product crystallized from the hot solution. The crude product was collected, washed with a small volume of ethanol (in which it is very soluble), and recrystallized from ethanol; yield, 40%. *Anal.* Calcd for $CoC_{15}H_{22}N_4Cl_2 \cdot H_2O$: C, 44.35; H, 5.96; N, 13.79. Found: C, 44.6; H, 6.39; N, 13.5.

**Co(CR)py($ClO_4$)$_2$.**—To a hot concentrated solution of 1 g of Co(CR)($ClO_4$)$_2 \cdot H_2O$ in acetone, a twofold excess of pyridine was added. Upon cooling, small dark maroon crystals formed. The mother liquor was concentrated under reduced pressure to obtain more of the product; yield, 50%. *Anal.* Calcd for $CoC_{15}H_{22}N_4(C_5H_5N)(ClO_4)_2$: C, 40.3; H, 4.57; N, 11.77. Found: C, 40.4; H, 4.45; N, 11.6.

**Co(CR)$NH_3$($ClO_4$)$_2$.**—One gram of Co(CR)$Br_2 \cdot H_2O$ was dissolved in ethanol and anhydrous ammonia gas was allowed to flow onto the surface of the solution. The color of the solution changed from red to dark maroon. A hot concentrated solution of sodium perchlorate in ethanol was added and the product precipitated immediately. The product was collected in air and washed thoroughly with ethanol in which it is very insoluble; yield, 80%. *Anal.* Calcd for $CoC_{15}H_{22}N_4(NH_3)(ClO_4)_2$: C, 32.7; H, 4.92; N, 12.70; Co, 10.69; Cl, 12.86. Found: C, 33.1; H, 4.62; N, 12.7; Co, 10.84; Cl, 12.94.

**Co(CR)Br($ClO_4$), Co(CR)Br($PF_6$), and Co(CR)BrB($C_6H_5$)$_4$.**—A warm concentrated solution of sodium perchlorate in ethanol, ammonium hexafluorophosphate in methanol, or sodium tetraphenylborate in methanol was added to a hot, concentrated solution of Co(CR)$Br_2 \cdot H_2O$ in the same solvent. A twofold excess of the salt was used. The product crystallized at once as a finely divided black solid; yield, 95%. *Anal.* Calcd for $CoC_{15}H_{22}N_4BrClO_4$: C, 36.27; H, 4.46; N, 11.28; Br, 16.09; Cl, 7.14. Found: C, 36.09; H, 4.03; N, 11.42; Br, 15.93; Cl, 7.15. Calcd for $CoC_{15}H_{22}N_4BrPF_6$: C, 33.22; H, 4.09; N, 10.33; F, 21.02. Found: C, 32.46; H, 4.15; N, 10.15; F, 20.95. Calcd for $CoC_{15}H_{22}N_4BrB(C_6H_5)_4$: C, 65.38; H, 5.97; N, 7.82; Br, 11.15. Found: C, 65.22; H, 6.01; N, 7.84; Br, 11.19.

**Zinc(II) Complex, Zn(CR)$I_2$.**—To a solution of 2,6-diacetylpyridine (0.80 g) in 150 ml of 50% ethanol–water, 1.49 g of Zn($NO_3$)$_2 \cdot 6H_2O$ dissolved in 50 ml of ethanol was added. While holding the temperature of the stirred solution near 70°, 3,3′-diaminodipropylamine (0.63 g) was added, 2–5 drops at a time, over a period of 30 hr. One drop of acetic acid was added occasionally to keep the solution clear. Heating was continued for an additional 15 hr. A large excess of sodium iodide (11 g) in ethanol solution was added and the solution was allowed to cool. Dark yellow crystals of the crude product formed. This crude product was recrystallized by dissolving it in a minimum volume of warm (60°) dimethylformamide. Five volumes of acetone was added and the solution was cooled in the refrigerator for several days. The bright yellow platelets which form were collected, washed with acetone, and dried; yield, 10%. *Anal.* Calcd for $ZnC_{15}H_{22}N_4I_2$: C, 31.2; H, 3.81; N, 9.70; Zn, 11.32; I, 44.95. Found: C, 31.0; H, 3.80: N, 9.69; Zn, 11.37; I, 41.22.

**2,12-Dimethyl-3,7,11-tetraazabicyclo[11.3.1]heptadeca-1(17),-13,15-trienecobalt(II) Bromide, Co(CRH)$Br_2$.**—Platinum oxide catalyst was added to a solution of Co(CRH)$Br_2 \cdot H_2O$ (2.0 g, 0.004 mol) in 200 ml of methanol. This solution was shaken on the Parr hydrogenation apparatus for 4 days. The solution was filtered to remove the catalyst and the volume of the filtrate was reduced until the solution was saturated at 60°. The solution was allowed to cool to room temperature and the reddish brown product was collected. The crude product was recrystallized from ethanol with addition of lithium bromide to induce crystallization. This purified product was collected, washed, and dried *in vacuo* over $P_4O_{10}$; yield, 70%. *Anal.* Calcd for $CoC_{15}H_{26}N_4Br_2$: C, 37.44; H, 5.44; N, 11.64; Co, 12.24; Br, 33.22. Found: C, 37.35; H, 5.53; N, 11.85; Co, 12.37; Br, 33.29.

**Co(CRH)Br($PF_6$).**—The preparation of this product was similar to that of Co(CRH)$Br_2$ with the following exceptions. A methanol solution of $NH_4PF_6$ was added to the filtrate after removing the catalyst. The bronze crystals which formed are very sparingly soluble in methanol and water; yield, 83%. *Anal.* Calcd for $CoC_{15}H_{26}N_4BrPF_6$: C, 33.0; H, 4.80; N, 10.3; Co, 10.79; Br, 14.63. Found: C, 33.2; H, 4.91; N, 10.3; Co, 10.72; Br, 14.62.

**Co(CRH)I($PF_6$).**—The preparation of this product is similar to that of Co(CRH)Br($PF_6$) with the following exceptions. Co(CR)$I_2$ was used for the hydrogenation. A microcrystalline brown product was obtained; yield, 45%. *Anal.* Calcd for $CoC_{15}H_{26}N_4IPF_6$: C, 30.37; H, 4.42; N, 9.45; I, 21.39. Found: C, 30.8; H, 4.69; N, 9.42; I, 21.40.

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# Perhaloarylmetal Chemistry. V. The Formation and Properties of Some σ-Perhaloaryl and Methyl Derivatives of Nickel[1,2]

By M. D. Rausch and F. E. Tibbetts

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A new series of air-stable, σ-bonded organic derivatives of nickel of the types $[CH_3(C_6H_5)_2P]_2Ni(aryl)Cl$, $[CH_3(C_6H_5)_2P]_2Ni(aryl)_2$, and $[CH_3(C_6H_5)_2P]_2Ni(aryl)CH_3$ is described. Their proton nmr spectra are consistent with a *trans*-planar configuration in each case. Factors affecting the relative stabilites of these products are discussed.

The chemistry of σ-bonded organonickel compounds has been the subject of an intensive research effort in recent years. These studies have been directed toward the possible utilization of such compounds as homogeneous catalysts, as well as toward a better understanding of the nature of the carbon–nickel σ bond. Chatt and Shaw[3] made a major contribution to this

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(1) Part IV: M. D. Rausch, Y. F. Chang, and H. B. Gordon, *Inorg. Chem.*, **8**, 1355 (1969).

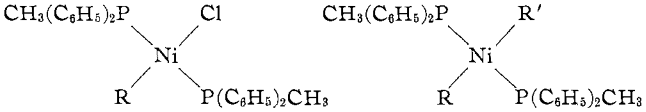
(2) Presented in part at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965, and in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968.

(3) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

area in 1960 when they found that certain organonickel compounds of the type $(R_3P)_2Ni(aryl)Cl$ and $(R_3P)_2Ni(aryl)_2$, where aryl is an *ortho*-substituted aromatic ligand, were relatively stable and isolable.

In continuation of our own studies in this area,[1,4] we have investigated the formation and properties of a series of $\sigma$-aryl and methyl derivatives of nickel derived from the nickel complex $[CH_3(C_6H_5)_2P]_2NiCl_2$. We reasoned that the *t*-phosphine ligands in this complex would provide carbon–nickel $\sigma$-bond stabilization of the type found earlier by Chatt and Shaw and further that the proton nmr spectra of the resulting organonickel derivatives would provide valuable information relating to their stereochemistries in solution, possible long-range $^1H-^{19}F$ coupling interactions, etc. Several organonickel derivatives containing diethylphenylphosphine ligands have likewise been prepared and examined. During the course of our studies, two other groups of investigators have also described some related $\sigma$-arylnickel complexes containing other *t*-phosphine ligands.[5,6]

Bis(diphenylmethylphosphine)dichloronickel (1) was synthesized by the procedure of Hayter and Humiec,[7] who postulated a *trans*-planar structure for this complex. Treatment of 1 with either pentafluorophenylmagnesium bromide, pentachlorophenyllithium, or mesityllithium readily produced good yields of the corresponding mono-aryl derivatives 2, 3, and 4, respectively. The monopentafluorophenyl complex 2 likewise served as a useful intermediate, since reactions of it with pentafluorophenyl- or pentachlorophenyllithium afforded the bis-aryl derivatives 5 and 6. Compound 6 represents the first example of an organo transition metal compound in which two different, highly electronegative aryl ligands are $\sigma$ bonded to the same transition metal, and only the second example of an organo transition metal compound containing two dissimilar $\sigma$-bonded aryl substituents.[8,9]



1, R = Cl
2, R = $C_6F_5$
3, R = $C_6Cl_5$
4, R = mesityl

5, R, R′ = $C_6F_5$
6, R = $C_6F_5$, R′ = $C_6Cl_5$
7, R = $C_6F_5$, R′ = $CH_3$
8, R = $C_6Cl_5$, R′ = $CH_3$
9, R = mesityl, R′ = $CH_3$

In contrast to the mode of formation of the bis-aryl derivatives 5 and 6, the chlorine atoms bonded to nickel in either 3 or 4 were found to be very inert to further $\sigma$-aryl substitution. In fact, the latter complexes were most conveniently prepared by employing an appreciable molar excess of organolithium reagent compared to 1. Attempted further arylations of 3 and 4 by phenyl-, pentafluorophenyl-, pentachlorophenyl-, and mesityllithium under a variety of conditions in no case produced detectable amounts of the corresponding bis-arylated product. In most cases, a high recovery of either 3 or 4 resulted, and in the case of 4, following hydrolysis, some decomposition to $Ni^{2+}$ was apparent as evidenced by dimethylglyoxime tests. Thus, while the bis-aryl complex 6 could be formed from a reaction between 2 and pentachlorophenyllithium (albeit in low yield), its presence could not be detected (*via* tlc, nmr, etc.) in a reaction between 3 and pentafluorophenyllithium under the same conditions, and 3 was recovered in 85% yield.

The lack of reactivity of 3 and 4 toward further arylation compared to 2 is most likely the result of steric factors, in agreement with theories developed by Chatt and Shaw.[3] An examination of molecular models of these systems indicates that the presence of two *bulky ortho* substituents (such as Cl or $CH_3$) on an aryl ligand effectively shields the axial coordination sites of the nickel atom from relatively bulky attacking reagents. Furthermore, the diphenylmethylphosphine ligands make a significant contribution to the total shielding of the nickel atom. As a consequence, aryl group substitution of the chlorine atom bonded to nickel in 3 and 4 by either an associative bimolecular mechanism or by an $S_N1$ mechanism should be greatly inhibited, since both processes involve additional coordination at the axial sites of the nickel atom.[3,10,11]

In this connection, Basolo, *et al.*,[12] have carried out kinetic studies of the reaction in ethanol solution between pyridine and planar complexes of the type $[(C_2H_5)_3P]_2M(aryl)Cl$ (M = Ni, Pd, and Pt). They observed a large steric effect on the relative rates of these reactions and noted that mesityl compounds consistently reacted more slowly than did analogous *o*-tolyl derivatives. Also, in a recent X-ray crystallographic study of a similar compound, bis(diethylphenylphosphine)bis($\sigma$-mesityl)cobalt, the mesityl liggands were found to be perpendicular to the coordination plane of the cobalt atom.[13] The *o*-methyl groups were noted to be in contact above and below the cobalt atom, thereby effectively shielding it.

All of the $\sigma$-arylnickel compounds 2–6 were found to exhibit relatively high thermal and oxidative stabilities, especially when compared to phenyl analogs[3] or to $\sigma$-arylnickel compounds in which no *t*-phosphine ligands are coordinated to the same nickel atom.[14] Any of these derivatives could be stored in air at room temperature for an indefinite period of time or in organic solvents for a period of several weeks without change, and each melted in a sealed tube under nitrogen without decomposition.

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Table I

Proton Nmr Spectra of Organonickel Complexes

| Compound | Solvent | Chemical shift[a] (multiplicity, $J$ (Hz)) | | |
|---|---|---|---|---|
| | | $CH_3$–P | $CH_3$–Ni | C–$CH_3$ |
| **2** | $CDCl_3$ | 7.92 (t, 3.8) | | |
| **3** | $CDCl_3$ | 7.90 (t, 3.8) | | |
| **4** | $CDCl_3$ | 8.79 (t, 4.0) | | 7.47 (s),[b] 7.98 (s)[c] |
| **5** | $CDCl_3$ | 8.33 (t, 3.8) | | |
| **6** | $CDCl_3$ | 8.08 (t, 3.8) | | |
| **7** | $C_6H_6$ | 8.50 (t, 3.6) | 10.37 (t, 9.5) | |
| **8** | $C_6H_6$ | 8.37 (t, 3.6) | 10.40 (t, 9.5) | |
| **8** | $CS_2$ | 8.28 (t, 3.6) | 10.80 (t, 9.5) | |
| **9** | $C_6H_6$ | 8.87 (t, 3.6) | 10.40 (t, 9.5) | 7.47 (s),[b] 7.67 (s)[c] |
| **9** | $CS_2$ | 9.00 (t, 3.6) | 11.02 (t, 9.5) | 7.80 (s),[b] 7.98 (s)[c] |

[a] Given in $\tau$ ppm units (estimated accuracy $\pm 0.02$ ppm); s = singlet, t = triplet. Integration of the resonances was consistent with proposed assignments in each case. Resonances for phenyl protons occurred as multiplets in the region near $\tau$ 2.6. [b] Assigned to the *o*-methyl protons of the mesityl group. [c] Assigned to the *p*-methyl protons of the mesityl group.

In contrast to the above-mentioned reactivity results of **2**–**4** toward further arylation, all three of these mono-aryl nickel intermediates underwent reaction with *methyllithium* in ethyl ether solution to afford a new and unique series of compounds of the type $[(C_6H_5)_2CH_3P]_2Ni(aryl)CH_3$ (**7**–**9**). Such a result is reasonable, since the steric requirements of a methyl group should be much less demanding than for an aryl group in the substitution process. It should be noted that metathetical reactions involving the chlorine atom in various compounds of the types $(R_3P)_2Ni(\sigma\text{-}C_6Cl_5)Cl$ and $(R_3P)_2Ni(\sigma\text{-mesityl})Cl$ have also been successful.[3,6] The methylnickel complexes **7**–**9** were characterized by elemenal analysis and by nmr spectroscopy (*vide infra*).

Our ability to isolate and characterize **7**–**9** is especially noteworthy in view of repeated failures by Chatt and Shaw to isolate alkylnickel compounds in their studies. Thus, whereas the addition of *trans*-$[(C_2H_5)_3P]_2NiBr_2$ to methylmagnesium bromide discharged the red color giving a yellow solution which evidently contained a methylnickel derivative, attempts to isolate the latter resulted in the rapid formation of greenish decomposition products, due presumably to the instability of the product.[3,15]

While our methylnickel complexes **7**–**9** have proved to be isolable, they are clearly of lower overall stability than any of the $\sigma$-arylnickel derivatives **2**–**6**. Qualitative stablity tests based on prolonged exposure to air at room temperature, storage in solution under nitrogen, etc., have indicated that the order of relative stability of these derivatives is **8** $\gg$ **9** > **7**. Compound **8** survived exposure to air at room temperature for a period of several months, and a benzene solution of **8** still exhibited a sharp, characteristic nmr spectrum after a 1-week period. Compound **8** thus appears to be one of the most stable alkylnickel derivatives that is yet known.

The remarkably high stabilities of the methylnickel compounds **7**–**9** are undoubtedly due to the simultaneous coordination of the two *t*-phosphine ligands as well as the *trans*-aryl ligand to nickel, and can probably best be accounted for by a combination of steric and electronic factors. On the basis of steric shielding of the axial coordination sites of the nickel atom, as discussed above, complexes **8** and **9** might be expected to be less prone to attack by external reagents or solvents. Strong support for such a postulation is the fact that the $\sigma$-organonickel compounds bis(trityl)nickel and tritylnickel chloride have been isolated, and the former was found to be stable in air at room temperature for several days.[16] Presumably, the steric bulk of the trityl group is responsible for this enhanced stability, since no *t*-phosphine ligands are present in the molecule. Also, assuming that a $\sigma$-perhaloaryl substituent can remove electron density either inductively (forming a polarized $\sigma$ bond) or by $d_\pi p_{\pi^*}$-type interaction from the nickel atom, the compound as a whole should be rendered more thermally stable.[3,17–21] Both factors should be operative in the case of the methylnickel complex **8** and may possibly account for its enhanced stability.

The proton nmr spectra of all the organonickel derivatives described in this paper have been recorded (Table I). The nmr spectrum of the starting material **1** in either carbon disulfide or deuteriochloroform proved to be abnormal in that broadened peaks, separated by large chemial shift values and exhibiting unusually large coupling constants, were observed. These and other results indicate a paramagnetic and probably tetrahedral structure for **1** in such solvents, in which ligand dissociation may also occur.[22] The nmr spectra of the other compounds **2**–**9** are consistent with diamagnetic, *trans*-planar structures in solution in each case. A symmetrical 1:2:1 triplet resonance in the vicinity of $\tau$ 8–9 is assigned to the phosphine methyl protons. The strong spin coupling of the two phos-

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(19) The concept of multiple bonding in the carbon–metal bond of various $\sigma$-aryl derivatives of transition metals has been the subject of dispute recently. See, for example, ref 4, 13, 20, and 21, as well as M. D. Rausch, A. K. Ignatowicz, M. R. Churchill, and T. A. O'Brien, *J. Am. Chem. Soc.*, **90**, 3242 (1968).

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phorus nuclei in *trans* positions in such complexes is well known, and since the phosphine methyl proton resonance thus depends on the spin state of both phosphorus nuclei, it appears as a triplet ("virtual coupling").[23] The assignment of *trans*-planar structures to compounds **2**–**9** is consistent with the results of previous dipole moment,[8] nmr,[6,24] and X-ray crystallographic studies[20,21] on analogous compounds.

In the proton nmr spectra of organonickel compounds **7**–**9**, a well-defined symmetrical 1:2:1 triplet resonance is also observed in each case at *ca.* $\tau$ 10.4–11. This resonance can be assigned to the methyl substituent σ bonded to nickel, since protons on methyl groups bonded to transition metals are known to resonate in this region.[25] The appearance of the resonance as a triplet is due to spin–spin interaction between the methyl nickel protons and the two adjacent phosphorus nuclei. Such a result indicates a relatively long preexchange lifetime of the methyl–nickel bond under these conditions.

During the early stages of the above investigation, some related studies were made on certain σ-bonded organonickel compounds containing diethylphenylphosphine rather than diphenylmethylphosphine as the ligand. These new substances are described in the Experimental Section.

## Experimental Section

Proton nmr spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Melting points were determined under nitrogen on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Mr. Charles Meade of the Chemical Analysis Laboratory, Office of Research Services, University of Massachusetts. Ethyl ether was purified by distillation from lithium aluminum hydride immediately before use. Benzene and *n*-hexane were purified by procedures described by Vogel.[26] The final fractional distillations were conducted under a nitrogen atmosphere into nitrogen-filled storage containers where the purified solvents were stored under nitogen until use.

All reactions were run in a small round-bottomed flask containing a magnetic stirring bar and fitted with a small-bore side arm containing a stopcock. When required, the apparatus could be equipped with a pressure-equalizing addition funnel or a reflux condenser. Before a reaction was begun, the apparatus was evacuated *via* a vacuum pump, flamed, and refilled with dry prepurified nitrogen; this process was repeated at least three times. All reactions were conducted under a positive flow of nitrogen, and for the methylnickel compounds **7**–**9**, a nitrogen atmosphere was utilized throughout the purification process.

*trans*-Bis(diphenylmethylphosphine)dichloronickel[7] and *trans*-bis(diethylphenylphosphine)dichloronickel[27] were prepared by published procedures. Methyl- and *n*-butyllithium were purchased from Alfa Inorganics, Inc.

***trans*-Bis(diphenylmethylphosphine)(σ-pentafluorophenyl)-chloronickel (2).**—To a stirred mixture of **1** (7.95 g, 15 mmol) and 40 ml of ethyl ether was added over a 20-min period a solution of pentafluorophenylmagnesium bromide[28] [prepared from magnesium turnings (0.486 g, 20 mg-atoms) and bromopentafluorobenzene (4.10 g, 17 mmol) in 25 ml of ethyl ether], a temperature of −15° being maintained. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was then stirred for 2 hr, after which the solvent was removed *in vacuo*. The residue was extracted with 65 ml of benzene, the extracted solution was filtered, the benzene was evaporated under reduced pressure, and the resulting residue was dried at 85° (0.3 mm). The product was recrystallized from *n*-hexane–benzene (2:1) to produce 8.43 g (85%) of **2**, mp 204–208°. An analytical sample was prepared by means of multiple recrystallization as brown crystals, mp 208–209°. *Anal.* Calcd for $C_{32}H_{26}ClF_5NiP_2$: C, 58.09; H, 3.96; Cl, 5.36; F, 14.36; Ni, 8.87; P, 9.36. Found: C, 58.20; H, 3.80; Cl, 5.75; F, 14.64; Ni, 8.47; P, 9.21. An infrared spectrum (KBr pellet) of **2** exhibited sharp, intense absorptions at 950 and 1498 cm$^{-1}$ and a doublet near 1050 cm$^{-1}$ which are characteristic of the pentafluorophenyl group.[29]

***trans*-Bis(diphenylmethylphosphine)(σ-pentachlorophenyl)-chloronickel (3).**—To a stirred solution of pentachlorophenyllithium[30] (15 mmol) in 300 ml of ethyl ether at −78° was added **1** (5.0 g, 9.5 mmol) in small portions over a 30-min period. The mixture was stirred at −78° for 2 hr and was then allowed to warm to room temperature over an additional 2-hr period. The solvent was evaporated and the residue was dried at 100° (0.3 mm). Workup as described above and subsequent recrystallization from ethyl ether resulted in 4.47 g (63%) of yellow-brown crystals, mp 215–217°. An analytical sample of mp 218–219° was prepared by multiple recrystallization of the product from *n*-hexane. *Anal.* Calcd for $C_{32}H_{26}Cl_6NiP_2$: C, 51.66; H, 3.52; Cl, 28.59; Ni, 7.89; P, 8.33. Found: C, 51.66; H, 4.02; Cl, 28.48; Ni, 8.19; P, 8.00. An infrared spectrum (KBr pellet) of **3** exhibited absorptions characteristic[30] of the pentachlorophenyl group at 1098, 874, and 690 cm$^{-1}$.

***trans*-Bis(diphenylmethylphosphine)(σ-mesityl)chloronickel (4).**—To a stirred solution of mesityllithium [prepared from 2-bromomesitylene (0.796 g, 4 mmol) and lithium shavings (0.056 g, 8 mg-atoms) in 20 ml of ethyl ether] was added in small portions 0.530 g (1 mmol) of **1**. The mixture was stirred at −15° for 1 hr, allowed to warm to room temperature over a 30-min period, and then heated to reflux for 15 min. Following the addition of 100 ml of ethyl ether, the mixture was cooled to −10°, hydrolyzed with saturated aqueous ammonium chloride, the organic portion was separated and dried, and the solvent was evaporated *in vacuo* to produce a residue. Recrystallization of the latter from *n*-hexane–benzene (4:1) produced yellow-brown crystals (0.195 g, 32%) of **4**, mp 195–199°. An analytical sample had a melting point of 199.5–201.5°. *Anal.*[31,32] Calcd for $C_{35}H_{37}ClNiP_2$: C, 68.49; H, 6.07; Cl, 5.78; Ni, 9.57; P, 10.09. Found: C, 65.50; H, 6.01; Cl, 6.02; Ni, 9.43; P, 10.30.

***trans*-Bis(diphenylmethylphosphine(bis)σ-pentafluorophenyl)-nickel (5).**—A solution of pentafluorophenyllithium[33] was prepared from bromopentafluorobenzene (0.25 g, 1.0 mmol), 1.0

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(31) For several compounds prepared in this study, suitable analyses were obtained for all elements determined with the exception of carbon, which was consistently several per cent lower than theory. In various organophosphorus compounds, low analytical values for carbon content are sometimes obtained, due to incomplete combustion resulting from difficulty in breaking the carbon–phosphorus bond.[32] For the same reason, low analytical values for carbon are sometimes obtained in organofluorine compounds.[32] Low values for carbon in various *t*-phosphine-stabilized, σ-arylpalladium compounds have been previously discussed.[8] Evidence for incomplete combustion in some of our products has been observed, despite the utilization of various oxidation catalysts in the analyses: C. Meade, personal communication.

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mmol of *n*-butyllithium in hexane, and a small amount of ethyl ether at −78°. To the stirred solution at this temperature was added 0.50 g (0.76 mmol) of **2** in small portions over a 10-min period. The reaction mixture was stirred at −78° for 1 hr and allowed to warm to room temperature; the solvent was then evaporated. The yellow residue was extracted with 60 ml of benzene, the solution was filtered and hydrolyzed with 5 ml of saturated aqueous ammonium chloride, and the organic portion was separated and dried. Evaporation of the solvent gave 0.41 g (74%) of **5**, mp 191–194°. An analytical sample was prepared by a subsequent recrystallization from *n*-hexane–benzene (2:1); lemon yellow crystals of mp 192–193° were obtained. This product was shown to be identical, by a mixture melting point determination as well as by a comparison of infrared and nmr spectra, with a sample of **5** prepared previously.[1]

*trans*-**Bis(diphenylmethylphosphine)(σ-pentachlorophenyl)(σ-pentafluorophenyl)nickel** (**6**).—Complex **2** (0.67 g, 1 mmol) was added in small portions over a 10-min period to a stirred solution of pentachlorophenyllithium (1.2 mmol) in 25 ml of ethyl ether maintained at −78°. The mixture was allowed to warm to room temperature over a 3-hr period, the solvent was evaporated, the residue was taken up in 20 ml of benzene, and the solution was filtered and hydrolyzed with saturated aqueous ammonium chloride. The organic layer was separated and dried and then was chromatographed on an 18-in. column of Florisil utilizing *n*-hexane–benzene (1:1) as the eluent. A small amount of hexachlorobenzene was eluted, followed by the product **6** as light yellow needles (0.132 g, 15%), mp 223–226°. A third band consisted of the starting material **2**. Further purification of **6** by preparative tlc and recrystallization from *n*-hexane produced an analytical sample, mp 187.5–189°. *Anal.* Calcd for $C_{38}H_{26}Cl_5F_5NiP_2$: C, 52.13; H, 2.99; Cl, 20.25; F, 10.85; Ni, 6.71; P, 7.08. Found: C, 51.85; H, 2.78; Cl, 19.87; F, 11.26; Ni, 6.95; P, 6.84. An infrared spectrum (KBr pellet) of **6** exhibited absorptions characteristic of the pentafluorophenyl group[29] at 950, 1050 (doublet), and 1499 $cm^{-1}$, as well as absorptions characteristic of the pentachlorophenyl group[30] at 692, 875, and 1100 $cm^{-1}$.

*trans*-**Bis(diphenylmethylphosphine)(methyl)(σ-pentafluorophenyl)nickel** (**7**).—To a stirred mixture of **2** (0.50 g, 0.75 mmol) and 30 ml of ethyl ether at −15° was added dropwise over a 10-min period a solution of 0.88 mmol of methyllithium in ethyl ether. The reaction mixture was stirred at −15° for 30 min and subsequently at 25° for 30 min, during which time all the solid **2** had dissolved, and the solution had become light red-brown. The solvent was then evaporated *in vacuo* and the residue was extracted with 40 ml of *n*-hexane at 40°. The extract was filtered through Filter-Cel to produce a light yellow solution. The latter was evaporated *via* a stream of nitrogen until crystals began to form and was then cooled to −20° to produce dark yellow-brown crystals. These crystals were dissolved in 20 ml of *n*-hexane and the filtration process was repeated. Subsequent cooling of the concentrated solution to −20° produced light yellow-brown crystals (0.056 g, 12%) of mp 94–98° dec. *Anal.* Calcd for $C_{33}H_{29}F_5NiP_2$: C, 61.81; H, 4.56; Ni, 9.15; P, 9.66. Found: C, 61.51; H, 4.81; Ni, 8.89; P, 9.93.

*trans*-**Bis(diphenylmethylphosphine)(methyl)(σ-pentachlorophenyl)nickel** (**8**).—Utilizing a reaction procedure and conditions identical with those described above, methyllithium (0.85 mmol) was caused to react with a mixture of **3** (0.50 g, 0.67 mmol) and 30 ml of ethyl ether. Evaporation of the solvent *in vacuo* and two recrystallizations from *n*-hexane (utilizing filtration through Filter-Cel) produced yellow-brown crystals (0.072 g, 15%). An analytical sample was prepared by an additional recrystallization from *n*-hexane; the product melted with decomposition over 121°. *Anal.* Calcd for $C_{33}H_{29}Cl_5NiP_2$: C, 54.78; H, 4.04; Cl, 24.50. Found: C, 54.71; H, 3.98; Cl, 24.30.

*trans*-**Bis(diphenylmethylphosphine)(methyl)(σ-mesityl)nickel** (**9**).—By means of a reaction procedure and conditions identical with those described for **7**, methyllithium (0.6 mmol) was caused to react with a mixture of **4** (0.307 g, 0.5 mmol) and 25 ml of ethyl ether. The solvent was evaporated *in vacuo* to produce a yellow-brown residue which was recrystallized from *n*-hexane–benzene (8:1) (utilizing filtration through Filter-Cel) and then twice from *n*-hexane to produce yellow crystals (0.117 g, 38%) of mp 118.5–120° dec. *Anal.* Calcd for $C_{36}H_{40}NiP_2$: C, 72.87; H, 6.80; Ni, 9.98; P, 10.44. Found: C, 72.69; H, 6.80; Ni, 9.47; P, 10.25.

*trans*-**Bis(diethylphenylphosphine)(σ-pentafluorophenyl)chloronickel.**—This substance was prepared in 72% yield from *trans*-bis(diethylphenylphosphine)dichloronickel and pentafluorophenylmagnesium bromide in a manner described for the synthesis of **2**; gold crystals were obtained, mp 106–107°. *Anal.*[31] Calcd for $C_{26}H_{30}ClF_5NiP_2$: C, 52.60; H, 5.10; Cl, 5.97; Ni, 9.89; P, 10.44. Found: C, 50.55; H, 5.15; Cl, 5.90; Ni, 9.29; P, 10.53.

*trans*-**Bis(diethylphenylphosphine)bis(σ-pentafluorophenyl)nickel.**—In a manner analogous to that described for the formation of **5**, a reaction between *trans*-bis(diethylphenylphosphine)(σ-pentafluorophenyl)chloronickel and pentafluorophenyllithium produced the organonickel derivative in 37% yield; the product was in the form of yellow crystals, mp 210–211°. *Anal.* Calcd for $C_{32}H_{30}F_{10}NiP_2$: C, 52.99; H, 4.18; F, 26.20; P, 8.54. Found: C, 53.05; H, 4.25; F, 26.11; P, 8.43.

*trans*-**Bis(diethylphenylphosphine)(methyl)(σ-pentafluorophenyl)nickel.**—This methylnickel derivative was prepared in low yield *via* the general method outlined for the synthesis of **7** in the form of small gold crystals, mp 116.5–118° dec. The product was not purified further, due to its sensitivity in solution, although a characteristic triplet resonance for the methylnickel protons was evident at τ 10.65 in benzene.

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