Reversible Oxidative Addition of Triphenylphosphine to Zero-Valent Nickel and Palladium Complexes[1]

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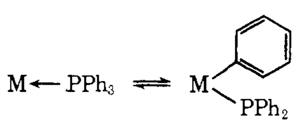
Received December 12, 1975

Abstract: Coordinatively unsaturated zero-valent nickel and palladium complexes can undergo a reversible oxidative–addition reaction with triphenylphosphine. Heating a hexane solution of $Ni(PEt_3)_3(PPh_3)$, **1**, which dissociates phosphine ligands in solution, results in the formation of biphenyl, PEt_3, and $Ni_2(\mu\text{-}PPh_2)_2(PEt_3)_3$, **2**. The products are assumed to be formed via the PPh_3 oxidative-addition product $Ni(C_6H_5)(PPh_2)(PEt_3)_2$, **3**. An attempted synthesis of **3** from *trans*-$NiBr(C_6H_5)(PEt_3)_2$ and $LiPPh_2{\cdot}OEt_2$ yielded **1**, **2**, and biphenyl. Compound **2** was independently synthesized by treating *trans*-$NiCl_2(PEt_3)_2$ with 2 equiv of $LiPPh_2{\cdot}OEt_2$, followed by reaction with 1 equiv of $Ni(PEt_3)_4$. The corresponding palladium chemistry is similar but is also subject to complicating side reactions. The reaction of $C_6F_5PPh_2$ with $Ni(PEt_3)_4$ was rapid and yielded **2** at room temperature. The reaction of $C_6F_5PPh_2$ with $Pd(PEt_3)_3$ yielded a mixture of products that included *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$. This compound was also synthesized from *trans*-$PdBr(C_6F_5)(PEt_3)_2$ and $LiPPh_2{\cdot}OEt_2$. Competitive PPh_3 oxidative addition in certain nickel- and palladium-promoted organic reactions can result in the formation of phenyl-containing by-products.

A complete understanding of all processes occurring in transition metal catalyzed organic reactions is yet to be realized. The important mechanistic steps leading from reactants to major products are quite well understood for many catalytic processes, while the steps leading to by-products often remain unrecognized. This latter chemistry is often related to catalyst decay and therefore cannot be ignored.

Zero-valent complexes of the nickel triad bearing triphenylphosphine ligands are effective catalysts for a myriad of organic transformations. We have observed that triphenylphosphine can undergo a reversible oxidative addition to zero-valent nickel and palladium complexes (eq 1), and that this reaction can eventually yield organic products and metal complexes in which the metal is in a different formal oxidation state.



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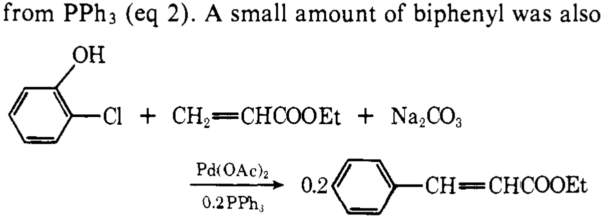
Results and Discussion

Occurrence in Metal-Promoted Organic Reactions. Several groups have described a palladium-catalyzed reaction of aryl halides with olefins that produces new olefins in which a vinylic hydrogen of the original olefin has been replaced by the aryl group of the halide.[2-4] While we were independently applying this concept to the synthesis of coumarin, several unexpected products were formed that could not be explained by conventional organometallic chemical processes. For example, when the synthesis of ethyl 2-hydroxycinnamate was attempted from 2-chlorophenol and ethyl acrylate using a $[Pd(PPh_3)_{0.2}]$ catalyst at 150°, ethyl cinnamate was produced quantitatively from PPh_3 (eq 2). A small amount of biphenyl was also observed, while the 2-chlorophenol was not consumed. Several similar examples have been reported by two other groups[5,6] for reactions of $[Pd(PPh_3)_2]$. The ethyl cinnamate formation is inhibited by excess PPh_3.[5]



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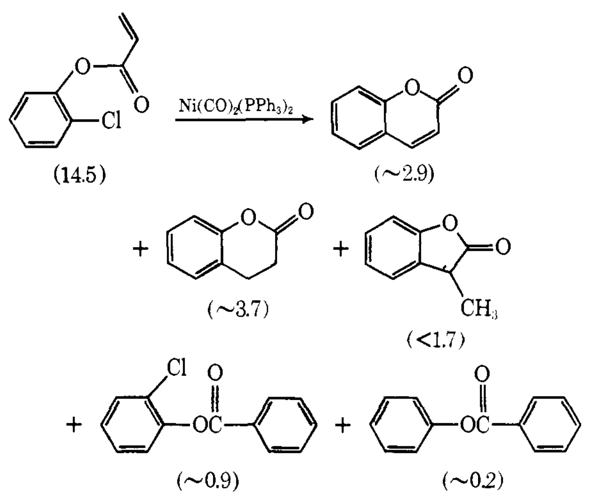
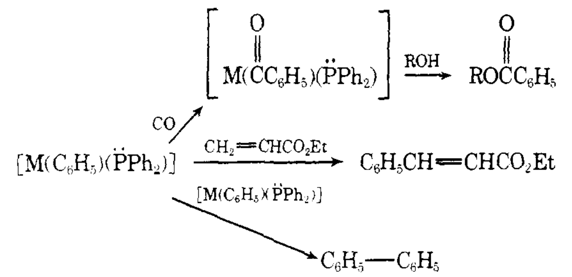
Related behavior appeared in some reactions with nickel complexes. After 2 h at 200°, the reaction of 2-chlorophenyl acrylate with a $Ni(CO)_2(PPh_3)_2$ catalyst yielded not only the normal products coumarin, 3,4-dihydrocoumarin, and 3-methyl-2(3*H*)-benzofuranone, but also small amounts of 2-chlorophenyl benzoate and phenyl benzoate (eq 3). The same reaction with $Ni(CO)_2(Ph_2PCH_2CH_2PPh_2)$ as catalyst produced only trace amounts of the normal products while 2-chlorophenyl benzoate and phenyl benzoate were formed in 7 and 4% yields, respectively. Very small amounts of biphenyl were detected among the products from these reactions. 2-Chlorophenol and phenol are released from 2-chlorophenyl acrylate during the reaction (small amounts of both have been detected by GLC analysis of the reaction mixture), and they account for the RO fragments of the benzoate esters. When these reactions were performed in the presence of excess PPh_3, the benzoate ester formation was completely inhibited.



(3)

In each of the above examples, the by-products (ethyl cinnamate, 2-chlorophenyl benzoate phenyl benzoate, and biphenyl) have incorporated a phenyl group from the triphenylphosphine. If a phenyl group migrates from phosphorus to the metal, then, through the well-established organometallic processes shown in eq 4, the mode of by-product formation can be understood. Phenyl migration is an integral component of the reversible PPh_3 oxidative–addition reaction depicted in eq 1.

Model Compound Studies. $Ni(PEt_3)_4$ is highly susceptible to oxidative-addition reactions with aryl halides[7,8] and thus was considered an attractive candidate with which to study



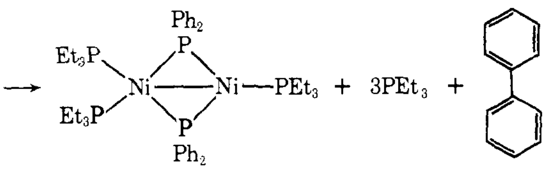
(4)

oxidative additions of PPh_3. When solutions of $Ni(PEt_3)_4$ are treated with 1 equiv of PPh_3, an orange-red $Ni(PEt_3)_3(PPh_3)$ complex, **1**, can be isolated in high yield. The complex undergoes reactions characteristic of phosphine complexed nickel(0) compounds; e.g., HCl treatment produces $NiCl_2(PEt_3)_2$, and reaction with certain organic halides yields normal oxidative-addition products. Benzene was not released during the HCl treatment, and the infrared C=C stretching bands of **1** are weak. These observations eliminate an alternative $Ni(C_6H_5)(PPh_2)(PEt_3)_3$ formulation (phenyl-nickel and -palladium complexes have medium intensity bands at 1560 cm^{-1} for C=C stretching vibrations[8,9]). In the ^1H NMR spectrum of **1**, no P-H coupling is observed as the ethyl proton resonances appear as a quartet (CH_2) and a triplet (CH_3). Absence of P-H coupling is consistent with phosphine dissociation in solution.

When heated, hydrocarbon solutions of **1** turn from orange-red to green as a result of the reaction shown in eq 5. After 8 h at 125° in hexane, $Ni_2(\mu\text{-}PPh_2)_2(PEt_3)_3$, PEt_3, and biphenyl were obtained in 77, 115, and 84% yields, respectively, based on the stoichiometry shown in the equation. After 5 h at 70–80° in hexane the yields were 46, 109, and 73%, respectively. Biphenyl and PEt_3 yields were determined by GLC, and the yield of $Ni_2(\mu\text{-}PPh_2)_2(PEt_3)_3$, **2**, is based on isolated material. The formulation of the dark green lustrous crystals of **2**[10] is based on C, H, and Ni analyses, spectroscopic and magnetic data, and on an independent synthesis described later in the report. The ir spectrum of **2** does not display a band at 1080 cm^{-1} characteristic of PPh_3 complexes, but does exhibit a medium-intensity C=C stretching vibration at 1580 cm^{-1} and other features characteristic of monosubstituted phenyl groups. The formal oxidation state of both nickel atoms in **2** is +1. However, the complex is diamagnetic and therefore must possess a strong nickel-nickel bond. Dissociation of PEt_3 ligands is suggested by the absence of fine structure for the PEt_3 proton resonances in the ^1H NMR spectrum of **2**. This is further confirmed by molecular weight determinations which gave values slightly less than half of theoretical for **2**. In a recent communication,[11] the crystal structure of $Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2\cdot C_6H_6$, obtained by thermolysis of $Pt(PPh_3)_4$, is described, and this complex also contains a strong metal-metal bond.

$2Ni(PEt_3)_3(PPh_3)$

1

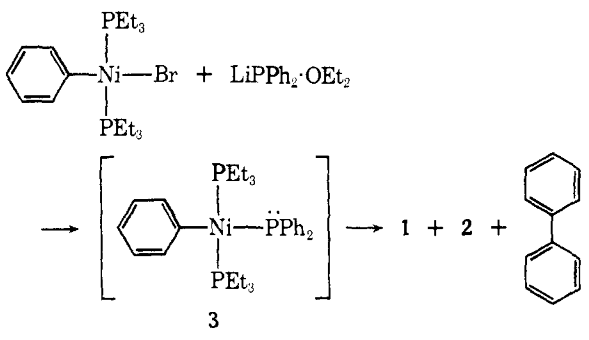


(5)

2

The analogous palladium chemistry is not as simple. Crystalline $Pd(PEt_3)_3(PPh_3)$ could not be prepared by treating $Pd(PEt_3)_3$ with PPh_3. Rapid ligand redistribution reactions occurred, and the most insoluble species precipitated. In this case, $Pd(PPh_3)_4$ along with other palladium complexes bearing more than one PPh_3 ligand were obtained. Undaunted, we heated an equimolar mixture of $Pd(PEt_3)_3$ and PPh_3 in hexane in a sealed vessel. After 68 h at 80°, a 13% biphenyl yield was obtained. Cooling the solution to −30° induced precipitation of a small amount of $Pd(PPh_3)_4$. Continued thermolysis in refluxing toluene somewhat improved the biphenyl yield, but also brought on the formation of unidentified by-products.

The reaction in eq 5 is assumed to occur via the intermediate **3**, $Ni(C_6H_5)(PPh_2)(PEt_3)_2$, the product of PPh_3 oxidative addition to nickel. An attempted direct synthesis of **3** from *trans*-$NiBr(C_6H_5)(PEt_3)_2$ and $LiPPh_2\cdot OEt_2$ instead yielded **1** (18%), **2** (5%), and biphenyl (eq 6). Repeating this reaction in the presence of 1 equiv of PEt_3 increased the yield of **1** to 74%. These results suggest that **3** is too labile to be isolated and that the PPh_3 oxidative-addition reaction is reversible. When *trans*-$PdBr(C_6H_5)(PEt_3)_2$ was mixed with $LiPPh_2\cdot OEt_2$ and then cooled to −72°, a gold mixture of $Pd(PR_3)_3$ complexes precipitated that contained PPh_3 and PEt_3 ligands in a ratio of about 1.1 to 1.9. Apparently a facile ligand redistribution reaction has again occurred with precipitation of the least soluble species.



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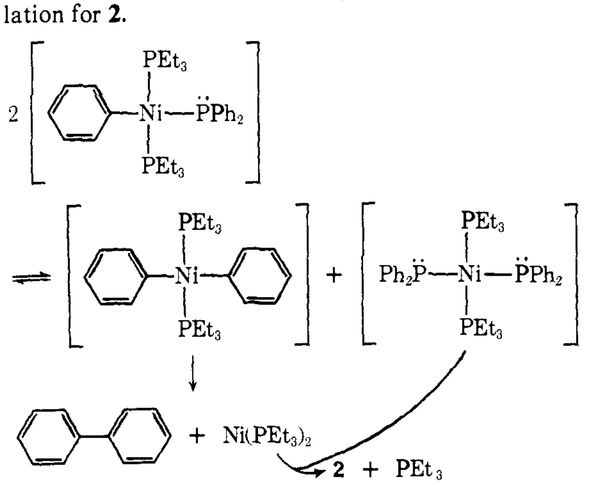
3

The path by which **3** leads to **2**, PEt_3, and biphenyl is suggested in eq 7. The first step is a redistribution reaction. The newly formed $Ni(C_6H_5)_2(PEt_3)_2$ complex would spontaneously decompose to biphenyl and (presumably) $Ni(PEt_3)_2$, as was previously observed by Chatt and Shaw.[12] A similar sequence of redistribution and reductive-elimination reactions was described by Parshall for some $NiX(aryl)(PEt_3)_2$ (X = Cl, CN) complexes.[7] Interaction of the $Ni(PEt_3)_2$ species with the other redistribution product then yields **2**. The soundness of this latter proposal was confirmed by treating *trans*-$NiCl_2(PEt_3)_2$ with 2 equiv of $LiPPh_2\cdot OEt_2$ and then treating the solution with $Ni(PEt_3)_4$. A 68% yield of $Ni_2(\mu\text{-}PPh_2)_2(PEt_3)_3$ was isolated. This independent synthesis confirms the formulation for **2**.



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Further support for the concept of PPh_3 oxidative addition was obtained by treating $C_6F_5PPh_2$ with both $Ni(PEt_3)_4$ and $Pd(PEt_3)_3$. Oxidative additions of aryl halides occur much more readily when the aryl halides are perfluorinated. For example, C_6F_5Br reacts much faster than C_6H_5Br with both $Ni(1,5\text{-}COD)(PEt_3)_2$[8] and $Pd(PEt_3)_3$ (see experimental section). Similarly, the reaction of $Ni(PEt_3)_4$ with $C_6F_5PPh_2$ was more rapid than with PPh_3 as the solution turned green in just a few minutes at 25°. The product mixture was messy, but an 8% yield of **2** was successfully isolated by column chromatography. From the reaction of $Pd(PEt_3)_3$ with $C_6F_5PPh_2$, a few milligrams of orange-red crystals precipitated at −30°. The ir spectrum of this product was the same as that of authentic *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$. Further cooling of the solution to −72° precipitated a 30% yield of an orange-red solid which appears to be *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$ contaminated with another compound (possibly the cis isomer). This proposal is based on comparison of NMR and ir data with those for *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$. Degradation of this product by HCl produced a 35% yield of C_6F_5H.[13] The progress of the reaction of $Pd(PEt_3)_3$ with $C_6F_5PPh_2$ has been monitored by periodic infrared analysis of the reaction mixture. In C_6F_5X compounds, an absorption occurring between 900 and 1000 cm^{-1} is very sensitive to the nature of X. During the first stages of the reaction, only one new absorption band appears which corresponds to the contaminant mentioned above [possibly *cis*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$]. Later, an absorption band for the trans isomer appears along with other bands due to by-products. Separation of individual components from the mixture has not been successful.

Authentic *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$ is yellow-orange and was prepared in 57% yield from *trans*-$PdBr(C_6F_5)(PEt_3)_2$ and $LiPPh_2{\cdot}OEt_2$. An alternative $Pd(PEt_3)_2(C_6F_5PPh_2)$ structure can be discounted by ^1H NMR evidence for trans PEt_3 groups and by the release of C_6F_5H (20% yield)[13] on reaction with HCl. In a similar attempt to prepare *trans*-$Ni(C_6F_5)(PPh_2)(PEt_3)_2$, only unreacted *trans*-$NiBr(C_6F_5)(PEt_3)_2$ was isolated.

Circumstances Favoring Triphenylphosphine Oxidative Addition. The primary prerequisite for the oxidative addition is the presence of a vacant coordination site on the metal. For **1,** vacation of sites (eq 8) by phosphine ligand dissociation was concluded earlier on the basis of NMR data. This dissociation should be suppressed in concentrated solutions, and the reaction shown in eq 4 is indeed slower under these conditions.

$$Ni(PEt_3)_3(PPh_3) \rightleftharpoons Ni(PEt_3)_2(PPh_3) + PEt_3 \qquad (8)$$

Product inhibition is also observed as a result of a mass action effect by PEt_3 product. A dilute solution of **1** in CD_3CN remained unchanged after several weeks at 35°, thus acetonitrile will also effectively occupy coordination sites on nickel. Finally, excess PPh_3 in the metal-promoted reactions inhibited the formation of organic by-products containing PPh_3 fragments. These observations convincingly argue the importance of metal coordinative unsaturation.

The other requirement for PPh_3 oxidative addition is the absence of other more favorable reactions. In the reaction of $Pd(PEt_3)_3$ with PPh_3, the low biphenyl yield and presence of other organic products suggest a competing process is also occurring, possibly an ortho-metalation reaction. In the $C_6F_5PPh_2$ reactions, insertion of the metal into a C–F bond[8] likely competes with insertion into the C–P bond.

Several other examples of a C–P bond cleavage in PPh_3 in the presence of a transition metal have appeared in the literature,[14] but none clearly indicates a distinct oxidative addition as described herein. Investigators should be aware of this possible reaction when pursuing studies of coordination-catalyzed reactions using PPh_3 complexes of transition metals or conducting related studies in organometallic chemistry.

Experimental Section

All of the organometallic compounds prepared in this work are sensitive to oxygen and/or water to varying degrees. Therefore all manipulations with these compounds were performed under argon, usually in a Vacuum-Atmospheres, Inc., recirculating-atmosphere drybox. Solvents and some reagents were dried and distilled, and all were purged with argon before use. Melting points were taken in open capillary tubes *in the drybox.* Infrared spectra of very air-sensitive compounds such as $Ni(PEt_3)_4$ were obtained without evidence of oxidation using carefully prepared Nujol mulls. ^1H NMR spectra are referenced to internal tetramethylsilane. Instruments used were a Perkin-Elmer 137 ir spectrophotometer, a Varian Associates T-60 NMR spectrometer, and a Hewlett-Packard Model 5750 gas chromatograph. Unless otherwise specified, GLC separations were accomplished on a 5 ft × 0.25 in. column packed with 10% Apiezon L on 60/80 Chromosorb G and temperature programmed from 100 to 240° at 10°/min. GLC yields were determined by comparisons to internal standards, and corrections for relative response factors were made. Elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory of Woodside, N.Y.

Metal Promoted Reactions. (a) Palladium Example. A 6-oz. Fischer-Porter aerosol compatibility bottle containing a stirred mixture of 2.24 g (10 mmol) of $Pd(OAc)_2$, 0.52 g (2.0 mmol) of PPh_3, 1.06 g (10 mmol) of Na_2CO_3, 0.91 g (10 mmol) of 2-chlorophenol, 1.00 g (10 mmol) of ethyl acrylate, 0.60 g of *cis*-decalin (internal standard), and 50 ml of ethanol under nitrogen was held at 150° for 3.5 h. After cooling, the mixture was analyzed by GLC on a 6 ft × 0.25 in. column of 15% SE-52 on HMDS treated Chromosorb P temperature programmed from 100° to 240° at 10°/min. Two products were detected: biphenyl (very small) and ethyl cinnamate (2.0 mmol). Products were identified by comparisons of GLC retention times with those of authentic samples on two columns.

(b) $Ni(CO)_2(PPh_3)_2$ Example. A 300-ml stirred autoclave was charged with 6.4 g (10 mmol) of $Ni(CO)_2(PPh_3)_2$, 2.66 g (14.5 mmol) of 2-chlorophenyl acrylate,[15] and 100 ml of *m*-xylene. After flushing the system with nitrogen, the reactor was heated to 200° for 2 h. GLC analysis of the reaction mixture showed the following major products (percent yields based on $Ni(CO)_2(PPh_3)_2$): coumarin (~29%), 3,4-dihydrocoumarin (~37%), 3-methyl-2(3*H*)-benzofuranone (overlapping unreacted 2-chlorophenyl acrylate) (~17%), 2-chlorophenyl benzoate (~9%), and phenyl benzoate (~2%). The products were isolated by preparative GLC and identified by comparing their spectra with those of authentic samples. Spectra of 3-methyl-2(3*H*)-benzofuranone have recently been published.[16]

(c) $Ni(CO)_2(Ph_2PCH_2CH_2PPh_2)$ Example. A 300-ml stirred autoclave was charged with 2.56 g (5.0 mmol) of $Ni(CO)_2(Ph_2PCH_2CH_2PPh_2)$, 1.33 g (7.3 mmol) of 2-chlorophenyl acrylate, and 100 ml of *m*-xylene. After flushing the system with nitrogen, the reactor was heated to 200° for 2 h. GLC analysis of the reaction mixture showed three major and several minor products. The major ones were (percent yield based on Ni): 2-chlorophenyl propanoate (5%), 2-chlorophenyl benzoate (7%), and phenyl benzoate (4%). The products were identified as in the preceding example.

Tris(triethylphosphine)(triphenylphosphine)nickel(0) (1). A 5-ml solution of 0.52 g (2.0 mmol) of PPh_3 in ether was slowly added to 0.83 g (1.6 mmol) of $Ni(PEt_3)_4$[17] in 5 ml of ether. On standing, 0.19 g of orange-red crystalline **1** precipitated that was suction filtered, washed with ether, and dried under vacuum. Concentration of the filtrate under reduced pressure and cooling to −30° allowed the collection of an additional 0.78 g of product. The total yield was 0.97 g (90%) of **1**: mp 95.5–97°; ir (Nujol) 2900 vs, 1585 vw, 1450 s, 1425 m, 1405 w, 1375 m, 1260 w, 1240 w, 1220 vw, 1080 w, 1040 w, 1030 m, 1000 vw, 985 vw, 965 vw, 757 m, 743 s, 717 m, 695 s cm^{-1}; NMR (C_6D_6) δ 7.7 (v br, 6), 7.15 (m, >9 due to CD_5H impurity), 1.58 (q, 18, J = 6.8 Hz), 1.05 (t, 27, J = 6.8 Hz).

Anal. Calcd for $C_{36}H_{60}NiP_4$: C, 64.01; H, 8.95; Ni, 8.69; P, 18.35. Found: C, 63.89; H, 9.28; Ni, 8.83; P, 18.37.

When the same synthesis was performed with product crystallization at −72°, $Ni(PEt_3)_4$ coprecipitated with **1**.

Thermolysis of 1. A closed vial containing 1.36 g (2.0 mmol) of **1** in 20 ml of hexane was suspended in a refluxing benzene bath. Within a few minutes, the orange solution had turned dark green. After 5 h, the solution was cooled to −72° and lustrous dark green crystals precipitated. The crystals were suction-filtered, washed with cold hexane, and dried in a stream of argon to yield 0.39 g (0.46 mmol) of $Ni_2(\mu\text{-}PPh_2)_2(PEt_3)_3$, **2**: mp 194–196° dec; ir (Nujol) 3040 w, 2910 vs, 2880 vs, 1580 m, 1455 s, 1425 m, 1375 m, 1150 w, 1075 w, 1055 w, 1030 s, 1000 w, 767 s, 763 s, 748 ms, 736 s, 724 m, 707 s, 700 vs, 694 s cm^{-1}; NMR (C_6D_6) δ 7.9 (v br, 6.6), 7.15 (v br, 17.4—includes C_6D_5H impurity), 1.00 (v br, 45); Ni $2p_{3/2}$ BE = 856.0 eV (FWHH

3.6 eV); compound is diamagnetic by Guoy susceptibility method.

Anal. Calcd for $C_{42}H_{65}Ni_2P_5$: C, 59.89; H, 7.78; Ni, 13.94; mol wt, 842. Found: C, 59.54; H, 7.78; Ni, 13.88; mol wt, (0.008 M) 378 and (0.013 M) 399.

The above filtrate was combined with 0.200 g of 2,2-diphenylpropane as an internal standard and analyzed by GLC. The solution contained 0.39 g (3.3 mmol) of PEt_3 and 0.113 g (0.73 mmol) of biphenyl. The solution was concentrated under reduced pressure and cooled to −72°. A few milligrams of biphenyl, identical with an authentic sample, precipitated and was filtered.

A similar thermolysis was performed with 2.72 g (4.00 mmol) of **1** in 100 ml of hexane. After 7 h at 85°, 1.30 g (1.54 mmol) of **2** was isolated. This was recombined with the reaction mixture and heated to 125° for 8 h. The mixture was cooled, spiked with an internal standard, and analyzed by GLC. The product yields were 0.81 g (6.9 mmol) of PEt_3 and 0.253 g (1.65 mmol) of biphenyl. Washing the solution with aqueous HCl before GLC analysis had no effect on the biphenyl yield.

Thermolysis of Tris(triethylphosphine)palladium(0) with Triphenylphosphine. A 5-ml ether solution containing 0.36 g (1.37 mmol) of PPh_3 was slowly added to 0.64 g (1.37 mmol) of $Pd(PEt_3)_3$[18] in 5 ml of ether at −30°. Pale yellow crystals of $Pd(PPh_3)_4$ (not pure) precipitated from solution. The entire mixture was evaporated to dryness under reduced pressure, and the residue was sealed in a vial with 18 ml of hexane. After 68 hr at 80°, GLC showed some (~13% yield) biphenyl had formed. Cooling the solution to −30° caused some $Pd(PPh_3)_4$ precipitation. The hexane was removed at reduced pressure, and the residue was sealed in a vial with 18 ml of toluene. Heating the mixture at 100° did not seem to significantly increase the biphenyl yield, and instead, two by-products were now evident with GLC retention times of 11.2 and 19.2 min (biphenyl, 13.6 min).

***trans*-Bromo(phenyl)bis(triethylphosphine)nickel(II).** This compound (mp 85–86°) was prepared from $Ni(PEt_3)_4$[17] and bromobenzene following a procedure similar to that used by Parshall[7] for other aryl halides. Details will be reported separately.[8,21]

Lithium Diphenylphosphide Diethyl Etherate. A 12.2-ml solution of 1.65 M *n*-butyllithium (20 mmol) in heptane was slowly added to 3.72 g (20 mmol) of $PHPh_2$ in 10 ml of hexane at ca. 10°. A yellow solid immediately precipitated that was collected by suction filtration (washing with hexane). Recrystallization of the solid from ether at −72° yielded 4.14 g (77.4%) of lemon yellow $LiPPh_2{\cdot}OEt_2$: mp 270° dec.

Anal. Calcd for $C_{16}H_{20}LiOP$: C, 72.18; H, 7.57. Found: C, 71.67; H, 7.35.

Reaction of *trans*-$NiBr(C_6H_5)(PEt_3)_2$ with $LiPPh_2{\cdot}OEt_2$. A solution of 0.45 g (1.0 mmol) of *trans*-$NiBr(C_6H_5)(PEt_3)_2$ and 0.27 g (1.0 mmol) of $LiPPh_2{\cdot}OEt_2$ in 10 ml of ether was agitated at 0°. The mixture turned brown and was cooled to −72°. Orange crystals formed that were suction filtered to yield 0.12 g (18%) of **1** identical with that described above. The filtrate was evaporated to dryness under reduced pressure, and the residue was dissolved in hexane, filtered, and cooled to −72°. Dark green crystals formed that were suction filtered to yield 0.02 g (5%) of **2** identical with that described above. The remaining filtrate was qualitatively analyzed by GLC, and a substantial quantity of biphenyl was observed.

Reaction of *trans*-$NiBr(C_6H_5)(PEt_3)_2$ with $LiPPh_2{\cdot}OEt_2$ and Triethylphosphine. A solution of 0.54 g (2.0 mmol) of $LiPPh_2{\cdot}OEt_2$ and 0.24 g (2.0 mmol) of PEt_3 in 7 ml of ether was added to 0.90 g (2.0 mmol) of *trans*-$NiBr(C_6H_5)(PEt_3)_2$ in 5 ml of ether at ca. 0°. The solution immediately turned dark brown and was cooled to −72°. The solution gradually turned green and precipitated a solid. An orange solid was collected by suction filtration which was washed with cold ether and vacuum dried to yield 1.00 g (74%) of **1** identical with that described above.

***trans*-Bromo(phenyl)bis(triethylphosphine)palladium(II).** A pale orange solution of 4.43 g (9.61 mmol) of $Pd(PEt_3)_3$[18] and 2.40 g (15.3 mmol) of bromobenzene in 10 ml of hexane was stirred overnight at 40°. The resulting pale yellow solution was diluted with 10 ml of ether, filtered, and cooled to −72°. Suction filtration of the mixture afforded 4.12 g (86%) of white crystalline *trans*-$PdBr(C_6H_5)(PEt_3)_2$: mp 105–107° (lit.[19] mp 103–104°).

Reaction of *trans*-$PdBr(C_6H_5)(PEt_3)_2$ with $LiPPh_2{\cdot}OEt_2$. A solution of 1.06 g (4.0 mmol) of $LiPPh_2{\cdot}OEt_2$ in 10 ml of ether was added to a stirred solution of 2.00 g (4.0 mmol) of *trans*-$PdBr(C_6H_5)(PEt_3)_2$ in 10 ml of ether at 0°. The solution rapidly turned dark brown, and it was cooled to −72°. Gold crystals formed that were collected by suction filtration to yield 0.77 g of what seems to be a mixture of average formula $Pd[(PEt_3)_{0.6}(PPh_3)_{0.4}]_3$: mp 130–133° dec (gradually turned purple between 76 to 124°); NMR ($CDCl_3$-reaction occurred on dissolution) δ 7.4 (m, 46), 1.9 and 1.17 (m, 54), corresponding to a PEt_3 to PPh_3 ratio of 0.54 to 0.46. Attempts to purify the product by recrystallization from toluene, hexane, and ether failed to yield a better defined complex.

Anal. Calcd for $Pd(PEt_3)_{1.9}(PPh_3)_{1.1}$: C, 60.50; H, 7.32. Found: C, 60.11; H, 6.60.

Synthesis of 2 from *trans*-Dichlorobis(triethylphosphine)nickel(II). A 25-ml ether solution containing 1.83 g (5.0 mmol) of *trans*-$NiCl_2(PEt_3)_2$ was treated with 2.66 g (10.0 mmol) of $LiPPh_2{\cdot}OEt_2$ in 30 ml of ether at ca. 0°. The solution immediately turned dark green. After 15 min, 2.66 g (5.0 mmol) of $Ni(PEt_3)_4$[17] was added to the stirred solution. The mixture was allowed to stand at 25° for 1 h and was then taken to dryness under reduced pressure. The residue was extracted with large amounts of hexane, and the extract was filtered and cooled to −72°. Suction filtration of the solution gave 1.54 g of lustrous dark green crystals of **2** identical with that described above. The mother liquor yielded additional product bringing the total yield of **2** to 2.86 g (68%).

Reaction of Pentafluorophenyldiphenylphosphine with Tetrakis(triethylphosphine)nickel(0). A solution of 1.06 g (2.0 mmol) of $Ni(PEt_3)_4$[17] in 5 ml of ether was treated with 0.70 g (2.0 mmol) of $C_6F_5PPh_2$ in 5 ml of ether at ca. 0°. The mixture turned brown and was warmed to 25° for a few minutes. The solution was cooled to −72° and was now green. No crystals formed, so the mixture was evaporated to dryness under reduced pressure. The residue was a dark-green gum that exhibited strong ir absorptions at 942 and 954 cm^{-1}. The residue was extracted with hexane, and the extract was chromatographed on a column of neutral alumina. A green solid eluted from the column with 5% ether in hexane. Recrystallization of the solid from hexane at −72° yielded 0.07 g (8%) of **2**.

Reaction of Pentafluorophenyldiphenylphosphine with Tris(triethylphosphine)palladium(0). A 2-ml hexane solution of 1.03 g (2.23 mmol) of $Pd(PEt_3)_3$[18] was added to 0.75 g (2.13 mmol) of $C_6F_5PPh_2$ in 5 ml of hexane to give an orange solution. The solution was maintained at 50–60° for 1 h and then stored overnight at −30°. A few milligrams of orange-red crystals had formed that had an ir spectrum identical with that of *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$ described below. Further cooling of the solution to −72° induced additional formation of crystals that were collected by suction filtration. The gummy product solidified after prolonged vacuum drying to yield 0.46 g (30% ?) of a mixture of *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$ with possibly the cis isomer: mp 105–112°; ir (Nujol) 953 s, 943 s cm^{-1}; NMR (C_6D_6, CD_3CN) δ 7.98 (br m, 4), 7.43 (m, 6), 1.54 (br m, 12), 1.05 (br quint, 18, apparent J = 8 Hz).

Anal. Calcd for $C_{30}H_{40}F_5PdP_3$: C, 51.85; H, 5.80. Found: C, 49.87; H, 5.98.

A 6-ml benzene solution containing 1.34 g (2.91 mmol) of $Pd(PEt_3)_3$[18] and 1.02 g (2.91 mmol) of $C_6F_5PPh_2$ was quickly prepared and a portion was loaded into an air-tight ir cell maintained at 25°. Spectra were periodically recorded to monitor the absorptions occurring between 850 and 1000 cm^{-1}. With the baseline at the 80% transmittance level, six bands appeared in this region with percent transmittances shown in Table I. Band assignments are: 984, $C_6F_5PPh_2$; 953, *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$; 945, tentatively *cis*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$; 922, 890, 882 cm^{-1}, unknowns.

***trans*-Bromo(pentafluorophenyl)bis(triethylphosphine)palladium(II).** A pale orange solution of 1.15 g (2.5 mmol) of $Pd(PEt_3)_3$[18] in 2 ml of hexane was slowly added to a stirred mixture of 0.62 g (2.5 mmol) of bromopentafluorobenzene in 5 ml of hexane. During the addition, the solution became warm, and a white precipitate formed. After the addition was complete, the mixture was cooled to −20° to precipitate additional product. Suction filtration of the solution yielded 1.21 g (82%) of white *trans*-$PdBr(C_6F_5)(PEt_3)_2$: mp 126–127° (lit.[19] 124–125°).

***trans*-(Pentafluorophenyl)(diphenylphosphido)bis(triethylphosphine)palladium(II).** A solution of 0.50 g (1.9 mmol) of $LiPPh_2{\cdot}OEt_2$ in 7 ml of ether was added to 1.12 g (1.9 mmol) of *trans*-$PdBr(C_6F_5)(PEt_3)_2$ in 12 ml of ether at 0°. An orange solid (0.22 g) immediately precipitated and was collected by filtration. The filtrate was cooled to −72°, and an additional 0.53 g of orange solid was obtained. The combined yield was 0.75 g (57%) of *trans*-$Pd(C_6F_5)(PPh_2)(PEt_3)_2$. This material was recrystallized from toluene/hexane at −72° to yield 0.44 g of yellow-orange *trans*-$Pd(C_6F_5)(PPh_2)$-

Table I

	Frequency, cm^{-1}					
Time, h	984	953	945	922	890	882
0.15	7		30	70		
1.0	8		13	61		
3.0	10		10	47		67
21	18	25	10	24	58	55
44	23	20	10	20	50	48
140	36	28	13	26	54	49

$(PEt_3)_2$: mp 114–115° dec; ir (Nujol) 3030 vw, 2900 vs, 1580 m, 1495 s, 1460 ms, 1440 vs, 1430 ms, 1380 m, 1335 m, 1255 w, 1095 w, 1070 m, 1050 s, 1040 s, 1010 w, 952 vs, 768 s, 748 w, 740 s, 724 ms, 708 w, 697 cm^{-1}; NMR ($CDCl_3$) δ 8.0–6.8 (m, 10), 1.53 (m, 12), 1.07 (quint, 18, J_{HH} = 8 Hz, $J_{PH} + J_{P'H}$ = 17 Hz).

Anal. Calcd for $C_{30}H_{40}F_5PdP_3$: C, 51.85; H, 5.80; F, 13.67; P, 13.37. Found: C, 51.63; H, 5.89; F, 13.29; P, 13.25.

***trans*-Bromo(pentafluorophenyl)bis(triethylphosphine)nickel(II).** This compound (mp 127–129° (lit.[20] mp 130–131°)) was prepared from Ni(1,5-COD)$(PEt_3)_2$ and bromopentafluorobenzene following a procedure to be reported separately.[8]

Attempted Preparation of *trans*-(Pentafluorophenyl)(diphenylphosphido)bis(triethylphosphine)nickel(II). A solution of 0.27 g (1.0 mmol) of $LiPPh_2 \cdot OEt_2$ in 3 ml of ether was added to 0.54 g (1.0 mmol) of *trans*-NiBr$(C_6F_5)(PEt_3)_2$ in 3 ml of ether at 0° causing the solution to turn green. On cooling to −72°, only a small amount of *trans*-NiBr$(C_6F_5)(PEt_3)_2$ was successfully isolated from the solution.

Acknowledgment. We are indebted to Mr. Bill Loffer for unusually competent and dedicated experimental assistance.

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Kinetics, Steric Course, and Mechanism of Stereoisomerization of Aluminum β-Diketonates[1]

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Abstract. The activation parameters for the stereoisomerizations of tris(2,6-dimethyl-3,5-heptanedionato)aluminum(III) and bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(2,6-dimethyl-3,5-heptanedionato)aluminum(III) have been determined by dynamic nuclear magnetic resonance (DNMR) spectroscopy and are reported. The reactions are found to be first order and intramolecular. Permutational analysis of the combined results of this study and those of all other DNMR studies of tris(β-diketonato)aluminum chelates reported reveal that the steric course of stereoisomerization involves the effective simultaneous interchange of the terminal groups within two of the three bidentate ligands and enantiomerization at the metal center. Consideration of the magnitudes of the activation parameters, the effective steric course, and a topological analysis leads to the following mechanistic conclusions. Chelates with alkyl or aryl substituents on the β-diketonate rings most likely stereoisomerize by a rhombic twist mechanism. Chelates with fluorocarbon substituents on the β-diketonate rings stereoisomerize by a bond-rupture mechanism which proceeds via an actual square pyramidal-apical five-coordinate intermediate.

Introduction

It has been more than 10 years since the pioneering study by Fay and Piper reported on the stereochemical nonrigidity of tris(β-diketonato)aluminum(III) chelates.[2] This work stimulated much interest in the dynamic stereochemistry of tris chelates in general,[3] and, subsequently, the "steric courses"[4] of the stereoisomerizations of other tris chelates, specifically certain tris(N,N-disubstituted dithiocarbamato) complexes,[5] and certain tris(α-substituted tropolonato) complexes,[6] have been uniquely determined. Nevertheless, despite more than a decade of investigation,[1b,2,7-12] the question of the steric course of the stereoisomerization of tris(β-diketonato)-

Springer et al. / Stereoisomerization of Aluminum β-Diketonates