaporated to dryness under vacuum, and the residual solid was washed with ethanol. The tetrahydrofuran and ethanol insoluble white solids had infrared spectra identical with that of authentic $[P(CH_3)(C_2H_5)_3][B(C_6H_5)_4]$ prepared from triethylphosphine, methyl iodide, and sodium tetraphenylborate in ethanol.

The ethanol soluble portion of the reaction product was evaporated to dryness under vacuum, the residue was extracted with 100 ml of *n*-pentane, and the filtered extract was cooled to −78° for 3 hr. A yellow crystalline solid formed. It was collected at −78°, washed with cold *n*-pentane, and dried at 25° (0.5 μ) for 2 hr to give 0.93 g (65%) of *trans*-$PdI(CH_3)[P(C_2H_5)_3]_2$: mp 63–65° to a yellow liquid; ir (Nujol) 1165 (m) cm^{-1} (δ CH_3); ^1H NMR (C_6D_6, external $Si(CH_3)_4$) δ −0.37 (t, $J = 6$ Hz, Pd–CH_3), −0.65 (quintet, $J = 9$ Hz, $PCH_2\mathit{CH_3}$), −1.5 (m, $P\mathit{CH_2}CH_3$). Anal. Calcd for $C_{13}H_{33}IP_2Pd$: C, 32.2; H, 6.9; I, 26.2. Found: C, 33.0; H, 7.0; I, 26.3. No evidence for the formation of $\{Pd(CH_3)[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$ was obtained.

Preparation of $\{PdCH_3[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$. In a nitrogen-filled glovebox, a yellow solution of 2.19 g (0.005 mol) of $PdBr(CH_3)[P(C_2H_5)_3]_2$[14] in 50 ml of absolute ethanol was treated with 1.18 g (0.01 mol) of triethylphosphine to give a colorless solution. Upon addition of a solution of 3.42 g (0.01 mol) of sodium tetraphenylborate in 25 ml of ethanol, a white crystalline precipitate formed and, after stirring for 15 min, the precipitate was collected and washed well with ethanol and diethyl ether. The crude product was extracted with ca. 50 ml of tetrahydrofuran, 200 ml of ethanol was added to the filtered extract, and the mixture was concentrated on a rotary evaporator to ca. 75 ml. The white, crystalline solid was collected, washed with ethanol, and dried at 25° (0.5 μ) for 1 hr to give 3.32 g (83%) of $\{Pd(CH_3)[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$: mp 110–111° dec; ^1H NMR (CD_2Cl_2, external $Si(CH_3)_4$) δ −0.06 (quartet, $J = 6$ Hz, Pd–CH_3), −1.6, 2.2 (m, PC_2H_5), −7.8 (m, B–C_6H_5). Anal. Calcd for

$C_{43}H_{68}BP_3Pd$: C, 65.0; H, 8.6; P, 11.7. Found: C, 64.6; H, 8.6; P, 12.6.

Preparation of $\{NiH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$ from $Ni[P(C_2H_5)_3]_4$. In a nitrogen-filled glovebox, a mixture of 6.39 g (0.012 mol) of $Ni[P(C_2H_5)_3]_4$, 8.1 g (0.024 mol) of sodium tetraphenylborate, and 100 ml of absolute ethanol was heated to ca. 50–55° and a solution of 0.010 mol of anhydrous hydrogen chloride in 25 ml of ethanol was added dropwise during ca. 15 min. The initial mixture of a purple solution and white solid became orange and upon cooling to 15° by evaporation a yellow, crystalline solid formed which was collected and washed with ethanol. The crude product was collected and dissolved in 100 ml of tetrahydrofuran. The filtered extract was mixed with 200 ml of ethanol, and the mixture was concentrated to ca. 150 ml on a rotary evaporator. An additional 200 ml of ethanol was added and the yellow crystalline solid was collected, washed with ethanol, and dried at 25° (0.1 μ) for 20 hr to give 6.95 g (79%) of $\{NiH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$: mp 85–88° (violet melt); ir (Nujol) 1956 cm^{-1} (ν_{NiH}); ^1H NMR $\{(CD_3)_2CO$, external $Si(CH_3)_4\}$ δ −7.0 (m, bd, $B-C_6H_5$), −1.0 (s, bd, C_2H_5), 14.58 (s, Ni–H). Anal. Calcd for $C_{42}H_{66}BNiP_3$: C, 68.8; H, 9.1; Ni, 8.0; P, 12.7. Found: C, 69.2; H, 9.2; Ni, 8.0; P, 12.8.

The complex is soluble in tetrahydrofuran, acetone, and acetonitrile and these solutions are decomposed by water; it is insoluble in ethanol, diethyl ether, and nonpolar organic solvents and appears to react with dichloromethane.

The nickel hydride salt is also obtained if the anhydrous hydrogen chloride is omitted but a lower yield is obtained. If the hydrogen chloride solution is added before the sodium tetraphenylborate, gas evolution occurs and a mixture of products is obtained. The complex was also obtained from $Ni[P(C_2H_5)_3]_4$ prepared in situ from bis(1,5-cyclooctadiene)nickel (see below). A solution of acetyl chloride in ethanol may be substituted for the anhydrous hydrogen chloride solution.

Preparation of $\{PdH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$ from $Pd[P(C_2H_5)_3]_3$. In a nitrogen-filled glovebox, a solution of 5.45 g (0.012 mol) of $Pd[P(C_2H_5)_3]_3$ and 100 ml of absolute ethanol was treated with 8.08 g (0.024 mol) of sodium tetraphenylborate. The solution became strongly basic and a white, crystalline solid formed. A solution of 0.012 mol of anhydrous hydrogen chloride in 25 ml of ethanol was then added dropwise over 10–15 min. More of the precipitate formed and the temperature rose slowly to 29°. After the addition was complete, the now neutral solution was stirred for 0.5 hr and filtered, and the product was washed with ethanol. The crude product was purified from tetrahydrofuran–ethanol as above for the nickel analogue to give 8.27 g (90%) of off-white crystalline $\{PdH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$: becomes pink at 80–87° and melts at 105° to a violet melt; ir (Nujol) 1966 (m) cm^{-1} (ν_{PdH}); ^1H NMR (CD_2Cl_2, external $Si(CH_3)_4$) δ 8.1 (d, $J_{H-P_{trans}} = 180$ Hz, Pd–H), −1.0, −1.6 (m, C_2H_5), −7.2 (m, C_6H_5). Anal. Calcd for $C_{42}H_{66}BP_3Pd$: C, 65.6; H, 8.5; P, 11.9. Found: C, 65.1; H, 8.7; P, 12.1.

The complex is soluble in tetrahydrofuran, acetonitrile, and dichloromethane and insoluble in diethyl ether and ethanol. It is moderately air stable as a solid but solutions slowly decompose, especially in the presence of water.

The hydride NMR resonance is consistent with square-planar geometry assuming $J_{H-P_{trans}} = 180$ Hz and $J_{H-P_{cis}} \approx 0$.

The complex is also obtained if hydrogen chloride is omitted but the yield is reduced to 69%; a solution of an equivalent amount of acetyl chloride in ethanol may be substituted for the anhydrous hydrogen chloride. $Pd[P(C_2H_5)_3]_4$ may be substituted for the tris complex with no reduction in yield.

In an attempt to prepare $\{PdH[P(C_6H_5)_3]_3\}[B(C_6H_5)_4]$ by a similar reaction using $Pd[P(C_6H_5)_3]_4$, no reaction occurred and the original Pd(0) complex was recovered.

Preparation of $\{PtH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$ from $Pt[P(C_2H_5)_3]_4$. In a nitrogen-filled glovebox, a yellow orange solution of 5.18 g (0.00786 mol) of $Pt[P(C_2H_5)_3]_4$ in 125 ml of ethanol was treated with a solution of 5.3 g (0.0165 mol) of sodium tetraphenylborate in 50 ml of ethanol. A white, crystalline precipitate formed immediately and, after stirring for 15 min, the product was collected and washed with ethanol. The crude product was dissolved in 50 ml of tetrahydrofuran and 200 ml of ethanol was added to the filtered extract. Concentration of the mixture to ca. 100 ml on a rotary evaporator and addition of 200 ml of ethanol gave a white, crystalline product which was collected and dried at 25° (0.1 μ) overnight to give 5.79 g (86%) of $\{PtH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$: mp 110–121°; ir 2163 (m) cm^{-1} (ν_{PtH}); ^1H NMR (CD_2Cl_2, internal $Si(CH_3)_4$, 60 MHz) δ 6.32 (d of multiplets, Pt–H), −1.0 (m, C_2H_5), −7.1 (m, C_6H_5). Anal. Calcd for $C_{42}H_{66}BP_3Pt$: C, 58.0; H, 7.6. Found: C, 58.1; H, 7.8.

The complex appears to be stable to air and moisture and is soluble in dichloromethane, acetonitrile, and tetrahydrofuran. The complex was previously obtained[16] by the reaction of $PtHCl[P(C_2H_5)_3]_2$ with $P(C_2H_5)_3$ and $NaB(C_6H_5)_4$.

At 220 MHz, the hydride NMR resonance (δ −6.22) is the expected doublet ($J = 16$ Hz) arising from the square-planar geometry of the cation and is comparable to that reported at 100 MHz.[16] The 60-MHz spectrum is more complicated and presumably arises from virtual coupling effects. All the hydride resonances show the expected satellites due to coupling of the hydride with ^{195}Pt ($J = {}^1/_2$).

Preparation of $\{NiH[P(CH_3)_3]_4\}[B(C_6H_5)_4]$ from Bis(1,5-cyclooctadiene)nickel. In a nitrogen-filled glovebox, a 250-ml Erlenmeyer flask was charged with 2.75 g (0.01 mol) of bis(1,5-cyclooctadiene)nickel and 100 ml of absolute ethanol. Upon the addition of 3.0 g (0.04 mol) of trimethylphosphine, the bright yellow slurry changed to a yellow solution and a pale-yellow, crystalline solid. After the addition of 4.0 g (0.0117 mol) of sodium tetraphenylborate, a solution of 0.8 g (0.01 mol) of acetyl chloride in 20 ml of ethanol was added dropwise. A new, bright-yellow, crystalline solid formed immediately and, after stirring the mixture for 0.5 hr, it was collected and washed well with ethanol. The crude product was extracted with 100 ml of tetrahydrofuran, 200 ml of ethanol was added to the filtered extract, and the mixture was concentrated to ca. 100 ml on a rotary evaporator. An additional 200 ml of ethanol was added and the yellow crystalline solid was collected, washed with ethanol, and dried for 6 hr at 25° (0.01 μ) to give 5.7 g (83%) of $\{NiH[P(CH_3)_3]_4\}[B(C_6H_5)_4]$: ir (Nujol) 1980 cm^{-1} (ν_{NiH}); ^1H NMR (acetone-d_6, internal $Si(CH_3)_4$, 220 MHz, 22°) δ 17.6, (s, bd, Ni–H). Anal. Calcd for $C_{36}H_{57}BNiP_4$: C, 63.3; H, 8.4; Ni, 8.6; P, 18.1. Found: C, 62.6; H, 8.3; Ni, 8.7; P, 17.8.

The product is an air-sensitive solid which is soluble in tetrahydrofuran and acetone; the solutions are decomposed by water.

Preparation of $\{NiH[P(CH_3)_2C_6H_5]_4\}[B(C_6H_5)_4]$ from Bis(1,5-cyclooctadiene)nickel. The procedure was similar to that described for the trimethylphosphine complex using 5.6 g (0.04 mol) of $P(CH_3)_2(C_6H_5)$ in place of the trimethylphosphine. The crude product was purified from tetrahydrofuran–ethanol to give 7.62 g (82%) of orange-red, crystalline $\{NiH[P(CH_3)_2(C_6H_5)]_4\}[B(C_6H_5)_4]$: ir (Nujol) 1955 cm^{-1} (ν_{NiH}); ^1H NMR (acetone-d_6, internal $Si(CH_3)_4$) δ 17.29 (s, bd, Ni–H). Anal. Calcd for $C_{56}H_{65}BNiP_4$: C, 72.2; H, 7.0; Ni, 6.3; P, 13.3. Found: C, 71.8; H, 7.1; Ni, 6.4; P, 13.5.

Preparation of $\{NiH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$ from Bis(1,5-cyclooctadiene)nickel. The procedure was similar to that described for the trimethylphosphine complex using 4.7 g (0.04 mol) of triethylphosphine instead of trimethylphosphine. The crude product was purified from tetrahydrofuran–ethanol to give 3.5 g (48%, due to mechanical losses) of $\{NiH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$ which was identical with the product described above.

Similar reactions with tripropylphosphine, diethylphenylphosphine, and tributylphosphine gave products which appeared to be nickel hydride complexes but they could not be satisfactorily purified and characterized.

Results and Discussion

Preparation of Zerovalent Triethylphosphine Complexes. The complexes $Pd[P(C_2H_5)_3]_4$ and $Pt[P(C_2H_5)_3]_4$ were prepared in high yield by the reaction of potassium metal in tetrahydrofuran with the preisolated $MCl_2[P(C_2H_5)_3]_2$ complexes or, more conveniently, with a mixture of the anhydrous metal chloride and triethylphosphine. Although the nickel complex, $Ni[P(C_2H_5)_3]_4$, was obtained in a similar reduction of either $NiBr_2[P(C_2H_5)_3]_2$ or a mixture of $NiBr_2$ and triethylphosphine, the reaction was erratic and often produced $NiBr[P(C_2H_5)_3]_3$ as the major product.[17] Consequently, the nickel(0) complex was normally prepared from bis(cycloocta-1,5-diene)nickel(0) and triethylphosphine as previously described.[2] However, the nickel complex has been prepared by the reduction of $NiBr_2[P(C_2H_5)_3]_2$ with sodium sand in *n*-heptane in 48% yield.[11]

The palladium complex was also prepared by the thermal decomposition of a mixture of *cis*- and *trans*-$Pd(CH_3)_2[P$-

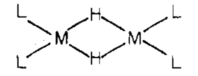
$(C_2H_5)_3]_2$ in triethylphosphine at 110°; ethane was the sole hydrocarbon product observed. No reaction occurred when *cis*-$Pt(CH_3)_2[P(C_2H_5)_3]_2$ and triethylphosphine were refluxed for 16 hr, or when they were heated in a sealed tube at 200° for 4 hr. When the mixture was heated to 250° for 8 hr, impure $Pt[P(C_2H_5)_3]_4$ was obtained; the volatile gases consisted of ca. 48% CH_4 and traces (<0.5% total) of C_3H_8, C_3H_6, C_4H_{10}, and C_4H_8. The formation of ethane from the palladium complex most likely occurs by an intramolecular reductive elimination mechanism as described for Pt(IV)[18] and Au(III)[19] methyl complexes. The decomposition of the platinum analogue at 250° may involve interaction of the ethyl groups of the triethylphosphine ligands as well.

Tris(triethylphosphine)nickel(0) was obtained as a waxy (sometimes semisolid), deep-purple, pyrophoric solid by careful vacuum thermolysis of $Ni[P(C_2H_5)_3]_4$. Cryoscopic molecular weight measurements in benzene solution in an argon atmosphere indicated that the complex is monomeric and not appreciably dissociated in solution. The complex reacts rapidly with nitrogen to give a brown, amorphous solid which exhibits an absorption at 2075 cm^{-1} in the infrared spectrum which is assigned to $\nu_{N\equiv N}$; the reaction is easily reversed under vacuum. The nitrogen complex is presumed to be $Ni(N_2)[P(C_2H_5)_3]_3$;[20] elemental analyses confirmed the Ni/P ratio but values for nitrogen were consistently low. When the pyrolysis of $Ni[P(C_2H_5)_3]_4$ was performed at 70°, more than 1 equiv of triethylphosphine was produced along with some ethane and ethylene. The residue was a soluble, pyrophoric, purple-brown oil which could not be satsifactorily characterized; interaction of the ethyl groups of the ligand with the metal undoubtedly occurred.[2]

Tris(triethylphosphine)palladium was obtained by vacuum thermolysis of $Pd[P(C_2H_5)_3]_4$ as a mobile, pale-orange, pyrophoric liquid. A similar preparation of the platinum analogue was previously reported.[3,4]

The palladium complexes, $Pd[P(C_2H_5)_3]_4$ and $Pd[P(C_2H_5)_3]_3$, are strong nucleophiles as observed with the nickel and platinum analogues. They reacted rapidly with benzonitrile and bromobenzene to give $PdCN(C_6H_5)[P(C_2H_5)_3]_2$ and $PdBr(C_6H_5)[P(C_2H_5)_3]_2$, respectively. The reaction of $Pd[P(C_2H_5)_3]_3$ with methyl iodide in the presence of sodium tetraphenylborate gave a modest yield of $PdI(CH_3)[P(C_2H_5)_3]_2$ rather than the expected $\{Pd(CH_3)[P(C_2H_5)_3]_3\}[B(C_2H_5)_4]$ salt. The latter complex was prepared by the reaction of $PdBr(CH_3)[P(C_2H_5)_3]_2$ with sodium tetraphenylborate and excess triethylphosphine in ethanol.

Metal hydride complexes were formed upon pressuring solutions of $Ni[P(C_2H_5)_3]_3$ and $Pd[P(C_2H_5)_3]_3$ with hydrogen in toluene solution to 150 psig at −63° in NMR tubes. New metal hydride resonances were observed at δ 11.86 ppm (quintet, J = 16 Hz) and δ 13.31 ppm (quartet, J = 13 Hz) for the nickel complex, and at δ 3.56 ppm (quintet, J = 32 Hz) for the palladium complex. It was previously reported[3] that hydrogen reacts with $Pt[P(C_2H_5)_3]_3$ to give $PtH_2[P(C_2H_5)_3]_3$ which was isolable but thermally unstable. No hydride complexes of nickel or palladium were isolable from the above solutions. At low temperatures, the hydride resonance of the platinum complex (δ 13.37 ppm) was a quartet (J = 13 Hz, with ^{195}Pt satellites) consistent with the five-coordinate complex, $PtH_2[P(C_2H_5)_3]_3$. The δ 13.31 ppm resonance observed for the nickel complex is also consistent with a five-coordinate species, $NiH_2[P(C_2H_5)_3]_3$. The quintet resonances observed for the nickel and palladium complexes imply splitting of the hydride resonance by four magnetically equivalent phosphorus nuclei but six-coordinate structures such as $MH_2[P(C_2H_5)_3]_4$ seem unlikely. A structure which would satisfy the observed spectrum is that of a hydrogen-bridged dimer.



$L = P(C_2H_5)_3$; M = Ni, Pd

Such a structure has been proposed for M = Ni, $L_2 = (C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$ (n = 2, 3, 4).[21] The hydride resonance for the complexes with m = 2 or 4 was also observed to be a quintet. Infrared evidence for the formation of a nickel hydride complex in the reaction of $Ni[P(C_2H_5)_3]_4$ and hydrogen at 1 atm has also recently been described.[2]

The zerovalent triethylphosphine complexes of nickel and palladium were readily protonated by ethanol to give four-coordinate cationic hydride complexes which were isolated as the tetraphenylborate salts, $\{MH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$ (M = Ni, Pd); a similar reaction was previously reported for the platinum analogue.[3] The yields of the nickel and palladium complexes were significantly improved by the careful addition of 1 equiv of anhydrous hydrogen chloride to the reaction mixture to neutralize the ethoxide ion formed in the reaction. The platinum analogue was also previously obtained from $PtH(Br)[P(C_2H_5)_3]_2$, triethylphosphine, and sodium tetraphenylborate.[16]

In the ^1H NMR spectra of the nickel hydride salt, the Ni–H resonance is temperature dependent; at room temperature only a single line is observed. The palladium analogue exhibits a doublet hydride resonance at room temperature ($J_{H-P_{cis}} \approx 0$) while the platinum resonance shows the expected pattern for a square-planar cation.[16] The hydride resonance in all three complexes is altered upon addition of free triethylphosphine. A detailed analysis of the inter- and intramolecular rearrangement processes involved is reported elsewhere.[22,23]

The nickel complex, $\{NiH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$, was also prepared by the reaction of bis(1,5-cyclooctadiene)nickel and excess triethylphosphine in ethanol, followed by the addition of sodium tetraphenylborate and anhydrous hydrogen chloride. Similar reactions using trimethylphosphine or dimethylphenylphosphine gave five-coordinate cationic nickel hydride complexes, $[NiHL'_4][B(C_6H_5)_4]$ ($L' = P(CH_3)_3$, $P(CH_3)_2(C_6H_5)$). At room temperature, the hydride resonances of these five-coordinate species were single lines indicating that a rapid inter- and/or intramolecular exchange process was occurring.

Acknowledgment. The author is indebted to Dr. Paul Meakin for obtaining the NMR spectra under hydrogen pressure, to Messrs. M. A. Cushing and E. R. Wonchoba for capable assistance in the preparation of some of the complexes, and to Dr. G. W. Parshall for many helpful discussions.

Registry No. $Pd(CH_3)_2[P(C_2H_5)_3]_2$, 29158-93-8; $P(C_2H_5)_3$, 554-70-1; $PdCl_2$, 7647-10-1; potassium, 7440-09-7; *cis*-$PtCl_2[P(C_2H_5)_3]_2$, 15692-07-6; $PtCl_2$, 10025-65-7; bis(1,5-cyclooctadiene)nickel(0), 1295-35-8; C_6H_5Br, 108-86-1; benzonitrile, 100-47-0; allyl bromide, 106-95-6; methyl iodide, 74-88-4; $PdBr(CH_3)[P(C_2H_5)_3]_2$, 29158-92-7; $Pt[P(C_2H_5)_3]_4$, 33937-26-7; $Ni[P(C_2H_5)_3]_4$, 51320-65-1; $Ni[P(C_2H_5)_3]_3$, 51340-83-1; $Pd[P(C_2H_5)_3]_3$, 52359-12-3; $PdBr(C_6H_5)[P(C_2H_5)_3]_2$, 57029-73-9; $Pd(CN)(C_6H_5)[P(C_2H_5)_3]_2$, 56960-34-0; $PdBr(C_3H_5)[P(C_2H_5)_3]_2$, 56960-35-1; *trans*-$PdI(CH_3)[P(C_2H_5)_3]_2$, 55500-72-6; $\{PdCH_3[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$, 56960-37-3; $\{NiH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$, 51404-95-6; $\{PdH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$, 51404-97-8; $\{PtH[P(C_2H_5)_3]_3\}[B(C_6H_5)_4]$, 22276-37-5; $\{NiH[P(CH_3)_3]_4\}[B(C_6H_5)_4]$, 56960-38-4; $\{NiH[P(CH_3)_2C_6H_5]_4\}[B(C_6H_5)_4]$, 56960-40-8; $Pd[P(C_2H_5)_3]_4$, 52230-29-2.

References and Notes

(1) This work was presented in part at the Sixth International Conference on Organometallic Chemistry, Amherst, Mass., August, 1973.

(2) C. S. Cundy, *J. Organomet. Chem.*, **69**, 305 (1974).

(3) D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 3543 (1971).

(4) L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 5665 (1972).

(5) G. W. Parshall, *J. Am. Chem. Soc.*, **96**, 2360 (1974).
(6) M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 179 (1975).
(7) M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 571 (1974).
(8) R. G. Pearson, W. Louw, and J. Rajaran, *Inorg. Chim. Acta*, **9**, 25 (1974).
(9) A. Musco, W. Kuran, A. Silvani, and M. W. Anker, *J. Chem. Soc., Chem. Commun.*, 938 (1973); W. Kuran and A. Musco, *Inorg. Chim. Acta*, **12**, 187 (1975).
(10) E. D. Dobrzynski and R. J. Angelici, *Inorg. Chem.*, **14**, 59 (1975).
(11) M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, **12**, 167 (1975).
(12) D. F. Shriver, "The Manipulation of Air-sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(13) R. A. Schunn, *Inorg. Synth.*, **15**, 5 (1972).
(14) G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).
(15) G. W. Parshall, *Inorg. Synth.*, **12**, 26 (1970).
(16) H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, **91**, 596 (1969).
(17) G. W. Parshall, private communication.
(18) M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 2457 (1974).
(19) A. Tamaki, S. A. Mangennis, and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 6487 (1973).
(20) C. A. Tolman, D. H. Gerlach, J. P. Jesson, and R. A. Schunn, *J. Organomet. Chem.*, **65**, C23 (1974).
(21) K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **9**, 312 (1970).
(22) P. Meakin, R. A. Schunn, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 277 (1974).
(23) P. Meakin, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, in press.

Contribution from the Department of Inorganic Chemistry,
The University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU

Ligand Site Preferences and Intramolecular Photochemical Rearrangements in Some Transition Metal Complexes. Simple Molecular Orbital Considerations

JEREMY K. BURDETT

Received April 29, 1975 AIC50296B

The angular overlap model is used to determine the relative stability of the following systems as a function of d orbital configuration; cis and trans octahedral MA_2B_4, isomers of MA_3B_3, axially and equatorially substituted square-pyramidal and trigonal-bipyramidal MAB_4, and square-planar MA_2B_4. The most stable isomer is determined in each case. These ligand site preferences as a function of d orbital occupation numbers are used to provide a ready explanation of some cis–trans photochemical isomerization processes in some d^6 and d^8 systems.

Introduction

Recently, we have shown that the angular overlap model of transition metal–ligand interaction is a very powerful tool with which to view the shapes of a variety of transition metal complexes as a function of d electron configuration and the number of coordinated orthaxial ligands.[1,2] We have also shown that it may be used to view relative bond strengths in some four-, five-, and six-coordinate complexes.[3] In particular, we have suggested that the so-called Jahn-Teller distortions of octahedral d^9 complexes and the square planar–octahedral isomerization of similar d^8 systems are probably two manifestations of the same effect within the d manifold of orbitals. We have also demonstrated[1] that simple Wolfsberg–Helmholz or extended Hückel molecular orbital calculations quite faithfully reproduce these minimum energy angular structures, and that simple plotting of d orbital energies as a function of distortion coordinate led to energy diagrams which could be used qualitatively to rationalize the observed molecular shapes. Hoffmann and coworkers using essentially the same computational method have recently arrived at similar conclusions.[4] In this paper we shall extend these angular overlap ideas to those situations, where the ligands coordinated to the central atom are not all identical, and inquire which of the positional ligand permutations gives rise to the most stable structure. While some of the arguments for specific systems will be qualitatively familiar we describe a quantitative unifying method with which to view these observations. We shall use these ideas to rationalize some cis–trans photochemical isomerization processes which occur in octahedral d^6 and square-planar d^8 complexes.

The Angular Overlap Method

We have previously shown[1,2] that the total orbital electronic stabilization energy due to d orbital–ligand σ interaction of a metal–ligand system is approximately given by the expression

$$\Sigma(\sigma) = \beta_\sigma \Sigma h_j S^2\,[\Gamma_j(\mathrm{M});\ \sigma(\Gamma_j)] \qquad (1)$$

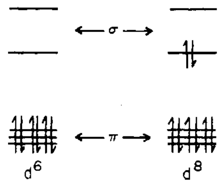
where h_j is the number of one-electron holes in the (predominantly d) metal ligand antibonding orbital of the jth representation. S is the overlap integral between the group of ligand σ orbitals transforming as Γ_j and the metal d orbital of the same symmetry species. β_σ is a parameter which measures the "strength" of the d orbital–ligand σ interaction. In the case of lower symmetry environments the following expression is simpler to handle

$$\Sigma(\sigma) = \sum_{\substack{\text{all d}\\ \text{orbitals}}} h_i \sum_{\substack{\text{all ligand}\\ \text{orbitals}}} S^2(\mathrm{X}_\sigma,\mathrm{d}_i)\beta_\sigma(\mathrm{X}) \qquad (2)$$

where we include the sum of the squared overlap integrals between the σ orbitals on each ligand X and the ith d orbital. The origin of these hole equations is readily seen in Figure 1 where the stabilization energy of the occupied bonding orbitals a, b, and c is canceled by occupation of their antibonding counterparts (a', b', c'). The total stabilization energy is given by $2D + 2E$, i.e., the destabilization energy times the number of holes in the unoccupied d orbitals. Similar equations to these hold when π interactions are considered. We will consider such interactions first since they are readily dismissed as being unimportant in determining site preferences of coordinated ligands in the geometries we have chosen to study.

π Bonding Effects within the d Orbital Manifold

In the spy and octahedral situation the lowest three d orbitals only are involved in π bonding and the highest two d orbitals exclusively in σ bonding. For the low-spin d^6 and d^8 configurations therefore all the d orbitals involved in π bonding are occupied. Thus, if the ligands are π donors then the total



π stabilization is zero ($\sum(\pi) = 0$) since the stabilization afforded by occupancy of the π bonding orbitals is completely