

N-end to Cl-end labilization applies as for the *trans*-Co(en)₂(NH₃)Cl²⁺ complex, the predicted N-end labilization should be $2.5 \times 10^{-4} \times 5.0$ or 12.5×10^{-4} . The discrepancy, 12.5×10^{-4} to 1.6×10^{-4} then indicates that 87% of the time labilization of the N-end terminates in recoordination of the ethylenediamine and hence no net reaction. We have used our preferred 80/20 isomer ratios in the above calculations, but use of the middle figures of the uncertainty ranges would not change the qualitative conclusions.

From the spectroscopic point of view, we would still suppose the lowest excited singlet state to be essentially the same as for Co(NH₃)₅Cl²⁺, although the microsymmetry is not exactly C_{4v} for the cis chloroammine complex. The position of the absorption band maxima is the same as for the chloropentammine, however, although the intensities are considerably higher.

Acknowledgment. This investigation was supported in part by Department of the Army Grant DA-ARO-D-31-124-G87, and by National Science Foundation Grants 27984X2 and GP-44348X to the University of Southern California.

References and Notes

(1) Author to whom correspondence should be addressed.

- (2) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1971.
- (3) J. Endicott in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975.
- (4) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 3027 (1974).
- (5) P. S. Sheridan and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 3032 (1974).
- (6) P. S. Sheridan and A. W. Adamson, *Inorg. Chem.*, **13**, 2482 (1974).
- (7) C. H. Langford and C. P. J. Vuik, *J. Am. Chem. Soc.*, **98**, 5409 (1976).
- (8) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).
- (9) J. I. Zink, *Inorg. Chem.*, **12**, 1018 (1973).
- (10) J. I. Zink, *J. Am. Chem. Soc.*, **96**, 4464 (1974).
- (11) A. D. Kirk and T. L. Kelly, *Inorg. Chem.*, **13**, 1613 (1974), and private communication.
- (12) S. C. Chan, *J. Chem. Soc. A*, 291 (1967).
- (13) M. L. Tobe, *J. Chem. Soc.*, 3776 (1959).
- (14) N. A. P. Kane-Maguire and C. H. Langford, *J. Chem. Soc., Chem. Commun.*, 351 (1973).
- (15) K. M. Cunningham and J. F. Endicott, *J. Chem. Soc., Chem. Commun.*, 1024 (1974).
- (16) J. C. Bailar, *Inorg. Synth.*, **2**, 222 (1946).
- (17) M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **34**, 3915 (1972).
- (18) A. Werner, *Justus Liebigs Ann. Chem.*, **1**, 386 (1912).
- (19) R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).
- (20) R. D. Cannon and J. E. Early, *J. Am. Chem. Soc.*, **88**, 1872 (1966).
- (21) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
- (22) W. T. Bolleter, C. J. Buchman, and P. W. Tidwell, *Anal. Chem.*, **33**, 592 (1961).
- (23) F. E. Clarke, *Anal. Chem.*, **22**, 553 (1950).
- (24) M. Tobe, private communication.
- (25) A. W. Adamson, A. Gutierrez, R. Wright, and T. Walters, unpublished work.

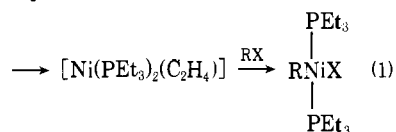
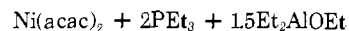
Oxidative Additions of Aryl, Vinyl, and Acyl Halides to Triethylphosphenickel(0) Complexes

Darryl R. Fahey* and John E. Mahan

Contribution from Research and Development, Phillips Petroleum Company, Bartlesville, Oklahoma 74004. Received August 2, 1976

Abstract: Aryl, vinyl, and acyl halides, but not alkyl halides, react with Ni(PEt₃)₂(C₂H₄), Ni(PEt₃)₂(1,5-C₈H₁₂), and Ni(PEt₃)₄ complexes to yield square-planar *trans*-NiX(R)(PEt₃)₂ compounds. Structure assignments are based on infrared and NMR spectra. Carbonylation of aryl nickel compounds provides aryl derivatives. Template, radical, and aromatic-nucleophilic-substitution processes are involved in the nickel-organic halide interactions.

Reactions of aryl halides with zero-valent nickel complexes have attracted considerable interest in organic¹ and organometallic² synthesis. Several years ago, one of us communicated a method for the preparation of aryl nickel complexes by the reaction of aryl halides with Ni(PEt₃)₂(C₂H₄), prepared and reacted in situ (eq 1).³ Since that time, a large



number of related examples have surfaced.⁴ This article presents details of our communicated method, and, more importantly, defines the scope of organonickel synthesis from nickel(0) complexes bearing triethylphosphine ligands, especially from Ni(PEt₃)₂(1,5-C₈H₁₂) and Ni(PEt₃)₄. Our studies were largely confined to complexes with triethylphosphine ligands, since this ligand imparts a high reactivity to nickel(0) reagents^{4j} and good stability to the organonickel(II) products.⁴ⁱ

Results and Discussion

Reactivities of Nickel(0) Reagents. (A) Ni(PEt₃)₂(1,5-C₈H₁₂). The addition of 2 molar equiv of triethylphosphine to a yellow solution of bis(1,5-cyclooctadiene)nickel(0) in hexane causes the solution to turn red-brown. The color change is attributed to the formation of Ni(PEt₃)₂(1,5-C₈H₁₂) as a 1,5-cyclooctadiene ligand is liberated.^{5,6} When this solution was added to an acyl halide, vinyl halide, or perfluoroaryl halide, rapid (sometimes exothermic) oxidative-addition reactions occurred. Products of formula NiX(R)(PEt₃)₂ were isolated in 61–83% yields by low temperature crystallization and filtration. When the final isolation steps were performed in air rather than under an inert atmosphere, the isolated yields dropped below 40% even for moderately air-stable compounds. The best results were always obtained when the nickel(0) reagent was added to the organic halide, thus keeping the organic halide present in excess at all times during the mixing process. The reaction of Ni(PEt₃)₂(1,5-C₈H₁₂) with chlorobenzene, bromobenzene, and the dichlorobenzenes required elevated temperatures (50–60 °C) or extended reaction times (24–48 h). Elemental nickel precipitated during these reactions and yellow-green impure products were isolated in 6–64% yields. Recrystallization of these products yielded the yellow-brown aryl nickel

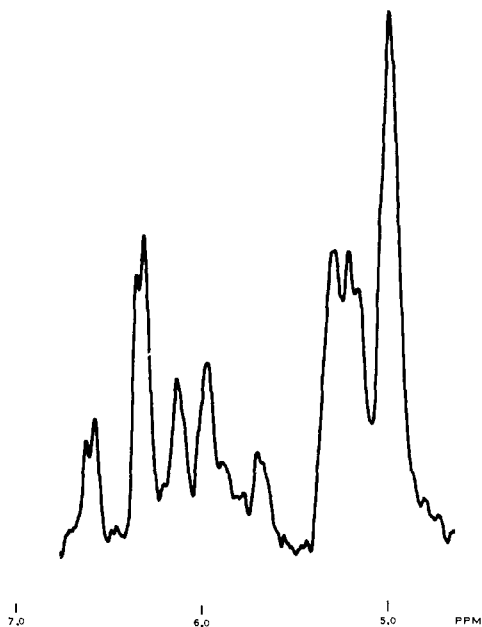


Figure 1. A portion of the ^1H NMR spectrum (C_6D_6) of *trans*- $\text{NiCl}[\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2](\text{PEt}_3)_2$. Peak assignments are: H_a , δ 6.50, dd (17, 3 Hz); H_b , 5.10, dd (11, 3 Hz); H_c , 5.93, dd (17, 11 Hz); H_d , 5.32, br s; H_e , 5.01 ppm, br s. See structural formula in text for proton labeling scheme.

complexes. Chlorobenzene reacted much more satisfactorily with solutions of $\text{Ni}(1,5\text{-C}_8\text{H}_{12})_2$ containing 3 or 4 equiv of triethylphosphine. In comparative reactions with 2, 3, and 4 equiv of triethylphosphine, the $\text{NiCl}(\text{C}_6\text{H}_5)(\text{PEt}_3)_2$ yields were 50, 70, and 79%, respectively. The first two of these reactions required gentle warming to promote the oxidative addition.

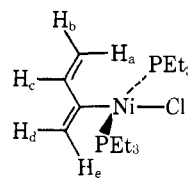
(B) $\text{Ni}(\text{PEt}_3)_4$. When $\text{Ni}(\text{PEt}_3)_4$ is dissolved in hydrocarbon solvents, a triethylphosphine ligand dissociates, and intensely purple solutions of $\text{Ni}(\text{PEt}_3)_3$ result.^{5,7} This reagent is more reactive than $\text{Ni}(\text{PEt}_3)_2(1,5\text{-C}_8\text{H}_{12})$, and it was found to react immediately with most aryl halides producing red to yellow-brown solutions sometimes accompanied by small amounts of white solids. When the solutions were cooled to low temperatures, aryl nickel complexes precipitated and were isolated in 70–85% yields. When $\text{Ni}(\text{PEt}_3)_4$ was added to carboxylic acid chlorides in hexane, copious quantities of acylphosphonium salts were formed as flocculent precipitates. Although acyl nickel complexes might be recoverable from this reaction, the isolation process would be more tedious than that from $\text{Ni}(\text{PEt}_3)_2(1,5\text{-C}_8\text{H}_{12})$ reactions.

(C) $\text{Ni}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)$. The reaction of $\text{Ni}(\text{acac})_2$ with AlEt_2OEt in the presence of 2 equiv of PEt_3 and under an ethylene atmosphere has previously been shown to yield $\text{Ni}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)$ as a yellow liquid.⁸ In our preliminary communication,³ $\text{Ni}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)$, prepared and reacted in situ, was shown to provide organonickel compounds from several aryl halides. Product yields were quite modest (6–19%), but this was at least partly due to product decomposition during column chromatography in air and possibly to too-short a reaction time. A recent publication describes 50–65% yields with this method but with longer reaction times and chromatography under nitrogen.⁴¹ This technique should be considered as a rapid and relatively simple method for organonickel synthesis from readily available starting materials.

Reactivities of Organic Halides. (A) Alkyl Halides. No alkyl nickel products were isolated from the reactions of $\text{Ni}(\text{PEt}_3)_2(1,5\text{-C}_8\text{H}_{12})$ with 1-bromoadamantane, $\text{Ni}(\text{PEt}_3)_4$ with 3-chloro-2-norbornanone, and $\text{Ni}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)$ with 1,1,2,2-tetrachloroethane. A detailed examination of the 3-

chloro-2-norbornanone reaction revealed that the major products were $\text{NiCl}_2(\text{PEt}_3)_2$ and 2-norbornanone.

(B) Vinyl Halides. Vinyl bromide and chloroprene both rapidly reacted with $\text{Ni}(\text{PEt}_3)_2(1,5\text{-C}_8\text{H}_{12})$ to afford halo(organo)bis(triethylphosphine)nickel(II) complexes. The products are air-sensitive, but the 2-(1,3-butadienyl) complex does survive brief exposures to air. The $\text{NiBr}(\text{CH}=\text{CH}_2)(\text{PEt}_3)_2$ complex melts near room temperature and, when allowed to stand as a melt at 25–30 °C, decomposes in less than 1 h. It is preferably prepared, isolated, and stored at temperatures below 10 °C. When the complex decomposes, it loses its C=C stretching vibration at 1550 cm^{-1} . The instability of the vinyl nickel complex prevented its complete characterization. The *trans*- $\text{NiCl}[\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2](\text{PEt}_3)_2$ complex, in contrast, is stable for months at 35 °C under argon. This compound is particularly enchanting since the nickel atom is σ -bonded to a potentially reactive diene. The diene fragment preferentially resides in a *s-trans* conformation judging from the low field ^1H NMR chemical shift of H_a . Its resonance



appears at δ 6.50 (Figure 1), approximately 1.3 ppm downfield from the corresponding proton resonance in isoprene. Only in the *s-trans* conformation does H_a deeply penetrate the induced paramagnetic field associated with the nickel atom.^{4h,i,9} Separate resonances occur for all five protons in the ^1H NMR spectrum at ambient temperature, indicating that the complex maintains a static σ -allyl structure. The infrared spectrum of the compound contains bands at 1592 and 1535 cm^{-1} for the C=C stretching vibrations, similar to the corresponding infrared absorptions of other 2-substituted-1,3-butadienes.¹⁰

No organonickel product was isolated from the reaction of $\text{Ni}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)$ with hexachlorocyclopentadiene. An attempt was made to prepare a chloro(1-methylene- η^3 -allyl)(triethylphosphine)nickel(II) complex by reacting chloroprene with a $\text{Ni}(1,5\text{-C}_8\text{H}_{12})_2$ solution containing 1 equiv of triethylphosphine. Again, no organonickel product was isolated.

(C) Aryl Halides. With the exception of pentafluorophenyl halides, aryl halides are less reactive than vinyl and acyl halides, and the $\text{Ni}(\text{PEt}_3)_4$ reagent proved to give the highest yields of aryl nickel products. Mono- and dihalobenzenes react smoothly and rapidly with $\text{Ni}(\text{PEt}_3)_4$ affording high yields of organonickel products. With increasing substitution of the benzene ring, the reaction is no longer instantaneous and the product yields decrease. 1,2,4-Trichlorobenzene produced only a 49% yield of organonickel product while hexachlorobenzene and hexabromobenzene produced none. Benzene, toluene, and tetrahydrofuran solutions of C_6Cl_6 were treated with $\text{Ni}(\text{PEt}_3)_4$ and the solutions turned brown or red within an hour. The major products were $\text{C}_6\text{Cl}_5\text{H}$ and $\text{NiCl}_2(\text{PEt}_3)_2$. An in situ reaction of $\text{Ni}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)$ and C_6Cl_6 did produce a trace amount of $\text{NiCl}(\text{C}_6\text{Cl}_4\text{H})(\text{PEt}_3)_2$ probably resulting from an oxidative-addition reaction with $\text{C}_6\text{Cl}_5\text{H}$. The yield is far too low for this latter synthesis to be of preparative value. 2-Bromo-*m*-xylene also resisted undergoing a normal oxidative addition reaction with $\text{Ni}(\text{PEt}_3)_4$. Instead a slow halogen abstraction process occurred, and a 51% yield of $\text{NiBr}(\text{PEt}_3)_3$ was isolated.

In aryl dihalides containing both chloride and bromide, the bromide reacts preferentially. Both 2-bromochlorobenzene and 4-bromochlorobenzene yielded the $\text{NiBr}(\text{C}_6\text{H}_4\text{Cl})(\text{PEt}_3)_2$ product from $\text{Ni}(\text{PEt}_3)_4$. Selectivity among the chlorides also

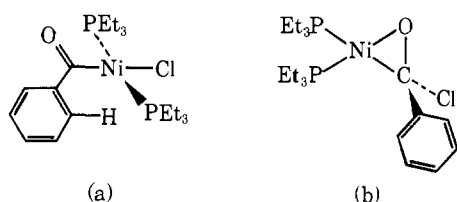
occurs in the reaction of 1,2,4-trichlorobenzene with $\text{Ni}(\text{PET}_3)_4$ as only the 2,5-dichlorophenyl nickel isomer was isolated. These results are in agreement with those from a quantitative study of halide selectivity in the reactions of 2-bromochlorobenzene and 1,2,4-trichlorobenzene with $\text{Ni}(\text{PET}_3)_2(\text{C}_2\text{H}_4)$ described in the communication.³

Pentafluorophenyl chloride and bromide are very reactive: treatment with $\text{Ni}(\text{PET}_3)_2(1,5\text{-C}_8\text{H}_{12})$ resulted in immediate oxidative-addition reactions. High yields of the pentafluorophenyl nickel complexes were obtained. With gentle warming, hexafluorobenzene could also be encouraged to react with $\text{Ni}(\text{PET}_3)_2(1,5\text{-C}_8\text{H}_{12})$, and a 7% yield of $\text{NiF}(\text{C}_6\text{F}_5)(\text{PET}_3)_2$ was obtained. This product gradually decomposed on standing at 30 °C.

Some kinds of functionality cannot be tolerated in these oxidative additions. 3,4-Dichloronitrobenzene readily reacted with $\text{Ni}(\text{PET}_3)_2(\text{C}_2\text{H}_4)$, but no organonickel products were isolated. Triethylphosphine oxide was formed in the reaction. 2-Chlorophenyl acrylate was immediately polymerized by $\text{Ni}(\text{PET}_3)_2(1,5\text{-C}_8\text{H}_{12})$. Free PET_3 also induces this polymerization so a reaction with $\text{Ni}(\text{PET}_3)_4$ was not examined.¹¹

A medium intensity band appears at 1560 cm^{-1} in the infrared spectra of the $\text{NiX}(\text{C}_6\text{H}_5)(\text{PET}_3)_2$ complexes (and the corresponding Pd complexes). This seems to be a typical feature of phenylnickel, -palladium, and -platinum complexes.¹² When substituents are present on the phenyl group, the intensity and frequency of this band varies.

(D) Acyl Halides. Rapid exothermic oxidative additions occurred as $\text{Ni}(\text{PET}_3)_2(1,5\text{-C}_8\text{H}_{12})$ was added to solutions containing acyl halides. In hexane solutions, some white solids precipitated during reactions, which, when the acyl halide was $(\text{CH}_3)_3\text{CCH}_2\text{COCl}$, was identified as $(\text{CH}_3)_3\text{CCH}_2\text{CO-PET}_3^+\text{Cl}^-$. In diethyl ether or hexane/acetonitrile mixtures, phosphonium salts did not precipitate. Very likely, the salts also acylated the nickel(0) complex. When the solutions were cooled to -72 °C, acyl nickel complexes usually precipitated in good yields. After recrystallization, most of these compounds were orange or yellow-brown, except those with bulky organic groups bonded to the carbonyl carbon, i.e., *tert*-butyl and 1-adamantyl (1-Ad), were red-brown. In addition to providing acyl nickel products, 2-chlorobenzoyl chloride and pivaloyl chloride yielded $\text{NiCl}(2\text{-ClC}_6\text{H}_4)(\text{PET}_3)_2$ and $\text{NiCl}_2(\text{PET}_3)_2$, respectively. Only $\text{NiCl}(\text{C}_6\text{F}_5)(\text{PET}_3)_2$ was isolated from pentafluorobenzoyl chloride. The 2- and 3-chlorobenzoyl nickel products were isolated as red-brown solids, but when these same compounds were prepared by carbonylation reactions (see below) they were orange. Attempts to obtain analytically pure samples of these two compounds were thwarted by sample decomposition during recrystallization. All three isomeric chlorobenzoyl nickel complexes as well as the two red-brown acyl complexes mentioned above melt with decomposition (gas evolution). Very unstable acyl nickel products were obtained from acetyl, acryloyl, and cinnamoyl chlorides. The isolated acetyl nickel product appeared to be pure, and it survived long enough at 25 °C to record its infrared spectrum. Previously, only four examples of stable $\text{NiX}(\text{COR})(\text{PR}_3)_2$ complexes have appeared in the literature,^{4k,12-14} as most synthetic attempts have given other products.^{4a,g,i,o,12,15}



Qualitative proof for the validity of assigning to the products acyl nickel halide structures (a) as opposed to simple nickel-

Table I. Selected Infrared Absorptions (cm^{-1}) of *trans*- $\text{NiX}(\text{R})(\text{PET}_3)_2$ Compounds

R	X	$\nu_{\text{C=O}}$	$\nu_{\text{Ni-X}}$	$\nu_{\text{Ni-P}}$
$[\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2]$	Cl		330	
C_6H_5	Cl		355	237
2- ClC_6H_4	Cl		327	230
3- ClC_6H_4	Cl		353	235
4- ClC_6H_4	Cl		337	228
2,5- $\text{Cl}_2\text{C}_6\text{H}_3$	Cl		358	224
C_6F_5	Cl		373	228
COC_6H_5	F	1605	<i>a</i>	<i>a</i>
COC_6H_5	Cl	1610	357	235
COC_6H_5	Br	1608	341?	
CO-2- ClC_6H_4	Cl	1600	377	227
CO-3- ClC_6H_4	Cl	1605, 1637	360	219
CO-4- ClC_6H_4	Cl	1607	362	221
COCH_3	Cl	1640	<i>a</i>	<i>a</i>
$\text{COCH}_2\text{C}(\text{CH}_3)_3$	Cl	1638, 1660, 1705	360	
$\text{COC}(\text{CH}_3)_3$	Cl	1635, 1660, 1725	<i>a</i>	<i>a</i>
CO-1-Ad	Cl	1620, 1642, 1665	350	

^a Low frequency region not examined.

(acyl halide) π -type complexes (b) was obtained with the $\text{NiCl}(\text{COC}_6\text{H}_5)(\text{PET}_3)_2$ complex. After heating this complex in ethanol, a GLC analysis of the solution showed the presence of ethyl benzoate. Both (a) and (b) are expected to produce this result. Degradation of the complex by anhydrous HCl in hexane yielded benzaldehyde, a result only expected from (a). Finally, the ^1H NMR spectrum of this complex shows substantial deshielding of the ortho proton resonances of the aryl group. Only in (a) would the ortho protons be strongly affected by the paramagnetic anisotropy of the nickel atom.⁹

Low temperature (-40 to -50 °C) crystallization of $\text{NiCl}(\text{COC}_6\text{H}_5)(\text{PET}_3)_2$ from solutions containing acetonitrile afforded a highly crystalline solid. As the crystals were warmed to 25 °C, they melted and formed a mobile solution. Subjecting this solution to a high vacuum caused it to resolidify. Apparently a low-melting crystalline acetonitrile complex or solvate is formed at low temperatures. This behavior was not observed with diethyl ether, tetrahydrofuran, hexane, or toluene.

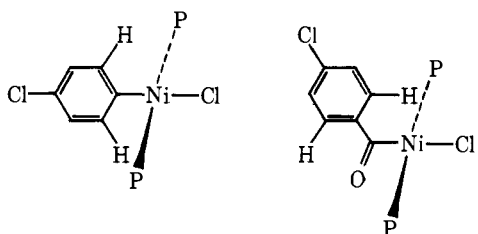
The IR spectra of the acyl nickel complexes all contain strong absorptions between 1600–1725 and 850–900 cm^{-1} (see Table I). The spectra of several of the acyl complexes displayed two or even three C=O stretching vibrations. This was unexpected, so the 1-adamantylcarbonyl complex, which had C=O absorptions at 1665 m, 1642 s, and 1620 s cm^{-1} , was chosen for further study. Repeated recrystallizations of the complex failed to alter the relative intensities of the three peak array. Essentially the same spectrum was observed in Nujol, KBr, hexane, and acetonitrile media. A molecular weight determination showed the complex to be monomeric in solution. The ^1H NMR spectrum is consistent with a structurally rigid *trans* square-planar configuration about nickel (see below). The IR spectrum remains puzzling, and in the absence of other likely explanations, we suggest that the multiple C=O vibrations might be due to conformational isomerism in the meshing of the adamantyl group with the triethylphosphine ligands.

Organonickel Carbonylation. Solutions of both $\text{NiCl}(\text{C}_6\text{H}_5)(\text{PET}_3)_2$ and $\text{NiCl}(3\text{-ClC}_6\text{H}_4)(\text{PET}_3)_2$ rapidly absorbed carbon monoxide at 1–2 atm and 25 °C to yield the benzoyl and 3-chlorobenzoyl nickel complexes, respectively, in high yields. The 2-chlorophenyl nickel complex was inert under these conditions, but could be forced to carbonylate at 15 atm of carbon monoxide. The orange 2- and 3-chlorobenzoylnickel products were isolated in higher purity than those obtained by the oxidative-addition reactions, but they still

decarbonylated on attempted recrystallization. The IR spectra of the acyl nickel complexes between 200 and 4000 cm^{-1} were independent of the method of preparation. The 2-(1,3-butadienyl)nickel complex absorbed carbon monoxide under a few atmospheres pressure but did not yield an acyl nickel complex. A pale yellow water-soluble solid precipitated, while the hydrocarbon-soluble products had an IR spectrum consistent with a mixture of $\text{Ni}(\text{CO})_2(\text{PEt}_3)_2$ ¹⁶ and $\text{Ni}(\text{CO})_3\text{PEt}_3$.¹⁷ We were unable to identify the water-soluble product.¹⁸

Structure/Spectra Correlations. All known $\text{NiX}(\text{R})(\text{PR}_3)_2$ complexes have adopted trans square-planar configurations about the nickel atom.² It is therefore reasonable to assume that all the complexes with this formula described here also possess this geometry. Direct rigorous proof for this assignment is, however, most desirable. In favorable cases, e.g., $\text{NiCl}(\text{CO}-1\text{-Ad})(\text{PEt}_3)_2$, the methyl proton resonances of the PEt_3 ligands appear as a pseudo 1:4:6:4:1 quintet in the ^1H NMR spectra. This pattern is characteristic^{2a} of *trans*- $\text{NiX}(\text{Y})(\text{PEt}_3)_2$ complexes, and the structural assignment is therefore confirmed. In most cases, e.g., $\text{NiCl}(2\text{-ClC}_6\text{H}_4)(\text{PEt}_3)_2$, the methyl and methylene proton resonances of the PEt_3 groups overlap and structural conclusions cannot be drawn from the spectra. It is possible to separate the methyl and methylene proton resonances by recording the spectra in the presence of the NMR shift reagent $\text{Eu}(\text{fod})_3$. Three $\text{NiCl}(\text{aryl})(\text{PEt}_3)_2$ complexes were examined and the downfield shifts induced by $\text{Eu}(\text{fod})_3$ increased in the order 2,5-dichlorophenyl < 2-chlorophenyl < mesityl. The mesityl complex was on hand from other work. In all cases, pseudo-quintets were apparent for the PEt_3 methyl proton resonances, although the resonance of a *tert*-butyl group in $\text{Eu}(\text{fod})_3$ now overlapped different portions of each quintet. In the mesityl compound, the magnitude of deshielding for each type of proton decreased in the order $\text{PCH}_2 > \text{ortho-CH}_3 > \text{PCH}_2\text{CH}_3 > \text{meta-H} > \text{para-CH}_3$. The ortho and para protons in $\text{NiCl}(2,5\text{-Cl}_2\text{C}_6\text{H}_3)(\text{PEt}_3)_2$ are each coupled to two equal P nuclei further confirming its *trans* structure. The pseudo-quintets can be observed in the spectra of the acyl nickel complexes without applying a shift reagent. However shift reagent studies were performed to ascertain the point of greatest Lewis basicity toward the reagent. For $\text{NiCl}[\text{COCH}_2\text{C}(\text{CH}_3)_3](\text{PEt}_3)_2$, the deshielding effect on the proton resonances decreased in the order $\text{COCH}_2 > \text{PCH}_2 \sim \text{C}(\text{CH}_3)_3 > \text{PCH}_2\text{CH}_3$. This order indicates that the acyl oxygen interacts more strongly with $\text{Eu}(\text{fod})_3$ than does chlorine bound to nickel. All the acyl nickel complexes gradually decomposed in the presence of $\text{Eu}(\text{fod})_3$.

The ^1H NMR spectra of many of these complexes show the effect of the paramagnetic anisotropy⁹ of the metal. Useful structural conclusions can be deduced from this phenomenon such as was done with the 2-(1,3-butadienyl)nickel complex (vide supra). The structure assignments for the benzoylnickel complexes are strongly supported by this effect. Particularly illustrative is a comparison of the spectrum of the 4-chlorophenylnickel complex with that of the 4-chlorobenzoyl derivative. For the 4-chlorophenyl compound, the resonances of the protons ortho to nickel appear at δ 7.23 ppm as a doublet,



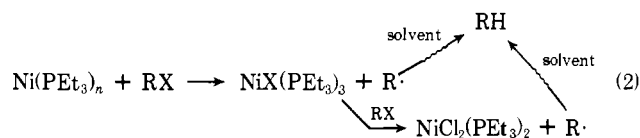
broadened by coupling with the phosphorus nuclei. In the 4-chlorobenzoyl complex, the doublet resonance for the corre-

sponding protons is sharp and is shifted downfield to δ 8.44 ppm. The structure of the benzoyl complex allows the ortho H atoms to more closely approach the nickel atom above the bonding plane of the complex.

In Table I, infrared absorptions assigned as nickel-chloride stretching vibrations are given for most of the organonickel complexes. These frequencies fall between 325 and 380 cm^{-1} and do not show the traditional influence from the *trans* organic ligands. Table I also contains a listing of asymmetric nickel-phosphorus stretching vibrations assigned to strong absorptions observed between 215 and 235 cm^{-1} for most of the $\text{NiCl}(\text{R})(\text{PEt}_3)_2$ complexes. When this vibration was not observed, we presume it fell outside the capability of our instrument (i.e., below 200 cm^{-1}).

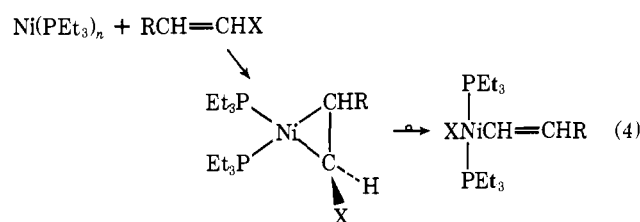
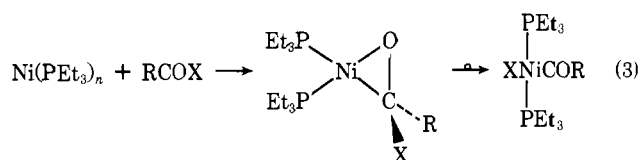
It would be desirable to assign *cis* vs. *trans* configurations to these complexes simply on the basis of their infrared spectra. After examining the spectra of more than 40 nickel complexes bearing two PEt_3 ligands, the only consistent differences we observed between *cis* and *trans* complexes were the relative intensities of three PEt_3 absorptions falling between 770 and 710 cm^{-1} . For *cis* complexes, the bands typically appear at 763 s, 743 ms, and 720 s cm^{-1} while for *trans* complexes they typically appear at 765 s, 727 ms, and 713 w cm^{-1} (Figure 2). In a few cases, vibrations of other ligands on nickel also occur in this region and mask this empirical correlation. The multiplicity of the δ_{CCP} vibration of the triethylphosphine ligands that occurs between 412 and 442 cm^{-1} should *not* be considered as a reliable method to diagnose *cis* vs. *trans* stereochemistry,^{2a} since a few *trans* complexes have now been encountered with more than one absorption in this region.

Mechanism. The combination of radical, template, and nucleophilic-substitution mechanisms previously outlined by Osborn¹⁹ for oxidative additions of organic halides to other low-valent metal complexes can also readily explain the results described herein. Alkyl halides appear to react by a radical process (likely initiated by a single electron transfer from Ni to RX) (eq 2) to form nickel(I) complexes of the type

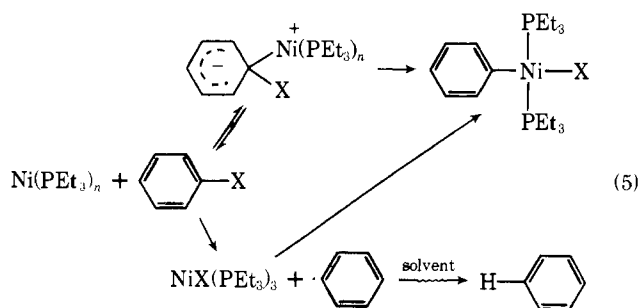


$\text{NiX}(\text{PR}_3)_3$. In some cases the nickel(I) complex can be isolated,²⁰ or it might react with another alkyl halide to form a $\text{NiX}_2(\text{PR}_3)_2$ complex as in the 3-chloro-2-norbornanone experiment. The alkyl radicals produced likely decay by hydrogen atom abstractions from the solvent or PR_3 groups. This was confirmed in the 3-chloro-2-norbornanone experiment. Previous reports of reactions of other nickel(0) complexes with alkyl halides have also described the formation of nickel(I) complexes,^{5,21} except in one case where the alkyl nickel complexes could be isolated.^{4d}

The acyl and vinyl halides probably react via a template¹⁹ mechanism (eq 3 and 4), i.e., coordination of the π system to



nickel followed by a rearrangement to the final product. Although the intermediate π complexes have not been isolated for these reactions, numerous generically related examples are known to exist.² The rearrangement step presumably occurs by an ionic process resembling nucleophilic substitution and not via radicals.^{2a} This has been strongly supported by the observation of retention of stereochemistry in the oxidative addition of *trans*- β -bromostyrene to a nickel(0) complex⁴ⁱ and by the isolation of high yields of acyl nickel complexes in the oxidative additions of pivaloyl chloride and 1-adamantylcarbonyl chloride reported here. A radical process would certainly allow double-bond isomerization in the bromostyrene experiment, while the two acid chlorides mentioned would be susceptible to decarbonylation in a radical reaction.²² The earlier failures to isolate acyl nickel products from acyl halides and nickel(0) complexes most likely are a consequence of product instability (stability is dependent on both the acyl and phosphine groups chosen) or an unsatisfactory synthetic procedure and were not caused by interference from an unproductive mechanism.



Two competing mechanisms complicate aryl halide oxidative additions (eq 5). When the aryl halide is activated by electron-withdrawing substituents, an aromatic nucleophilic-substitution mechanism is dominant. This regime was first inferred from the dramatic selectivities observed between halogens in reactions of multihalobenzenes³ and has now been confirmed by a rigorous kinetic study.²³ Sterically crowded and unactivated aryl halides appear to react by a radical process (probably initiated by single electron transfer to the aromatic system).²⁴ Both mechanisms can provide the aryl nickel product, but collapse of the radical pair is unfavorable for sterically hindered aryl radicals. Thus 2-bromo-*m*-xylene and hexachlorobenzene did not produce aryl nickel products even though the expected 2,6-dimethylphenyl- and pentachlorophenylnickel products would be exceptionally stable. Radical intermediates can also explain the formation of the cyclized organic products obtained in the reaction of Ni(PPh₃)₄ with 2-chlorophenyl acrylate.^{25,26} It is probable that both mechanisms occur simultaneously in the oxidative additions of several of the aryl halides. The isolation of only *trans* complexes from these reactions is probably a thermodynamic consequence and therefore has no mechanistic relevance. The high stability of nickel(I) complexes compared to those of palladium and platinum likely makes radical reactions even more attractive for nickel than for palladium and platinum.¹⁹

Conclusion

The oxidative-addition reaction of aryl, acyl, and vinyl halides is an excellent practical method for the synthesis of many organonickel compounds of the type *trans*-NiX(R)(PR'₃)₂. When radical processes are favored by steric or electronic considerations, the oxidative-addition reaction may not provide the expected organonickel product. The formation of benzoyl nickel complexes by carbonylation of phenylnickel complexes supports the intervention of these species in the nickel-catalyzed carbonylation of aryl halides.^{1b}

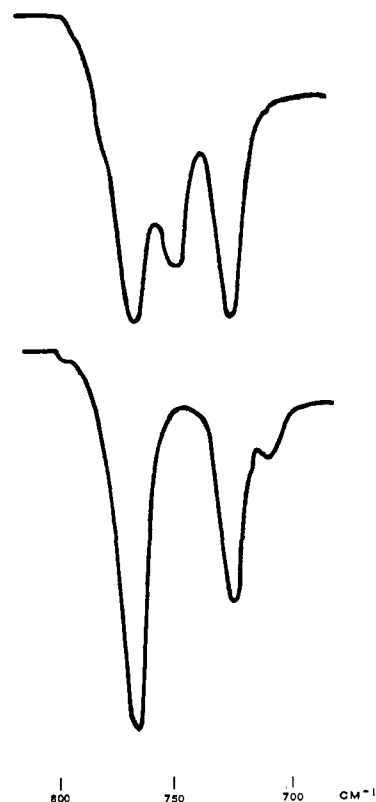


Figure 2. Examples of infrared spectra (700–800-cm⁻¹ region) for nickel complexes bearing *cis* (upper) and *trans* (lower) PEt₃ ligands.

Experimental Section

Unless otherwise specified, all manipulations of air-sensitive 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. Literature procedures were used to prepare Ni(1,5-C₈H₁₂)₂²⁷ and Ni(PEt₃)₄.⁵ Melting points were determined in open capillary tubes *in the drybox*. Most infrared spectra were run on KBr or CsI pellets, but very air-sensitive compounds required Nujol mulls pressed tightly between salt plates to avoid oxidation. Instruments used were Perkin-Elmer Models 137 and 621 infrared spectrophotometers, a Varian Associates T-60 NMR spectrometer, and a Hewlett-Packard Model 5750 gas chromatograph. Elemental analyses were performed by Dr. T. V. Irons at Phillips Research Center, except very air-sensitive compounds which were analyzed by Schwarzkopf Microanalytical Laboratory of Woodside, N.Y. Table II presents physical properties and elemental analyses of all new compounds prepared. Some of the samples gradually decomposed at ambient temperatures under argon and could not be satisfactorily analyzed. In spite of this, some analyses were attempted, and the results are given in Table II. A complete tabulation of infrared and NMR data for most of the compounds reported is given in Tables III and IV. (See paragraph at end of paper regarding supplementary material.)

In Situ Reactions with Ni(PEt₃)₂(C₂H₄). (a) **With 1,2-Dichlorobenzene.** Complete details are given only for one example. A mixture of 2.57 g (10 mmol) of Ni(acac)₂, 2.36 g (20 mmol) of PEt₃, and 50 mL of ether was stirred under an ethylene atmosphere at 0 °C, and 10 mL of a 25% solution of Et₂AlOEt in isopentane was slowly added. The product from this reaction has been shown to be Ni(PEt₃)₂(C₂H₄).⁸ The mixture was stored overnight at -78 °C. The solution was then warmed to 0 °C, and 3.0 mL of 1-butanol and 3.9 g (27 mmol) of 1,2-dichlorobenzene were added. The mixture was warmed to 35 °C and stirred until gas evolution ceased. The reaction was quenched with dilute aqueous HCl, and the organic phase was concentrated to a yellow-brown oil under vacuum. The concentrate was chromatographed on a column of acid-washed alumina, and a yellow-brown oil was eluted with 1:1 ether-pentane. Crystallization of the oil from methanol afforded 0.83 g (19%) of yellow *trans*-chloro(2-chlorophenyl)bis(triethylphosphine)nickel(II): mp 91–92 °C.

Table II. Properties and Analyses of New Compounds

Compound	Mp, °C	Color	Calcd (Found) Analyses		
			% C	% H	% Ni
<i>trans</i> -NiBr(CH=CH ₂)(PEt ₃) ₂	~32	Yellow-brown			
<i>trans</i> -NiCl[C(CH=CH ₂)=CH ₂](PEt ₃) ₂	68–68.5	Yellow-brown	50.10 (50.35)	9.19 (9.16)	
<i>trans</i> -NiCl(C ₆ H ₅)(PEt ₃) ₂ ^a	75–75.5	Yellow-brown	53.08 (53.39)	8.60 (8.87)	14.41 (14.14)
<i>trans</i> -NiBr(C ₆ H ₅)(PEt ₃) ₂	85–86	Brown	47.82 (47.92)	7.81 (7.86)	12.99 (13.27)
<i>trans</i> -NiCl(2-ClC ₆ H ₄)(PEt ₃) ₂	91–92	Yellow-brown	48.91 (48.81)	7.75 (7.93)	
<i>trans</i> -NiBr(2-ClC ₆ H ₄)(PEt ₃) ₂	109–110	Yellow-brown	44.44 (44.35)	7.04 (6.82)	
<i>trans</i> -NiCl(3-ClC ₆ H ₄)(PEt ₃) ₂	94–95	Yellow-brown	48.91 (49.05)	7.75 (7.51)	13.28 (13.58)
<i>trans</i> -NiCl(4-ClC ₆ H ₄)(PEt ₃) ₂	86–87.5	Yellow-brown	48.91 (48.86)	7.75 (7.89)	13.28 (13.50)
<i>trans</i> -NiBr(4-ClC ₆ H ₄)(PEt ₃) ₂	118–120 dec	Brown	44.44 (45.25)	7.04 (6.80)	
<i>trans</i> -NiCl(2,5-Cl ₂ C ₆ H ₃)(PEt ₃) ₂	101–102	Yellow	45.37 (45.18)	6.98 (6.64)	
<i>trans</i> -NiF(C ₆ F ₅)(PEt ₃) ₂	64–66	Yellow	44.94 (44.51)	6.29 (6.71)	12.20 (12.7)
<i>trans</i> -NiCl(COCH ₃)(PEt ₃) ₂	<30	Orange			
<i>trans</i> -NiCl[COCH ₂ C(CH ₃) ₃](PEt ₃) ₂	100–101	Orange	50.32 (51.36)	9.62 (10.11)	13.67 (13.80)
<i>trans</i> -NiCl[CO(C(CH ₃) ₃)](PEt ₃) ₂	73–74 dec	Red-brown	49.13 (49.39)	9.46 (9.76)	14.13 (14.43)
<i>trans</i> -NiCl(CO-1-Ad)(PEt ₃) ₂ ^b	148–149 dec	Red-brown	55.95 (56.35)	9.19 (9.34)	11.89 (11.4)
<i>trans</i> -NiF(COC ₆ H ₅)(PEt ₃) ₂	55.5–57	Yellow-brown			
<i>trans</i> -NiCl(COC ₆ H ₅)(PEt ₃) ₂ ^c	73.5–75	Orange	52.39 (52.58)	8.10 (8.34)	
<i>trans</i> -NiBr(COC ₆ H ₅)(PEt ₃) ₂	77–80	Yellow-brown	47.54 (48.28)	7.35 (7.25)	
<i>trans</i> -NiCl(CO-2-ClC ₆ H ₄)(PEt ₃) ₂ ^d	84–86.5 dec	Orange	48.55 (49.75)	7.29 (7.96)	12.49 (12.71)
<i>trans</i> -NiCl(CO-3-ClC ₆ H ₄)(PEt ₃) ₂ ^e	84–86	Orange	48.55 (49.20)	7.29 (7.85)	12.49 (12.89)
<i>trans</i> -NiCl(CO-4-ClC ₆ H ₄)(PEt ₃) ₂	101–110 dec	Orange	48.55 (48.56)	7.29 (7.34)	

^a Cl: calcd 8.70 (found 8.90). P: calcd 15.21 (found 14.92). ^b Mol wt: calcd 494 (found 493). ^c Mol wt: calcd 436 (found 417). ^d Cl: calcd 15.09 (found 15.38). ^e Cl: calcd 15.09 (found 15.64).

(b) **With 1,2,4-Trichlorobenzene.** A similar reaction with 1,2,4-trichlorobenzene produced a 6% yield of *trans*-chloro(2,5-dichlorophenyl)bis(triethylphosphine)nickel(II), mp 101–102 °C. Protonolysis of this recrystallized product by HCl in benzene yielded *p*-dichlorobenzene, a trace of *m*-dichlorobenzene, and no *o*-dichlorobenzene (by GLC analysis).

(c) **With 2-Bromochlorobenzene.** A similar reaction with 2-bromochlorobenzene produced a 9% yield of *trans*-bromo(2-chlorophenyl)bis(triethylphosphine)nickel(II); mp 108–109 °C.

(d) **With Bromopentafluorobenzene.** A similar reaction with bromopentafluorobenzene produced an 11% yield of *trans*-bromo(pentafluorophenyl)bis(triethylphosphine)nickel(II); mp 130–131 °C (lit.²⁸ mp 130–131 °C).

(e) **With Other Organic Compounds.** Similar reactions with hexachlorobenzene and hexabromobenzene yielded small amounts of tetrahalophenylnickel compounds which were not thoroughly characterized. 1,1,2,2-Tetrachloroethane, hexachlorocyclopentadiene, 1,2-dichloro-4-nitrobenzene, and tetracyanoethylene did not yield organonickel products with this procedure.

In Situ Reactions with Ni(PEt₃)₂(1,5-C₈H₁₂). (a) **With Chloropentafluorobenzene.** Complete details are given for one example only. A solution of Ni(PEt₃)₂(1,5-C₈H₁₂) was prepared by stirring 1.10 g (4.01 mmol) of Ni(1,5-C₈H₁₂)₂ and 0.94 g (8.0 mmol) of PEt₃ in 3 mL of hexane. The homogeneous yellow-brown solution was then slowly added to a stirred solution of 0.83 g (4.10 mmol) of chloropentafluorobenzene in 5 mL of hexane at 25 °C. The solution became very warm. After the addition was complete, the brown solution was cooled to –72 °C, and a yellow solid precipitated. The solid was collected by suction filtration and was washed with hexane to yield 1.58 g (79%) of *trans*-chloro(pentafluorophenyl)bis(triethylphosphine)nickel(II). Recrystallization of the solid from ether afforded yellow platelets; mp 113–114 °C (lit.²⁸ mp 112–113 °C).

(b) **With Bromopentafluorobenzene.** A similar reaction with bromopentafluorobenzene produced a 77% yield of *trans*-bromo(pentafluorophenyl)bis(triethylphosphine)nickel(II), mp 127–129 °C.

(c) **With Hexafluorobenzene.** A similar reaction with hexafluorobenzene was allowed to stand at 30–35 °C for several days. The mixture was filtered and cooled to –72 °C which induced the formation of yellow-brown crystals. The mother liquor was removed by syringe and the crystals were dried on a clay plate affording a 7% yield of *trans*-fluoro(pentafluorophenyl)bis(triethylphosphine)nickel(II), mp 60–61.5 °C. The compound gradually decomposed on standing at 30 °C under argon. The IR spectrum of this product is nearly

identical with that of the chloro and bromo analogues (see Table III).

(d) **With Other Aryl Halides.** Similar reactions with chlorobenzene, bromobenzene, *o*-, *m*-, and *p*-dichlorobenzene, and 1,2,4-trichlorobenzene required 40–60 °C temperatures over several hours to several days to react. The expected organonickel products were obtained in very impure forms in 6–64% yields. Recrystallizations from ether afforded low yields of pure products. Organonickel products were not isolated from hexachlorobenzene or hexabromobenzene with this procedure. 2-Chlorophenyl acrylate was polymerized by Ni(PEt₃)₂(1,5-C₈H₁₂).

(e) **With Vinyl Bromide.** Vinyl bromide (0.50 g, 4.7 mmol) was added to a solution of 4.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) in 5 mL of hexane at –50 °C. The solution turned brown and was cooled to –72 °C. No precipitate formed, so the solution was gradually warmed to 10 °C and then was again cooled to –72 °C. Brown crystals formed which were suction filtered, washed with hexane, and vacuum dried at temperatures below –25 °C yielding 1.23 g (76%) of *trans*-bromo(vinyl)bis(triethylphosphine)nickel(II), mp 32–37 °C. The product rapidly decomposes at 30 °C under argon. Attempts to recrystallize the product were unsuccessful.

(f) **With 2-Chloro-1,3-butadiene.** From the reaction of 20 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) and 23 mmol of triply distilled 2-chloro-1,3-butadiene in 20 mL of ether was obtained 6.35 g (83%) of *trans*-chloro[2-(1,3-butadienyl)]bis(triethylphosphine)nickel(II), mp 68–68.5 °C.

(g) **With 1-Bromoadamantane.** A reaction similar to (a) was performed with 1-bromoadamantane in 20 mL of hexane–benzene. The solution turned brown-black, but no crystals formed on cooling to 5–10 °C. The mixture was taken to dryness under vacuum, and the residue was treated with 5–10 mL of hexane. The solution was decanted from some black solids and cooled to –55 °C. Crystal formation could not be induced.

(h) **With Acetyl Chloride.** A reaction similar to (a) was performed with 2.0 mmol of acetyl chloride and 2.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂). Orange-brown crystals of *trans*-chloro(acetyl)bis(triethylphosphine)nickel(II) precipitated at –72 °C and were collected by suction filtration at low temperature. When warmed to 25 °C, the product melted and gradually decomposed. The yield was not determined.

(i) **With *tert*-Butylacetyl Chloride.** A reaction similar to (h) was performed with 2.0 mmol of *tert*-butylacetyl chloride. A white solid immediately precipitated which was removed by filtration. The solid was identified as (CH₃)₃CCH₂COPEt₃⁺Cl[–] (10% yield). The filtrate

yielded 0.60 g (70%) of dark orange *trans*-chloro(*tert*-butylacetyl)-bis(triethylphosphine)nickel(II), mp 100–101 °C.

(j) **With Pivaloyl Chloride.** A reaction similar to (h) was performed with 2.0 mmol of pivaloyl chloride. The solution yielded 0.55 g (66%) of red-brown platelets of *trans*-chloro(pivaloyl)bis(triethylphosphine)nickel(II), mp 73–74 °C dec. The filtrate was allowed to stand at 40 °C for 30 h. On cooling to –72 °C, the solution precipitated 0.12 g (17%) of red *trans*-dichlorobis(triethylphosphine)nickel(II).

(k) **With 1-Adamantanecarbonyl Chloride.** A reaction similar to (h) was performed with 2.0 mmol of 1-adamantanecarbonyl chloride. The solution yielded 0.75 g (76%) of red-brown *trans*-chloro(1-adamantanecarbonyl)bis(triethylphosphine)nickel(II), mp 148–149 °C dec.

(l) **With Benzoyl Chloride.** A 20-mL solution containing 20 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) was slowly added to 20 mmol of benzoyl chloride in 50 mL of hexane. A white precipitate formed but redissolved when 5–10 mL of acetonitrile was added. Cooling the solution to –72 °C caused orange crystals to precipitate and these were collected by suction filtration. On warming to room temperature the crystals began to melt. They resolidified when subjected to a high vacuum affording 6.83 g (78%) of *trans*-chloro(benzoyl)bis(triethylphosphine)nickel(II). The melting of the crystals on warming to room temperature was unexpected and is believed to be caused by the formation of a low-melting acetonitrile solvated complex. Recrystallization from acetonitrile containing solvents reproduced the same behavior. Recrystallization from ether gave orange crystals, mp 73.5–75 °C.

(m) **With Benzoyl Bromide.** From 4.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) and 4.0 mmol of benzoyl bromide was obtained 0.66 g (34%) of *trans*-bromo(benzoyl)bis(triethylphosphine)nickel(II). Recrystallization from ether afforded yellow-brown crystals: mp 77–80 °C.

(n) **With Benzoyl Fluoride.** From 4.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) and 4.1 mmol of benzoyl fluoride was obtained 1.15 g (69%) of brown *trans*-fluoro(benzoyl)bis(triethylphosphine)nickel(II), mp 55.5–57 °C. The complex decomposed on standing.

(o) **With 2-Chlorobenzoyl Chloride.** From 2.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) and 2.0 mmol of 2-chlorobenzoyl chloride was obtained 0.62 g (66%) of impure (unsatisfactory C, H analyses) red-brown *trans*-chloro(2-chlorobenzoyl)bis(triethylphosphine)nickel(II), mp 78–80 °C dec. The filtrate yielded 0.06 g (7%) of *trans*-chloro(2-chlorophenyl)bis(triethylphosphine)nickel(II).

(p) **With 3-Chlorobenzoyl Chloride.** From 2.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) and 2.0 mmol of 3-chlorobenzoyl chloride was obtained 0.57 g of impure orange-brown *trans*-chloro(3-chlorobenzoyl)bis(triethylphosphine)nickel(II). Recrystallization from ether produced orange crystals of the product that were still impure (unsatisfactory C analysis), mp 80–86 °C.

(q) **With 4-Chlorobenzoyl Chloride.** From 2.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) and 2.0 mmol of 4-chlorobenzoyl chloride was obtained 0.67 g (71%) of orange *trans*-chloro(4-chlorobenzoyl)bis(triethylphosphine)nickel(II), mp 101–110 °C dec.

(r) **With Pentafluorobenzoyl Chloride.** From 2.0 mmol of Ni(PEt₃)₂(1,5-C₈H₁₂) and 2.0 mmol of pentafluorobenzoyl chloride was obtained 0.26 g (26%) of yellow *trans*-chloro(pentafluorophenyl)bis(triethylphosphine)nickel(II), mp 110–111.5 °C.

(s) **With Acryloyl and Cinnamoyl Chlorides.** The products from these reactions appeared to be very unstable and no well-defined solid nickel complexes were obtained.

Reactions of Ni(PEt₃)₄. (a) **With Chlorobenzene.**²⁹ Complete details are given for this example only. A purple solution of 1.06 g (2.0 mmol) of Ni(PEt₃)₄ in 5 mL of hexane was slowly added to a stirred solution of 0.23 g (2.0 mmol) of chlorobenzene in 2 mL of hexane. The resulting red-brown solution was stirred for a few minutes and then cooled to –72 °C. Yellow-brown crystals formed that were collected by suction filtration, washed with cold hexane, and dried under vacuum. Some additional product was recovered from the filtrate yielding a total of 0.69 g (85%) of *trans*-chloro(phenyl)bis(triethylphosphine)nickel(II), mp 64–65 °C. Recrystallization of the sample from ether gave a pure product, mp 75–75.5 °C.

(b) **With Bromobenzene.** From 2.0 mmol of Ni(PEt₃)₄ and 0.32 g (2.0 mmol) of bromobenzene was obtained 0.65 g (72%) of brown *trans*-bromo(phenyl)bis(triethylphosphine)nickel(II), mp 85–86 °C (lit.^{1h} mp 82–83 °C dec).

(c) **With 1,2-Dichlorobenzene.** From 2.0 mmol of Ni(PEt₃)₄ and 0.59 g (4.0 mmol) of 1,2-dichlorobenzene was obtained 0.62 g (70%)

of yellow-brown *trans*-chloro(2-chlorophenyl)bis(triethylphosphine)nickel(II), mp 89–90 °C.

(d) **With 1,3-Dichlorobenzene.** From 2.0 mmol of Ni(PEt₃)₄ and 0.59 g (4.0 mmol) of 1,3-dichlorobenzene was obtained 0.67 g (76%) of yellow-brown *trans*-chloro(3-chlorophenyl)bis(triethylphosphine)nickel(II), mp 94–95 °C.

(e) **With 1,4-Dichlorobenzene.** A solution of 2.0 mmol of Ni(PEt₃)₄ in 5 mL of hexane was slowly added to a stirred solution of 0.30 g (2.0 mmol) of 1,4-dichlorobenzene in 2 mL of hexane. Some white solids precipitated which were filtered off. Cooling the brown filtrate to –72 °C afforded 0.73 g (83%) of *trans*-chloro(4-chlorophenyl)bis(triethylphosphine)nickel(II), mp 80–83 °C. Recrystallization of the sample from ether gave a pure product, mp 86–87.5 °C.

(f) **With 1,2,4-Trichlorobenzene.** From 2.0 mmol of Ni(PEt₃)₄ and 0.37 g (2.0 mmol) of 1,2,4-trichlorobenzene was obtained 0.47 g (49%) of yellow *trans*-chloro(2,5-dichlorophenyl)bis(triethylphosphine)nickel(II). Recrystallization of the sample from ether gave a pure product, mp 98–100 °C.

(g) **With 2-Bromochlorobenzene.** From 2.0 mmol of Ni(PEt₃)₄ and 0.38 g (2.0 mmol) of 2-bromochlorobenzene was obtained 0.78 g (80%) of yellow-brown *trans*-bromo(2-chlorophenyl)bis(triethylphosphine)nickel(II). Recrystallization of the sample from ether gave a pure product, mp 109–110 °C.

(h) **With 4-Bromochlorobenzene.** From 2.0 mmol of Ni(PEt₃)₄ and 0.38 g (2.0 mmol) of 4-bromochlorobenzene was obtained 0.82 g (84%) of brown *trans*-bromo(4-chlorophenyl)bis(triethylphosphine)nickel(II). Recrystallization of the sample from toluene/ether gave a pure product, mp 118–120 °C dec.

(i) **With 2-Bromo-*m*-xylene.** A solution of 2.0 mmol of Ni(PEt₃)₄ and 0.40 g (2.2 mmol) of 2-bromo-*m*-xylene in 7 mL of hexane was stirred overnight at 25 °C. The color gradually turned from purple to brown. Some white solids were removed by filtration, and the filtrate was cooled to –72 °C. Yellow-brown platelets precipitated which were collected by suction filtration to yield 0.50 g (51%) of NiBr(PEt₃)₃: mp 46–48 °C; IR (Nujol) 2930 vs, 1460 vs, 1420 m, 1380 s, 1250 w, 1055 w, 1030 s, 1000 w, 980 w, 763 s, 752 ms, 727 ms, 707 ms, 678 m cm⁻¹.

Anal. Calcd for C₁₈H₁₄BrNiP₃: C, 43.85; H, 9.20; Br, 16.20; Ni, 11.91. Found: C, 43.53; H, 9.08; Br, 15.78; Ni, 11.32.

(j) **With Hexachlorobenzene.** From 2.0 mmol of Ni(PEt₃)₄ and 0.57 g (2.0 mmol) of hexachlorobenzene in 10 mL of toluene was obtained 0.34 g of a mixture of red and white crystals. An IR spectrum of this sample identified it as a mixture of pentachlorobenzene and *trans*-NiCl₂(PEt₃)₂. Repeating the reaction in 50 mL of tetrahydrofuran yielded 0.15 g of the same mixture.

(k) **With 3-Chloro-2-norbornanone.** A solution of 0.75 g (1.4 mmol) of Ni(PEt₃)₄ and 1.5 g (10 mmol) of 3-chloro-2-norbornanone were stirred in 20 mL of ether. After the slightly exothermic reaction had subsided, the solution was stored overnight at –25 °C. Suction filtration of the solution produced 0.40 g (79%) of *trans*-NiCl₂(PEt₃)₂ which was identified by its IR spectrum and satisfactory C, H, Ni, P analyses. The mother liquor was filtered through alumina, and the filtrate was evaporated to an oil. GLC analysis of the oil was performed on a 0.25 in. × 5 ft column packed with 10% Apiezon L on 60/80 Chromosorb G temperature programmed from 100 to 250 °C. In addition to unreacted 3-chloro-2-norbornanone, one predominant and several minor products were detected. The major product was isolated by preparative GLC and was found to be identical with authentic 2-norbornanone.

Carbonylations. (a) **Of *trans*-NiCl(C₆H₅)(PEt₃)₂.** A 21-mL glass pressure tube containing 0.81 g (2.0 mmol) of *trans*-NiCl(C₆H₅)(PEt₃)₂ in 5 mL of hexane was flushed with carbon monoxide and then pressured to 15 psig with carbon monoxide and allowed to stand at 25 °C. Orange crystals formed overnight, and the tube was cooled to –72 °C. The crystals were collected by suction filtration, were washed with cold ether, and were dried under vacuum to yield 0.70 g (80%) of orange *trans*-chloro(benzoyl)bis(triethylphosphine)nickel(II), mp 73–75 °C. Its IR spectrum is identical with the benzoyl nickel complex prepared by oxidative addition.

(b) **Of *trans*-NiCl(2-C₆H₄)(PEt₃)₂.** An experiment identical with (a) with 0.44 g (1.0 mmol) of *trans*-NiCl(2-C₆H₄)(PEt₃)₂ resulted in the recovery of 0.39 g (89%) of starting material. Repeating the experiment with 1.05 g (2.38 mmol) of *trans*-NiCl(2-C₆H₄)(PEt₃)₂ and 10 mL of hexane in an aerosol compatibility bottle at 20 psig of carbon monoxide led to a rapid but small pressure drop and some orange crystal precipitation. After standing overnight, the excess CO

was vented and the mixture was cooled to $-20\text{ }^{\circ}\text{C}$ and suction filtered. Orange crystals contaminated with black and green impurities were collected (0.80 g). The product was dissolved in ether and filtered. The solution evolved CO during this process. The filtrate was resubjected to a 200 psig pressure of CO, cooled to $-72\text{ }^{\circ}\text{C}$, and suction filtered to yield 0.10 g (9%) of orange *trans*-chloro(2-chlorobenzoyl)bis-(triethylphosphine)nickel(II), mp $84\text{--}86.5\text{ }^{\circ}\text{C}$ dec.

(c) **Of *trans*-NiCl(3-CIC₆H₄)(PEt₃)₂.** An experiment similar to (a) with 0.44 g (1.0 mmol) of *trans*-NiCl(3-CIC₆H₄)(PEt₃)₂ was performed. When the tube was pressured to 16 psig with carbon monoxide, rapid stirring caused the pressure to fall to 3 psig in a few minutes. The reaction produced 0.43 g (92%) of orange *trans*-chloro(3-chlorobenzoyl)bis(triethylphosphine)nickel(II), mp $83\text{--}88\text{ }^{\circ}\text{C}$. Recrystallization of the sample from ether at low temperature gave a purer product, mp $84\text{--}86\text{ }^{\circ}\text{C}$.

(d) **Of *trans*-NiCl[C(CH=CH₂)=CH₂](PEt₃)₂.** An aerosol compatibility tube containing 2.0 g (5.2 mmol) of *trans*-NiCl[C(CH=CH₂)=CH₂](PEt₃)₂ in 8 mL of hexane was pressured to 50 psig with carbon monoxide. After 0.5 h, the pressure had fallen to 14 psig and a yellow solid had formed. The solution was filtered and 1.22 g of an unidentified water-soluble yellow solid was collected. The filtrate was evaporated to dryness and the yellow-brown oil residue exhibited IR absorptions at 2030 s, 2000 vs, and 1925 ms cm⁻¹ plus PEt₃ absorptions suggesting the oil is a mixture of Ni(CO)_n(PEt₃)_m complexes. A weak absorption was also present at 1800 cm⁻¹.

Acknowledgments. We are indebted to Mr. Bill Loffer for outstanding laboratory assistance and to Mr. J. P. Butler for recording many of the infrared spectra.

Supplementary Material Available. Tables III and IV, infrared and NMR spectra (10 pages). Ordering information is given on any current masthead page.

References and Notes

- See, e.g., (a) L. Cassar, S. Ferrara, and M. Foà, "Homogeneous Catalysis-II", *Adv. Chem. Ser.*, **No. 132**, 252-273 (1974); (b) L. Cassar and M. Foà, *J. Organomet. Chem.*, **51**, 381 (1973); (c) L. Cassar, *ibid.*, **93**, 253 (1975); (d) K. Tamao, K. S. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4374 (1972); (e) M. F. Semmelhack, P. M. Helquist, and L. D. Jones, *ibid.*, **93**, 5908 (1971); (f) M. F. Semmelhack, R. D. Stauffer, and T. D. Rogerson, *Tetrahedron Lett.*, 4519 (1973); (g) R. Cramer and D. R. Coulson, *J. Org. Chem.*, **40**, 2267 (1975); (h) D. G. Morrell and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 7262 (1975).
- Reviews: (a) D. R. Fahey, *Organomet. Chem. Rev., Sect. A*, **7**, 245 (1972); (b) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. I, Academic Press, New York, N.Y., 1974, pp 169-171.
- D. R. Fahey, *J. Am. Chem. Soc.*, **92**, 402 (1970).
- (a) J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3019 (1969); (b) J. Browning, M. Green, and F. G. A. Stone, *ibid.*, 453 (1971); (c) M. Hidai, T. Kashiwagi, T. Ikeuchi, and Y. Uchida, *J. Organomet. Chem.*, **30**, 279 (1971); (d) P. W. Jolly, K. Jonas, C. Krüger, and Y.-H. Tsay, *ibid.*, **33**, 109 (1971); (e) W. B. Hughes, *J. Org. Chem.*, **36**, 4073 (1971); (f) P. S. Fitton and E. A. Rick, U.S. Patent 3 674 825 (1972); (g) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *J. Am. Chem. Soc.*, **95**, 3180 (1973); (h) D. R. Fahey, *J. Organomet. Chem.*, **57**, 385 (1973); (i) L. Cassar and A. Giarrusso, *Gazz. Chim. Ital.*, **103**, 793 (1973); (j) G. W. Parshall, *J. Am. Chem. Soc.*, **96**, 2360 (1974); (k) S. Otsuka, K. Tani, I. Kato, and O. Teranaka, *J. Chem. Soc., Dalton Trans.*, 2216 (1974); (l) R. G. Miller, D. R. Fahey, H. J. Golden, and L. C. Satek, *J. Organomet. Chem.*, **82**, 127 (1974); (m) K. J. Klabunde, J. Y. F. Low, and H. F. Efner, *J. Am. Chem. Soc.*, **96**, 1984 (1974); (n) M. Uchino, K. Asagi, A. Yamamoto, and S. Ikeda, *J. Organomet. Chem.*, **84**, 93 (1975); (o) W. B. Hughes and D. R. Fahey, U.S. Patent 3 887 441 (1975).
- C. S. Cundy, *J. Organomet. Chem.*, **69**, 305 (1974); Cundy described the color of Ni(PEt₃)₂(1,5-C₈H₁₂) as orange.
- C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 1647 (1970).
- C. A. Tolman, D. H. Gerlach, J. P. Jesson, and R. A. Schunn, *J. Organomet. Chem.*, **65**, C23 (1974).
- G. Herrmann, Ph.D. Dissertation, Technische Hochschule, Aachen, 1963.
- R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *J. Am. Chem. Soc.*, **92**, 1511 (1970).
- C. A. Aufdermarsh, *J. Org. Chem.*, **29**, 1994 (1964).
- A bis(triphenylphosphine)(2-chlorophenyl acrylate)nickel(0) complex can be isolated from the reaction of 2-chlorophenyl acrylate and Ni(PPh₃)₂(1,5-C₈H₁₂) or Ni(PPh₃)₄ with no acrylate polymerization. However, the reaction of 2-iodophenyl acrylate with Ni(PPh₃)₂(1,5-C₈H₁₂) yielded Ni(PPh₃)₃ and polymer.
- B. Corain and G. Favero, *J. Chem. Soc., Dalton Trans.*, 283 (1975).
- H. F. Klein, *Angew. Chem., Int. Ed. Engl.*, **12**, 402 (1973).
- M. Hidai, Y. Uchida, and I. Ogata in "Prospects in Organotransition-Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, pp 265-271.
- B. Corain and M. Martelli, *Inorg. Nucl. Chem. Lett.*, **8**, 39 (1972).
- M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964).
- C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
- This product seems to be a phosphonium salt. We have found that Ph₃PCH=CH₂⁺Br⁻ can be produced from PPh₃ and vinyl bromide in the presence of a catalytic amount of a nickel(0) complex. A similar catalysis with aryl halides has been described by L. Cassar and M. Foà, *J. Organomet. Chem.*, **74**, 75 (1974).
- J. A. Osborn, ref 14, pp 65-76.
- We have isolated NiBr(PPh₃)₃·C₆H₆ from the reaction of 1-bromoadamantane with Ni(PPh₃)₂(1,5-C₈H₁₂) in benzene.
- C. S. Cundy and H. Nöth, *J. Organomet. Chem.*, **30**, 135 (1971).
- At 25 °C, decarbonylation of the pivaloyl radical occurs faster than radical termination reactions: H. Schuh, E. J. Hamilton, Jr., H. Paul, and H. Fisher, *Helv. Chim. Acta*, **57**, 2011 (1974).
- M. Foà and L. Cassar, *J. Chem. Soc., Dalton Trans.*, 2572 (1975).
- I. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organomet. Chem.*, **84**, C7 (1975).
- Evidence for radical processes becomes more compelling as the phosphine ligand is changed to the bulkier and less basic triphenylphosphine. With PPh₃, the nickel(I) complexes are more easily isolated²⁰ and the bulkier ligands seem to hinder ionic reaction paths. For examples (in benzene solutions), the reactions of Ni(PPh₃)₄ with chloroprene and 2-iodophenyl acrylate yielded NiCl(PPh₃)₃·C₆H₆ and NiI(PPh₃)₃, respectively.
- D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, **98**, 4499 (1976), and unpublished results.
- B. Bogdanović, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966).
- J. R. Phillips, D. T. Rosevear, and F. G. A. Stone, *J. Organomet. Chem.*, **2**, 455 (1964).
- This reaction has been previously disclosed without details: D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muettterties, *J. Am. Chem. Soc.*, **93**, 3543 (1971).