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Unanticipated Formation of Dibromo[1,2-bis(diphenylphosphino)ethane]nickel(II) by Sequential Michael Reversion and Michael Addition of Dibromobis(diphenylvinylphosphine)nickel(II)

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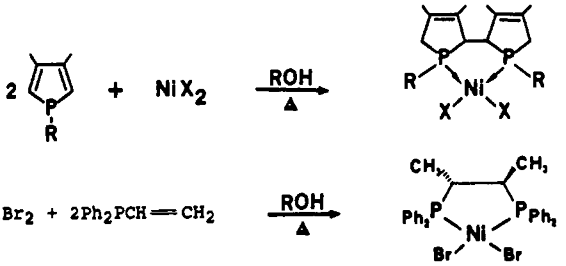
Thermolysis of dibromobis(diphenylvinylphosphine)nickel(II) in 1-butanol at 135 °C produces dibromo[1,2-bis(diphenylphosphino)ethane]nickel(II), Ni(dppe)Br_2, by sequential Michael reversion and addition reactions. Ni(dppe)Br_2 was characterized by elemental analyses, physical properties, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The crystal structure of Ni(dppe)Br_2·CH_2Cl_2 was determined from three-dimensional X-ray data collected by counter methods. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.150$ (3) Å, $b = 15.509$ (3) Å, $c = 15.532$ (3) Å, $\beta = 104.58$ (2)°, and $Z = 4$. The structure was refined by least-squares methods with $R(F) = 0.035$ for 2900 reflections with $I > 3\sigma(I)$. The Ni-Br (2.3205 (7) Å, 2.3360 (7) Å) and Ni-P (2.141 (1) Å, 2.156 (1) Å) distances are not equivalent. The molecule shows a slight tetrahedral distortion with the dihedral angle between the Br-Ni-Br and P-Ni-P planes being 4.01 ± 0.47°. The five-membered chelate ring is puckered with the two carbon atoms lying out of the coordination plane by 0.404 (5) Å and 0.391 (5) Å. The ligand, 1,2-bis(diphenylphosphino)ethane, was liberated by cyanide displacement and characterized by melting point, mass spectrometry, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

Nickel,[2-4] palladium,[5] platinum,[6] and especially rhodium,[7-10] complexes containing optically active (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane [(*S*,*S*)-chiraphos] have been widely used in catalysis. They catalyze asymmetric Grignard cross coupling,[2] nucleophilic substitution,[5] asymmetric hydroformylation of alkenes,[8] and asymmetric intramolecular cycloaddition reactions.[9] A major inconvenience in using (*S*,*S*)-chiraphos complexes lies in the synthesis of (*S*,*S*)-chiraphos itself. The best reported[10] yield is only 14%, and the synthesis is lengthy and tedious. Due to the great utility of this compound, a better synthesis would be welcome.

The formation[11,12] of Ni[(2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]X_2 by thermolysis of dihalobis(1-phenyl-3,4-dimethylphosphole)nickel(II) (reaction 1) suggested that thermolysis of $NiBr_2$ with diphenylvinylphosphine (Ph_2VyP) in alcohol might produce dibromo(chiraphos)nickel(II) according to reaction 2.



Experimental Section

(A) Reagents and Physical Measurements. All chemicals were of reagent grade and were used as received or synthesized as described below. Far-infrared spectra were recorded on a Perkin-Elmer 1800 FT infrared spectrometer as polyethylene pellets. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 and 75 MHz, respectively, on a General Electric GN-300 spectrometer, and the $^{31}P\{^1H\}$ NMR spectra, at 40.26 MHz on a JEOL FX-100 spectrometer, all as $CDCl_3$ solutions. Proton and carbon chemical shifts are relative to internal Me_4Si, while the phosphorus chemical shifts are relative to external Ph_3P ($\delta = -6$ ppm) and corrected to 85% H_3PO_4 with a positive value being downfield of the respective references. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Mass spectra were obtained at 70 eV on a Finnigan 4023 GC-MS instrument. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921.

Table I. Crystallographic Data for Ni(dppe)Br_2·CH_2Cl_2

chem formula:	space group: $P2_1/c$
$C_{27}H_{26}Cl_2Br_2NiP_2$	$\lambda = 1.5418$ Å
formula weight: 701.89	$\rho_{calcd} = 1.589$ g cm^{-3}
$a = 12.150$ (3) Å	$\mu = 73.173$ cm^{-1}
$b = 15.509$ (3) Å	abs min/max: 0.85/1.20
$c = 15.532$ (3) Å	$R(F) = 0.035$
$\beta = 104.58$ (2) °	$R_w(F) = 0.068$
$Z = 4$	GOF = 1.578
$T = -100$ °C	

(B) Synthesis. Ni(dppe)Br_2. To 2.31 g (10.6 mmol) of anhydrous $NiBr_2$ suspended in 35 mL of 1-butanol under N_2 was added 4.50 g (21.2 mmol) of diphenylvinylphosphine (Strem Chemicals). The resultant mixture was stirred magnetically at 135 °C for 2 h in a sealed thick-walled glass pressure vessel. The dark red solution was allowed to cool to room temperature. The brick red precipitate that formed was isolated by filtration and washed with anhydrous ethanol and diethyl ether. The complex was recrystallized from CH_2Cl_2/CH_3OH, isolated by filtration, and vacuum-dried overnight: yield 1.86 g (28.3%); dec pt 278 °C; IR (polyethylene) ν_{NiBr} 292, 260 cm^{-1} (lit.[13] 289.7, 266.1 cm^{-1} (^{58}Ni)); ^1H NMR ($CDCl_3$) δ 2.08 (d, $|^2J_{PH} + {}^3J_{PH}| = 17.6$ Hz, CH_2, 4 H), 7.2-8.3 (m, Ar H, 20 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.72 (t, "J_{PC}" = 45.9 Hz, CH_2), 129.21 (t, "J_{PC}" = 10.8 Hz, C_m), 129.52 (t, "J_{PC}" = 51.8 Hz, C_i), 132.13 (s, C_p), 134.20 (t, "J_{PC}" = 8.8 Hz, C_o), "J_{PC}" = $|^nJ_{PC} + {}^{n+2}J_{PC}|$; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 64.9 (s). Anal. Calcd for $C_{26}H_{24}Br_2NiP_2$·CH_2Cl_2: C, 50.63; H, 3.89; Br, 25.91; P, 10.04. Found: C, 50.85; H, 3.76; Br, 25.67; P, 9.95.

1,2-Bis(diphenylphosphino)ethane. Ni(dppe)Br_2 (0.75 g (1.21 mmol) was dissolved in approximately 200 mL of CH_2Cl_2, and the mixture was placed into a pressure-equalizing funnel. To this solution was added 125 mL of saturated aqueous NaCN. N_2 was bubbled vigorously through the mixture to promote mixing. After approximately 1 h the CH_2Cl_2 layer became colorless. It was separated from the pale yellow aqueous layer and filtered under N_2 into a Schlenk flask through a fritted column containing Celite and anhydrous $MgSO_4$. The solvent was removed by rotary evaporation, and the resulting colorless solid was recrystallized from hot absolute ethanol and vacuum-dried overnight: yield 0.35 g (72.6%); mp 142-144 °C (lit.[14] 140-142 °C); ^1H NMR ($CDCl_3$) δ 2.28

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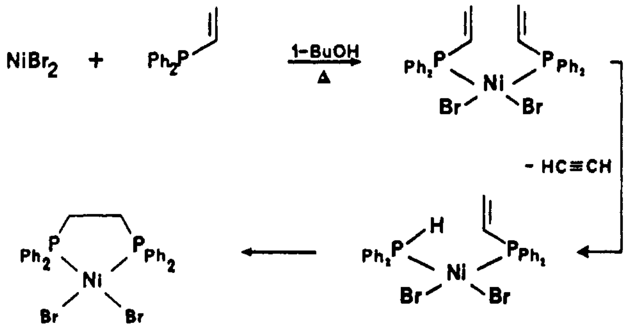
Table II. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^{2a}
Ni	0.21843 (6)	0.19920 (5)	0.37747 (4)	2.05 (2)	C11	0.3937 (5)	0.4378 (4)	0.2723 (4)	4.3 (1)
Br1	0.04158 (4)	0.14263 (3)	0.30799 (3)	3.15 (1)	C12	0.3610 (4)	0.3666 (3)	0.3140 (4)	3.6 (1)
Br2	0.31423 (4)	0.13647 (3)	0.28042 (3)	3.09 (1)	C13	0.0151 (4)	0.3304 (3)	0.4244 (3)	2.3 (1)
P1	0.37732 (9)	0.24989 (8)	0.45312 (8)	2.08 (2)	C14	0.0265 (4)	0.4138 (3)	0.3941 (3)	2.9 (1)
P2	0.14097 (9)	0.26595 (7)	0.46888 (8)	1.82 (2)	C15	−0.0681 (5)	0.4628 (4)	0.3575 (4)	4.1 (1)
CB	0.2434 (4)	0.3410 (3)	0.5352 (3)	2.4 (1)	C16	−0.1754 (4)	0.4293 (4)	0.3508 (4)	3.8 (1)
CA	0.3590 (4)	0.2951 (3)	0.5573 (3)	2.7 (1)	C17	−0.1868 (4)	0.3494 (4)	0.3811 (4)	4.0 (1)
C1	0.4976 (4)	0.1787 (3)	0.4861 (3)	2.7 (1)	C18	−0.0922 (4)	0.2993 (3)	0.4178 (4)	3.3 (1)
C2	0.5057 (6)	0.1237 (4)	0.5582 (5)	4.8 (2)	C19	0.1083 (4)	0.1909 (3)	0.5489 (3)	2.09 (9)
C3	0.5978 (6)	0.0702 (4)	0.5871 (5)	5.9 (2)	C20	0.0646 (4)	0.2193 (3)	0.6178 (3)	2.8 (1)
C4	0.6823 (6)	0.0695 (5)	0.5458 (6)	6.8 (2)	C21	0.0406 (4)	0.1636 (4)	0.6772 (3)	3.4 (1)
C5	0.6763 (5)	0.1209 (5)	0.4760 (6)	6.2 (2)	C22	0.0559 (5)	0.0762 (3)	0.6676 (4)	3.6 (1)
C6	0.5838 (5)	0.1770 (4)	0.4431 (4)	4.3 (1)	C23	0.0981 (5)	0.0468 (3)	0.5991 (3)	3.9 (1)
C7	0.4223 (4)	0.3412 (3)	0.3981 (3)	2.4 (1)	C24	0.1233 (4)	0.1041 (4)	0.5398 (4)	3.3 (1)
C8	0.5178 (4)	0.3880 (4)	0.4386 (4)	3.3 (1)	C25	0.2350 (6)	0.7121 (6)	0.3227 (6)	7.2 (2)
C9	0.5518 (4)	0.4596 (4)	0.3989 (4)	4.1 (1)	Cl1	0.2093 (2)	0.6249 (2)	0.3895 (2)	11.43 (9)
C10	0.4898 (5)	0.4834 (3)	0.3154 (4)	4.5 (1)	Cl2	0.3519 (2)	0.6913 (2)	0.2811 (2)	8.30 (6)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Scheme I



(t, $|^2J_{PH} + {}^3J_{PH}|$ = 8 Hz, CH_2, 4 H), 7.46 (s, Ar H, 20 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.82 (s, CH_2), 128.35 (t, "J_{PC}" = 8.8 Hz, C_m), 128.54 (s, C_p), 132.74 (t, "J_{PC}" = 18.6 Hz, C_o), 138.11 (t, "J_{PC}" = 12.7 Hz, C_i); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −13.2 (s) (lit.[15] δ −12.5); mass spectrum[16] (*m/e* (assignment, relative intensity)) 398 (M, 37), 370 (M − C_2H_4, 16), 321 (M − Ph, 2), 289 (M − PhPH, 44), 275 (M − $PhPCH_3$, 23), 262 (M − $PhPCH_2CH_2$, 37), 185 (Ph_2P^+, 53), 183 (PhP^+Ph, 100), 152 (Ph = Ph, 12), 108 ($PhP^{\bullet+}$, 29). Anal. Calcd for $C_{26}H_{24}P_2$: C, 78.42; H, 6.03. Found: C, 78.28; H, 6.15.

(C) Crystal Structure Analyses. Dary red crystals of $Ni(dppe)Br_2\cdot CH_2Cl_2$ were isolated from a CH_2Cl_2/CH_3OH solution. Crystal data and additional details of data collection are given in Table I. The structure was solved by Patterson and Fourier techniques. Hydrogen atoms were inserted at calculated positions (d(CH) = 0.95 Å) with isotropic temperature factors, $B(H) = 1.38B_{eqv}(C)$, but were not refined. Final refinement was by least-squares methods minimizing $\sum w(|F_o| - |F_c|)^2$, with $w(F^2) = (\sigma^2_{count} + (0.08F^2)^2)^{-1}$. For all computations the Enraf-Nonius SDP/VAX package was used.[17] Scattering factors were taken from reference 18. Final atom coordinates are given in Table II.

Results and Discussion

The formation[11,12] of Ni[(2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]X_2 by thermolysis of the phosphole and NiX_2 in alcoholic solvents suggested that $NiBr_2$ might promote formation of $Ni(chiraphos)Br_2$ by a similar reaction. Accordingly, $NiBr_2$ and diphenylvinylphosphine were heated for 2 h at 135 °C in 1-butanol. To our surprise, $Ni(dppe)Br_2$ was formed instead.

A mechanism by which this reaction might occur is outlined in Scheme I. The first step involves the formation of the $(Ph_2VyP)_2NiBr_2$ complex. This is followed by loss of acetylene via a reverse Michael reaction to form a secondary phosphine complex. Michael reactions are reversible processes[19] that can be promoted by base[20] and in some cases by elevated temperature.[21] In a similar system it has been shown[22,23] that direct addition of Ph_2PH to PhC≡CH produces a vinylphosphine. Given the fact that Michael reactions are reversible, it is not unreasonable to assume the reverse process taking place to produce an acetylene and a secondary phosphine. In the final step, an intramolecular Michael reaction between the coordinated Ph_2PH and $Ph_2PCH{=}CH_2$ groups produces $Ni(dppe)Br_2$. This latter reaction has precedent[24] in the palladium- and platinum-promoted intramolecular Michael additions of coordinated secondary phosphines to alkynylphosphines.

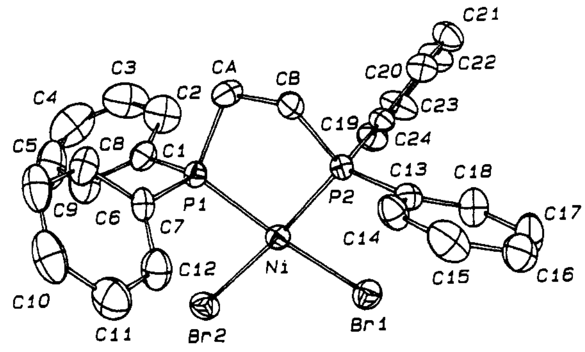


Figure 1. ORTEP plot of the structure of $Ni(dppe)Br_2$, showing the atom-labeling scheme (50% probability ellipsoids). Hydrogens are not shown.

As a final conformation of this reaction, an X-ray crystal structure of the product was obtained. As shown in Figure 1, $Ni(dppe)Br_2$ was indeed formed. This complex has the expected[25] tetrahedrally distorted square-planar structure with inequivalent Ni–Br (2.3205 (7), 2.3360 (7) Å) and Ni–P (2.141 (1), 2.156 (1) Å) bond distances. The dihedral angle between the Br–Ni–Br and P–Ni–P planes (4.01 ± 0.47°) is considerably less than the corresponding Cl–Ni–Cl/P–Ni–P dihedral angle[11] in Ni[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]Cl_2. This is because the chelate ring is rigid and nearly planar in the latter

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complex. For Ni(dppe)Br_2, the five-membered chelate ring is puckered with the two carbon atoms lying out of the coordination plane by 0.404 (5) and 0.391 (5) Å.

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Supplementary Material Available: Listings of X-ray experimental parameters, bond distances and angles, hydrogen coordinates, and thermal parameters (6 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Intramolecular [4 + 2] Diels-Alder Cycloaddition Reactions of Phospholes with Vinylphosphines Promoted by Palladium and Platinum

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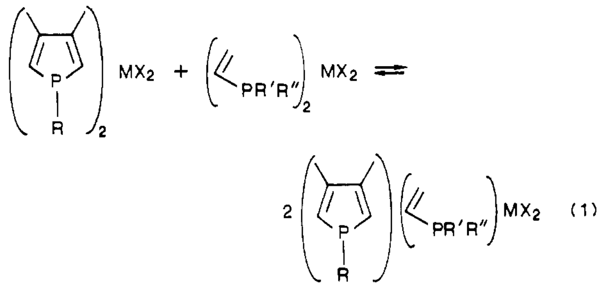
Reactions of (vinylphosphine)$_2$MX_2 complexes with (1-R-3,4-dimethylphosphole)$_2$MX_2 complexes (where vinylphosphine = Ph_2VyP, PhVy$_2$P, Et_2VyP; R = Ph, Bzl, *t*-Bu; X = Cl, Br, I; M = Pd, Pt) produce dihalo[2-(R',R''-phosphino)-5,6-dimethyl-7-R-7-phosphabicyclo[2.2.1]hept-5-ene]metal(II) complexes via an intramolecular Diels-Alder [4 + 2] cycloaddition. These reactions occur at ambient temperature with very high diastereoselectivity, providing a facile route to a new class of rigid chiral bidentate phosphines. These substituted 7-phosphanorbornene palladium and platinum complexes have been characterized by elemental analysis, physical properties, infrared spectroscopy, mass spectrometry, thermal analysis, and ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{1}H/^{13}C HETCOR, COSY, and 2-D *J* nuclear magnetic resonance spectroscopy. The structures of two palladium complexes have been confirmed by X-ray crystallography. Dichloro[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) crystallizes in the monoclinic space group $P2_1/c$ in a unit cell of dimensions a = 11.184 (4) Å, b = 10.972 (5) Å, c = 23.351 (8) Å, β = 103.17 (3)°, and ρ(calcd) = 1.58 g cm^{-3}, with Z = 4. Refinement converged to R = 0.060 with 1886 independent observed ($I/\sigma(I) \geq 3.0$) reflections. The donor abilities of the two phosphorus donors are not significantly different; the PdP distances are 2.213 (4) and 2.251 (4) Å, the CPC angle for the bridging phosphorus is small (82.5 (6)°), and the PdCl distances (2.344 (4), 2.351 (4) Å) are not significantly different. The chelate ring is rigid, and the molecule contains four asymmetric centers. Dichloro[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]palladium(II) crystallizes in the orthorhombic space group *Fdd*2 in a unit cell of dimensions a = 28.737 (5) Å, b = 32.979 (8) Å, c = 10.253 (2) Å, and ρ(calcd) = 1.44 g cm^{-3}, with Z = 16. Refinement converged to R = 0.036 with 2011 independent observed reflections. The donor abilities of the two phosphorus donors are not significantly different; the PdP distances are 2.224 (2) and 2.236 (2) Å, the CPC angle for the bridging phosphorus is small (82.3 (4)°), and the PdCl distances (2.356 (2), 2.366 (2) Å) are not significantly different. The chelate ring is rigid, and the molecule contains five asymmetric centers. Two of the ligands have been liberated from the complexes and converted to their respective disulfides with retention of stereochemical configuration. Thermal analyses (TG and DSC) show that the complexes and disulfides polymerize upon melting, probably by extrusion of phosphinidine. A mechanism for the [4 + 2] Diels-Alder cycloaddition is proposed.

Introduction

In the course of our studies of the coordination chemistry of phospholes[2,3] and their novel reactions,[4-9] we have investigated the redistribution reactions[10] of palladium and platinum phosphole complexes with palladium and platinum complexes of vinylphosphines (reaction 1). We observed that these mixed phosphole-vinylphosphine complexes undergo a very facile [4 + 2] Diels-Alder cycloaddition reaction[11] (reaction 2) to produce a new class of rigid chiral diphosphines and report the details of these novel reactions herein.



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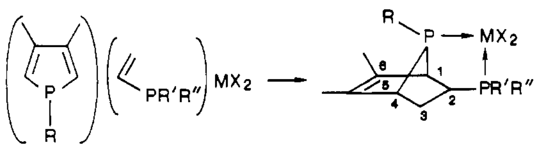

(2)

Experimental Section

(A) Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or sythesized as described below. Diphenylvinylphosphine, phenyldivinylphosphine, diethylvinylphosphine, and diallylphenylphosphine were obtained from Organometallics, Inc. The phospholes were prepared as previously described.[12] All reactions involving the phosphines were conducted under an N_2 atmosphere.

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