σ-Aryl Compounds of Nickel, Palladium, and Platinum. Synthesis and Bonding Studies

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Abstract: The reactions of fluorohalobenzenes with the zerovalent complexes, $M(PEt_3)_4$ (M = Ni, Pd, Pt), give the fluoroaryl complexes *trans*-$MX(C_6H_4F)(PEt_3)_2$ in high yields. Fluorobenzonitriles react similarly to give *trans*-$M(CN)(C_6H_4F)(PEt_3)_2$ complexes. The reaction rates decrease in the sequences Ni > Pd > Pt and I > Br > Cl > CN ≫ F. Reaction of the bromo complexes with phenylmagnesium bromide and with methyllithium has been used to prepare the *trans*-$M(R)(C_6H_4F)(PEt_3)_2$ compounds in which R is C_6H_5 and CH_3. The methyl derivatives of nickel and palladium decompose slowly in solution at room temperature to give fluorotoluenes. The ^{19}F nmr chemical shifts of the fluoroaryl compounds and the derived substituent constants indicate that the $-MX(PEt_3)_2$ group is an electron donor to the aromatic ring. The differences between Ni, Pd, and Pt are small, but the σ_R^0 values suggest that nickel(II) is the most effective in π-bonding.
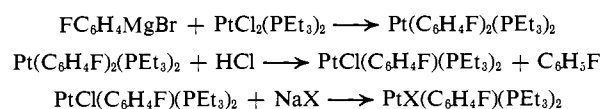
A n unusual opportunity to study exactly analogous σ-aryl complexes of the nickel, palladium, and platinum triad metals has been provided by a recent discovery.[1] The readily available[2] zerovalent complexes, $M(PEt_3)_4$, react with halobenzenes to give the *trans*-$MX(C_6H_5)(PEt_3)_2$ derivatives (M = Ni, Pd, Pt; X = Cl, Br, I, CN). This paper elaborates the original finding and describes the synthesis of a series of *m*- and *p*-fluorophenyl compounds of nickel, palladium, and platinum in which the trans ligand (X) includes chloride, bromide, iodide, cyanide, phenyl, and methyl. Study of the ^{19}F nmr shielding parameters of these compounds has given quantitative comparisons of the metal–aryl bond characteristics in the series.
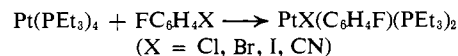
Synthesis by Oxidative Addition

Oxidative addition of halobenzenes to zerovalent complexes of nickel, palladium, and platinum provides a simple, high yield synthesis of the monoaryl derivatives. Tetrakis(triethylphosphine)metal(0) complexes generally react with aryl halides under milder conditions than do the corresponding triphenylphosphine complexes which have been studied previously. For example, Pt-$(PEt_3)_4$[1] and $Pd(PEt_3)_4$[2] react with chlorobenzene in a few minutes in boiling toluene to give *trans*-$MCl(C_6H_5)$-$(PEt_3)_2$ while $Pt(PPh_3)_3$[1] and $Pd(PPh_3)_4$[3] are inert under these conditions. Similarly the oxidative addition of chlorobenzene to $Ni(PEt_3)_4$ is virtually instantaneous at room temperature whereas the reaction with $Ni(PPh_3)_4$ requires hours.[4] The oxidative addition of benzonitrile to the triethylphosphine complexes to give phenylmetal cyanide complexes does not occur in the triphenylphosphine series.

In the present work, it was found that fluorophenyl-metal(II) compounds are conveniently available by oxidative addition of fluorohalobenzenes to $M(PEt_3)_4$ complexes (M = Ni, Pd, Pt). An extensive series of

fluorophenylplatinum complexes had been prepared previously[5] by a conventional sequence.[6]

$$FC_6H_4MgBr + PtCl_2(PEt_3)_2 \longrightarrow Pt(C_6H_4F)_2(PEt_3)_2$$

$$Pt(C_6H_4F)_2(PEt_3)_2 + HCl \longrightarrow PtCl(C_6H_4F)(PEt_3)_2 + C_6H_5F$$

$$PtCl(C_6H_4F)(PEt_3)_2 + NaX \longrightarrow PtX(C_6H_4F)(PEt_3)_2$$

However, with the recent development of a good, one-step synthesis of $Pt(PEt_3)_4$ from $PtCl_2$, Et_3P, and potassium,[2] the oxidative addition route

$$Pt(PEt_3)_4 + FC_6H_4X \longrightarrow PtX(C_6H_4F)(PEt_3)_2$$
$$(X = Cl, Br, I, CN)$$

became attractive. It gave the trans isomer in high yield (50–90%) in a convenient procedure. There appeared to be no significant difference in the ease of oxidative addition between the *m*- and *p*-halofluorobenzenes, but the rate of the reaction varied with the halide in the sequence: I > Br > Cl > CN.

The *m*- and *p*-fluorophenylpalladium halide and cyanide compounds were readily prepared by oxidative addition of the halofluorobenzenes or fluorobenzonitriles to tetrakis(triethylphosphine)palladium(0). As with the platinum series, the reactions were clean and the *trans*-fluorophenylhalobis(triethylphosphine)-palladium(II) complexes were formed in high yield. The same chloro and bromo complexes were also obtained by reaction of the fluorophenylmagnesium halides with *trans*-$PdCl_2(PEt_3)_2$ because the Grignard reagents react much more readily with the first Pd–Cl bond than with the second.[7] The products of these reactions were characterized as the trans isomers by their proton nmr spectra. The methyl signals appeared as pseudoquintets due to coupling of the trans ^{31}P nuclei. As further confirmation of the trans configuration of the products, the proton-decoupled ^{19}F nmr signals appeared as triplets due to equivalent coupling with the two ^{31}P nuclei.

The reactions of halofluorobenzenes and fluorobenzonitriles with tetrakis(triethylphosphine)nickel(0) were

$$FC_6H_4X + Ni(PEt_3)_4 \longrightarrow NiX(C_6H_4F)(PEt_3)_2$$

(1) D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971).
(2) R. A. Schunn, Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 13, 1973.
(3) P. Fitton and E. A. Rick, *J. Organometal. Chem.*, **28**, 287 (1971); U. S. Patent 3,674,825 (1972).
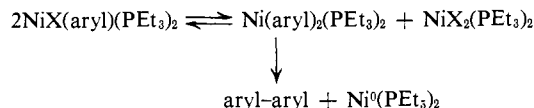(4) M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, *J. Organo-metal. Chem.*, **30**, 279 (1971).

(5) G. W. Parshall, *J. Amer. Chem. Soc.*, **88**, 704 (1966).
(6) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).
(7) G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).

almost instantaneous at room temperature. (The reactions of chlorobenzenes with ethylenebis(triethylphosphine)nickel(0) proceed under similarly mild conditions.[8]) The bromo and iodo complexes were formed cleanly and in good yield but the chloro and cyano complexes were generally contaminated by small amounts of the dichloro- or dicyanobis(triethylphosphine)nickel(II). The formation of these by-products did not seem to be affected by the ratio of halobenzene to nickel(0) complex and was not promoted by addition of m-fluorobenzonitrile to a preformed solution of $trans$-p-$FC_6H_4Ni(CN)(PEt_3)_2$ in benzene. It seems more likely that the by-products were formed by successive redistribution and reductive elimination reactions.[9]

$$2NiX(aryl)(PEt_3)_2 \rightleftharpoons Ni(aryl)_2(PEt_3)_2 + NiX_2(PEt_3)_2$$

$$\downarrow$$

$$aryl\text{-}aryl + Ni^0(PEt_3)_2$$

This proposal is quite consistent with the finding[10] that $NiBr(C_6H_5)(PPh_3)_2$ decomposes thermally (80°, 12 min) in toluene solution to give a quantitative yield of biphenyl and with our stability studies on the aryl methyl complexes. Despite the problems involved in their isolation, the fluorophenylnickel complexes are quite stable when pure. Although not air stable like ortho-substituted aryl nickel compounds,[11] the crystalline complexes are stable for months at room temperature in a nitrogen atmosphere.
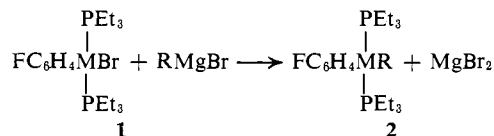
In these oxidative addition reactions of halobenzenes and benzonitriles, the $M(PEt_3)_4$ compounds or, more likely, the $M(PEt_3)_3$ derivatives formed by ligand dissociation,[12] behave like powerful nucleophiles. The reactivity sequence for the metal(0) complexes is Ni $\gg$ Pd > Pt and that for halobenzenes appears to be I > Br > Cl > CN $\gg$ F. The reactions of the zerovalent nickel and palladium complexes are similar to the recently reported reaction of free nickel and palladium atoms.[13]

$$M \text{ atoms} \xrightarrow{C_6F_5Br} [C_6F_5MBr]_n \xrightarrow{Ph_3P} MBr(C_6F_5)(PPh_3)_2$$
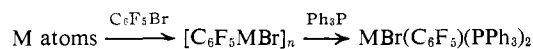
This similarity seems to support the qualitative concept of $M(PR_3)_n$ complexes as solvated metal atoms.[14]

Diaryl and Aryl Methyl Complexes

The reactions of phenyl and methyl Grignard reagents with the $MBr(C_6H_4F)(PEt_3)_2$ complexes provide a convenient synthesis of compounds bearing two C-bonded ligands.

$$\begin{array}{ccc} PEt_3 & & PEt_3 \\ | & & | \\ FC_6H_4MBr + RMgBr & \longrightarrow & FC_6H_4MR + MgBr_2 \\ | & & | \\ PEt_3 & & PEt_3 \\ \mathbf{1} & & \mathbf{2} \end{array}$$

This synthesis method, which has been used extensively for platinum complexes,[5,6] seems equally applicable to

(8) D. R. Fahey, *J. Amer. Chem. Soc.*, **92**, 402 (1970); U. S. Patent 3,686,245 (1972).

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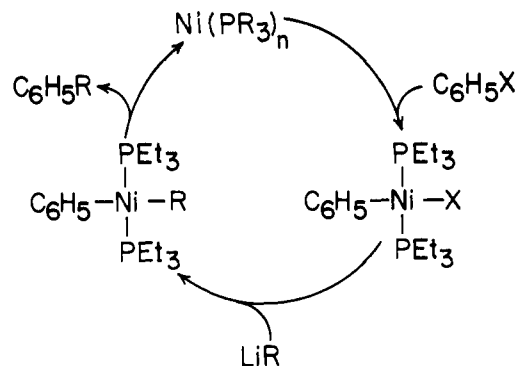(14) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968).

Figure 1. Cycle for alkylation, arylation, and cyanation of halobenzenes catalyzed by zerovalent nickel complexes. R = alkyl, aryl, CN.

the palladium analogs. Both phenyl- and methylmagnesium bromides react smoothly with the m- and p-fluorophenylpalladium bromides in mixed benzene-ether solvent at 25° to give **2** (M = Pd, R = C_6H_5, CH_3) in good yield. The converse reaction of p-fluorophenylmagnesium bromide with $trans$-bromophenylbis(triethylphosphine)palladium(II) also gives **2** (M = Pd, R = C_6H_5) cleanly. The products are white crystalline solids which are moderately stable in the solid state. However, in solution, the compounds slowly decompose with formation of metallic palladium. The trans configuration is apparent from the proton nmr spectrum (pseudoquintet C-CH_3 signal due to virtual coupling of the ^{31}P nuclei) and from the proton-decoupled ^{19}F signal which is a symmetrical triplet.

Similarly, in the nickel series, the bromo complexes (**1**) react with ethereal phenylmagnesium bromide in benzene to give the corresponding trans-diaryl compounds (**2**, M = Ni, R = C_6H_5) as red-brown crystalline solids. The cis-trans isomerism of the diaryl derivatives was not assignable from the proton nmr spectra, even at 220 MHz, because the CH_2 and CH_3 signals of the triethylphosphine ligands exactly coincide. However, the triplet signals in the proton-decoupled ^{19}F spectra indicate the trans configuration.

The reaction of methylmagnesium bromide with the bromo nickel complexes (**1**) did not seem to proceed to completion under the mild conditions needed to avoid thermal decomposition of the products. However, methyllithium in pentane reacts smoothly to give the aryl methyl nickel complexes (**2**) in good yield. Both the Ni-CH_3 proton nmr signals and the ^{19}F signals are 1-2-1 triplets consistent with a trans structure.

In contrast to the very stable platinum analogs,[6] the nickel and palladium complexes (**2**) with two carbon-bonded ligands are unstable in solution at room temperature.[7,9b] The decomposition appears to proceed by reductive elimination[12] of the σ-alkyl and aryl ligands.

$$M(R)(C_6H_4F)(PEt_3)_2 \longrightarrow R\text{-}C_6H_4F + M^0(PEt_3)_n$$

The palladium compounds deposit metallic palladium on standing in anaerobic C_6D_6 solution at 25° but the nickel complexes give soluble, deep-red species, probably $Ni(N_2)(PEt_3)_2$.[15] The methyl derivatives of both metals gave m- or p-fluorotoluene. The appearance of the organic product was conveniently followed by its proton nmr absorption. The growth of the toluene

(15) C. A. Tolman, D. H. Gerlach, J. P. Jesson, and R. A. Schunn, *J. Organometal. Chem.*, **65**, C23 (1974).

CH$_3$ signal and disappearance of the M–CH$_3$ signal were complementary. The decomposition of the four methyl complexes (2, M = Ni, Pd; meta and para isomers) was monitored for 5 weeks. Half-lives of *ca.* 4 weeks at 25° were noted for the methyl nickel complexes. No definitive comparative data were obtained for the palladium compounds because of metal deposition after about 1 week. The decomposition was strongly enhanced by impurities.

The diaryl complexes (2, R = C$_6$H$_5$) also showed some decomposition during 30 days at 25°. As with the methyl derivatives, the palladium compounds deposited metal. The metal may have had an autocatalytic influence because, with its appearance between day 15 and day 22, a major change in the ^{1}H nmr spectrum of the solution occurred. The normal Pd–aryl signals completely disappeared and were replaced by complex signals assigned to the respective *m*- and *p*-fluorobiphenyls. The characteristic features of the *trans*-M(PEt$_3$)$_2$ absorption also disappeared and were replaced by a broad, nondescript signal. The nickel complexes showed only a small amount of biphenyl formation and no metal deposition in 30 days.

These results, like those obtained by Coates[7] and by Schunn[2] for the dimethylpalladium complexes, suggest reductive elimination as a major reaction mode in the MR$_2$(PR′$_3$)$_2$ series. The sequence of oxidative addition, metathesis, and reductive elimination involved in the formation of toluene (Figure 1) closely resembles that proposed for the catalytic cyanation of aryl halides in the presence of zerovalent nickel and palladium compounds.[16] Similar mechanisms have been proposed in the nickel salt catalyzed selective coupling reactions of arylmagnesium halides with vinyl halides and halobenzenes.[17]

The oxidative addition of a halobenzene to a nickel(0) complex proposed as the first step in the series has been demonstrated in the present work as well as in previous studies in which phosphine,[4,9,14] isocyanide,[10] carbon monoxide,[18] and cyclooctadiene[19] ligands were present. Replacement of the halide ligand (X) with a cyanide,[16] alkyl, or aryl group is similarly well documented. The reductive elimination of the two C-bonded ligands from C$_6$H$_5$NiR(PEt$_3$)$_2$ also has extensive precedent in the chemistry of nickel,[9b] palladium,[2,7] platinum,[20] and rhodium.[21] Such couplings of ligands to form C–C bonds have extensive synthetic application in organic chemistry.[22]

^{19}F Nmr Studies

It was recognized over 20 years ago[23] that the ^{19}F nmr chemical shifts of substituted fluorobenzenes correlate

well with the classical Hammett substituent constants determined from reactivity sequences of substituted benzoic acids, phenols, and anilines. This correlation has been greatly extended and refined by Taft and coworkers.[24] In the first application of this technique to transition metal derivatives, the ^{19}F shielding parameters of the fluorophenyl platinum compounds 3 and 4
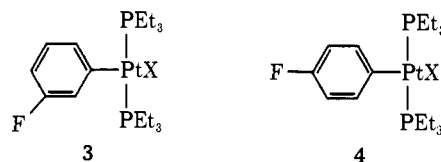
indicated that the –PtX(PEt$_3$)$_2$ substituent was a strong electron donor to the aromatic ring in both inductive and resonance modes.[5]

The shielding parameters for 3 and 4 also showed a marked dependence on the nature of the trans ligand (X).[5] The magnitude of the chemical shift for 3 was proposed as a measure of the σ-donor capacity of X and the difference between the shielding parameters of 3 and 4 was suggested to be a function of the π-acceptor (or donor) character of X.[5] The theoretical basis for these proposals has been challenged with regard to the mechanism of transmission of electronic effects across the aromatic ring[25] and across the metal atom.[26] However, there does not seem to be a consensus as to the correct mechanisms for such effects.

Despite the uncertainties involved in the interpretation of the effects, the ^{19}F nmr chemical shifts are among the most sensitive probes available for detection of changes in electron density on a metal induced by changes in ligands. When applied to rigorously analogous series of compounds which have a high electron density on the central metal atom, the results are thoroughly consistent with those derived from other techniques.[27] The technique has been applied extensively in recent years (Table I). Within the stated limitations, consistent results have been obtained between series as disparate as the bis(triethylphosphine) platinum complexes 3 and 4 and the cobalt(III) Schiff base complexes. Interestingly, most of the transition metals[28] (in contrast to mercuric ion[29]) are electron donors when viewed as substituents on a fluorobenzene ring. The least satisfactory results have been obtained when the electron density on the central metal atom has been lowered by a formal charge as in [FC$_6$H$_4$PtL(PEt$_3$)$_2$]$^+$ or by strongly electron-withdrawing ligands as in FC$_6$H$_4$-Mn(CO)$_4$L.

The availability of strictly analogous FC$_6$H$_4$MX-(PEt$_3$)$_2$ complexes of nickel, palladium, and platinum presented a rare opportunity to compare electronic effects in a vertical triad of metals. The *m*- and *p*-fluorophenyl analogs of 3 and 4 in which the metal is nickel or palladium and in which X includes I, Br, Cl, CN, CH$_3$,

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(17) (a) R. J. P. Corriu and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 144 (1972); (b) K. Tamao, M. Zembayashi, Y. Kiso, and M. Kumada, *J. Organometal. Chem.*, **55**, C91 (1973).

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(29) D. N. Kravtsov, B. A. Kvasov, L. S. Golovchenko, and E. I. Fedin, *J. Organometal. Chem.*, **36**, 227 (1972).

Table I. [19]F Nmr Studies of Fluorophenyl Metal Compounds

Fluorobenzene substituent	[19]F shielding parameters[a] meta	para	Ref
-MnL(CO)₄	0.70–2.86	7.63–9.97	28
-FeL(CO)(C₅H₅)	2.35–4.47	10.95–13.84	28, b, c
-CoX(chelate)	0.50–3.05	9.29–11.3	d
-Ni(PPh₃)(C₅H₅)	3.71	12.35	28
-Cu	-0.05	5.37	e
-MoL(CO)₂(C₅H₅)	3.10	9.9	f
-WL(CO)₂(C₅H₅)	1.84–3.70	7.50–9.5	f
-PtX(PEt₃)₂	-0.23–3.93	6.96–11.70	5, j
-[PtL(PEt₃)₂]⁺	-0.79–0.59	4.56–6.84	26
-Pt(C₆H₄F)(YEt₃)₂	2.30–2.75	9.70–10.40	g
-AuL	2.10–2.35	2.60–4.04	h, i
-HgX	1.0–0.5	-1.1–0.5	29

[a] Positive values to high field from fluorobenzene. [b] E. S. Bolton, G. R. Knox, and C. G. Robertson, *Chem. Commun.*, 664 (1969). [c] A. N. Nesmeyanov, I. F. Leshcheva, I. V. Polovyanyuk, Yu. A. Ustynyuk, and L. G. Makarova, *J. Organometal. Chem.*, **37**, 159 (1972). [d] H. A. O. Hill, K. G. Morallee, and G. Pelliyer, *J. Amer. Chem. Soc.*, **94**, 277 (1972). [e] A. Cairncross and W. A. Sheppard, *ibid.*, **90**, 2186 (1968). [f] A. N. Nesmeyanov, L. G. Makarova, N. A. Ustynyuk, B. A. Kvasov, and L. V. Bogatyreva, *J. Organometal. Chem.*, **34**, 185 (1972). [g] A. D. Westland and M. Northcott, *Can. J. Chem.*, **48**, 2907 (1970). [h] L. G. Vaughan and W. A. Sheppard, *J. Amer. Chem. Soc.*, **91**, 6151 (1969). [i] D. I. Nichols, *J. Chem. Soc. A*, 1216 (1970). [j] C. Eaborn, M. R. Harrison, P. N. Kapoor, and D. R. M. Walton, *J. Organometal. Chem.*, **63**, 99 (1973).

and C₆H₅ were prepared (Synthesis section). The ^{19}F nmr chemical shifts of these compounds (Table II) were

Table II. [19]F Nmr Parameters[a] for

Ligand (X)	Chemical shift (ppm) Ni	Pd	Pt	J(19F–195Pt)
	Meta Isomers			
CH₃	4.18	3.90	4.20	27
C₆H₅	3.58	3.48	3.71	26
CN	2.06	1.89	2.49	36
Cl	2.22	1.60	2.52	48
Br	2.00	1.36	2.28	49
I	1.72	1.15	2.03	49
	Para Isomers			
CH₃	12.59	11.10	11.68	18
C₆H₅	11.72	10.52	10.96	16
CN	10.59	8.99	9.29	19
Cl	11.52	9.55	10.23	26
Br	11.37	9.30	9.96	28
I	11.12	9.01	9.61	27

[a] Spectra measured at 94.1 MHz with proton decoupling on *ca.* 10% solutions in cyclohexane containing 20% C₆H₅F. All values are to high field from the fluorobenzene reference signal.

measured in cyclohexane solution under conditions which permitted much higher precision than those used in the original study.[5] (No significant discrepancies between the two sets of measurements on the platinum complexes were noted.) The meta and para isomers of each compound were studied in the same solution as well as separately in order to provide a direct measurement of the chemical shift $\delta_p - \delta_m$.

The ^{19}F chemical shifts (Table II) and the derived substituent constants, σ_I (Table III), for the *m*-fluoro-

Table III. Inductive and Resonance Substituent Parameters[a] for *trans*-MX(PEt₃)₂ Groups

Ligand (X)	σ₁ Ni	Pd	Pt	σ_R⁰ Ni	Pd	Pt
CH₃	-0.50	-0.46	-0.51	-0.28	-0.24	-0.25
C₆H₅	-0.42	-0.40	-0.44	-0.28	-0.24	-0.25
CN	-0.20	-0.18	-0.27	-0.29	-0.24	-0.23
Cl	-0.23	-0.14	-0.27	-0.32	-0.27	-0.26
Br	-0.20	-0.11	-0.24	-0.32	-0.27	-0.26
I	-0.16	-0.08	-0.20	-0.32	-0.27	-0.26

[a] Derived from the Taft[24] equations: $\delta_{meta} = -7.10\sigma_I + 0.60$ and $\delta_{para} - \delta_{meta} = -29.5\sigma_R^0$.

phenyl compounds show striking similarities for nickel and platinum. The smaller chemical shifts for the palladium derivatives suggest a slightly lower degree of electron donation to the aromatic ring. The effect of changes in the anionic ligand X are roughly the same for all three metals.

The chemical shifts and Taft substituent constants σ_R^0 for the *p*-fluorophenyl compounds of palladium and platinum are quite similar. The chemical shifts and σ_R^0 values for the nickel complexes are generally larger, indicating greater transfer of electron density to the para carbon. (The σ_R^0 values display less dramatic variations relative to the σ_I constants than the chemical shifts would suggest because of the way in which they are calculated.)

The present results confirm the previous observation, based on less precise data, that the halides give higher σ_R^0 values than do the other ligands. The halide ligands are also distinctive in that they lead to much larger [195]Pt–[19]F coupling constants in compounds **3** and **4**. The large coupling constants suggest a greater involvement of platinum s orbitals in Pt–C bonding with a reciprocal decrease in s orbital involvement in Pt–X bonding for halide relative to C-bonded ligands. The chemical shift and coupling constant effects are consistent in defining an "nmr trans influence series:"[21] I, Br, Cl < CN < C₆H₅, CH₃.

Overall, the similarities between the three metals are more conspicuous than the differences. Perhaps the most significant difference is that the σ_R^0 parameters are significantly larger for the nickel compounds. At risk of provoking further controversy, it is tempting to speculate that nickel is more effective in π interactions with ligands than are palladium and platinum. This proposal parallels one made previously on the basis of studies of zerovalent nickel, palladium, and platinum in M(C₂H₄)(PPh₃)₃ complexes[30] although it is not obvious that divalent and zerovalent complexes should show the same trend.

The ^{19}F nmr chemical shifts of the *p*-fluorophenyl-platinum complexes correlate nicely with the ^{13}C chemical shifts of the para carbon of the analogous phenyl-platinum complexes for a series of *trans*-PtX(C₆H₅)-(PEt₃)₂ compounds recently studied by Coulson and Jesson.[31] A plot of [19]F *vs.* [13]C shielding parameters defines a straight line over the entire range of substituents studied here. A similar, but less exact, correlation exists for the analogous meta chemical shifts. Thus, it appears that the ^{13}C and ^{19}F probes produce compara-

(30) C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, **94**, 2669 (1972).
(31) D. R. Coulson and J. P. Jesson, unpublished results.

Table IV. Analyses of $FC_6H_4PdX(PEt_3)_2$ Isomers

Ligand (X)	% calcd C	H	% found meta C	H	para C	H	Mp, °C meta	para
Cl	45.68	7.24	45.87	7.24	46.02	7.33	89–90	99–100
Br	41.76	6.62	41.74	6.67	42.08	6.70	93–94	108–109
I	38.28	6.07	38.83	6.17	38.54	6.14	111–112	131–132[a]
CN	49.20	7.39	49.47	7.47	49.40	7.54	109–110	118–121[a]
	(N 3.02)		(N 3.20)		(N 3.03)		($\nu_{C\equiv N}$ 2130)[b]	($\nu_{C\equiv N}$ 2130)[b]
CH₃	50.51	8.25	50.04	8.18	49.85	8.18	60–61[a]	72–73[a]
C₆H₅	55.98	7.63	55.90	7.67	55.90	7.69	107–108[a]	103[a]

[a] Melting point accompanied by decomposition. [b] Nujol mull, cm⁻¹.

Table V. Analyses of $FC_6H_4NiX(PEt_3)_2$ Isomers

Ligand (X)	% calcd C	H	% found meta C	H	para C	H	Mp, °C meta	para
Cl	50.80	8.05	50.05[a]	7.96	49.33[a]	7.81	95–96[b]	87–91[b]
	(Cl, 8.33)		(Cl 9.32)					
Br	45.95	7.29	46.46	7.42	46.08	7.43	93–94	95–96
I	41.77	6.63	42.32	6.63	42.11	6.77	106–107[b]	116–117[b]
CN	54.84	8.24	53.98[a]	8.26	54.54	8.25	85–88[b]	106–107
	(N 3.37)		(N 3.44)		(N 3.54)		(ν_{CN} 2130)	(ν_{CN} 2130)
C₆H₅	61.70	8.41	61.64	8.45	61.20	8.36	136–137[b]	138–139[b]

[a] Satisfactory analyses were not obtained due to contamination by the difficultly separable dichloro- or dicyanobis(triethylphosphine)-nickel complexes. [b] Melting accompanied by decomposition.

ble information for this series of compounds. The ¹³C probe appears to be more convenient because it involves synthesis of only one series of compounds. However, the ¹⁹F technique will be preferred in situations in which the fluorine substituent contributes stability, as with aryl nickel compounds.

Experimental Section

M(PEt₃)₄ Complexes. The tetrakis(triethylphosphine)metal(0) complexes of nickel, palladium, and platinum were prepared by the method of Schunn.[2] The dihalobis(triethylphosphine)metal-(II) compounds were prepared *in situ* by reaction of excess triethylphosphine with nickel(II) bromide, palladium(II) chloride, or platinum(II) chloride in boiling tetrahydrofuran. The solutions were cooled to room temperature and excess potassium was added, and the mixture was stirred and boiled under reflux under nitrogen for *ca.* 2 hr. The resulting mixtures were filtered under nitrogen and the filtrates were evaporated to dryness under vacuum. Recrystallization of the residues from pentane with cooling to −78° gave the M(PEt₃)₄ compounds in 50–90% yields.

Fluorophenylplatinum Halides and Cyanides. The oxidative additions of *m*- and *p*-fluorohalobenzenes to tetrakis(triethylphosphine)platinum(0) were carried out in boiling toluene. The reactions of *m*- and *p*-fluorobenzonitrile with the platinum(0) complex required the higher reaction temperature afforded by boiling xylene. All the products were characterized by comparison of the ¹H and ¹⁹F nmr spectra, infrared spectra, and melting points with those of authentic *trans*-FC₆H₄PtX(PEt₃)₂ compounds prepared by other methods.[5] The detailed synthesis procedure is illustrated for *trans*-bromo-*p*-fluorophenylbis(triethylphosphine)platinum(II).

A solution of 2.63 g (15 mmol) of *p*-bromofluorobenzene and 3.84 g (5.75 mmol) of tetrakis(triethylphosphine)platinum(0) in 20 ml of deoxygenated toluene was boiled under reflux for 1 hr. (Generally, heating was continued until the orange color imparted to the solution by the platinum(0) complex faded to pale yellow.) The solution was evaporated to dryness under vacuum and the residue was recrystallized from hexane to give 2.7 g (78%) of the bromo-*p*-fluorophenyl complex, mp 103–104.5° (lit. value[5] 102–104°). No precautions were required to protect the product from air.

Fluorophenylpalladium Halides and Cyanides. The oxidative additions of fluorohalobenzenes and the *m*- and *p*-fluorobenzonitriles to tetrakis(triethylphosphine)palladium(0) were carried out in toluene solution with 1–2-hr reflux periods. The elemental analyses, melting points, and ν_{CN} infrared stretching frequencies of the

products are shown in Table IV. The proton nmr spectra, measured in acetone-d_6 solution, were very similar to those of their platinum analogs. The methyl signals of the triethylphosphine ligands showed the characteristic five-line patterns noted for *trans*-bis(triethylphosphine) complexes in the platinum series as a result of virtual coupling between trans ³¹P nuclei. The general procedure is illustrated by the preparation of *trans*-iodo-*p*-fluorophenylbis-(triethylphosphine)palladium(II).

A solution of 2.9 g (5.0 mmol) of tetrakis(triethylphosphine)-palladium(0) and 3.33 g (15 mmol) *p*-fluoroiodobenzene in 15 ml of toluene was boiled under reflux under nitrogen for 1 hr. (This period was adequate for all except the cyano compounds.) The pale yellow solution was evaporated under reduced pressure and the residue was recrystallized from hexane to give yellow-orange crystals of the iodo complex, mp 131–132°, with decomposition, yield 2.56 g (91%). The 60-MHz proton nmr spectrum (acetone-d_6) showed alkyl and aryl signals in a 30:3.8 intensity ratio (*vs.* 30:4 theory). The aryl proton signals appeared as a pair of apparent triplets at δ 7.30 and 6.93, the CH₂ signal was a complex multiplet at δ 1.78, and the CH₃ signal as an apparent quintet with 7.6 Hz spacing at δ 1.17.

Fluorophenylnickel Halides. The reactions of halofluorobenzenes with tetrakis(triethylphosphine)nickel(0) proceeded much more readily than with the zerovalent palladium and platinum compounds. As judged by color change, the reaction required only a few minutes at room temperature. The products, such as *trans*-chloro-*p*-fluorophenylbis(triethylphosphine)nickel(II) (described in detail below), are very air-sensitive and appear to decompose slowly in solution even in the absence of air.³² Chromatography on activity grade 4 neutral alumina gave the bromo and iodo complexes in relatively pure form (Table V), but the chloro complexes were not obtained completely pure. Although the CH₂ and CH₃ proton nmr signals of the triethylphosphine ligands were closely spaced, the CH₃ signal recorded at 220 MHz of all six complexes showed the characteristic five-line pattern assigned to the trans isomer for the palladium complexes.

The chloro-*p*-fluorophenyl complex was prepared by allowing 1.96 g (15 mmol) of *p*-chlorofluorobenzene and 2.66 g (5.0 mmol) of tetrakis(triethylphosphine)nickel(0) to react in 25 ml of hexane at room temperature. The color rapidly changed from purple to brown. After 1 hr, the solution was evaporated to dryness under vacuum (temperature <40°). The residue was dissolved in deoxygenated hexane and was applied to a chromatographic column of grade 4 neutral alumina. Difluorobiphenyl was eluted first,

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

but hexane or 5% benzene in hexane eluted the desired product from the column. Recrystallization from hexane gave 1.13 g (53%) of yellow-orange crystals, mp 87–91°. Both the elemental analysis (Table V) and the ratio (30:3.6) of alkyl to aryl proton signals in the nmr spectrum indicated 5–10% contamination by dichlorobis(triethylphosphine)nickel(II) which was not removed by repeated recrystallization.

The ^{1}H nmr spectrum (220 MHz, C_6D_6 solution, internal Me_4Si standard) showed aryl signals as a δ 6.73 triplet ($J = 9$ Hz) with additional fine structure and a poorly resolved triplet at δ 7.14. The ethyl signals were a quintet at δ 0.96 and a multiplet at δ 1.27 assigned to CH_3 and CH_2 protons, respectively. The signals did not shift or change structure when small amounts of triethylphosphine were added.

Fluorophenylnickel Cyanides. The reactions of the *m*- and *p*-fluorobenzonitriles with tetrakis(triethylphosphine)nickel(0) occurred readily but the products were often contaminated with dicyanobis(triethylphosphine)nickel(II). In contrast to the halide complexes, the cyanides appeared to undergo rapid exchange with triethylphosphine as judged by the nmr spectral changes.

A solution of 2.66 g (5.0 mmol) of tetrakis(triethylphosphine)-nickel(0) and 1.82 g (15 mmol) of *m*-fluorobenzonitrile in 25 ml of toluene was stirred at 25° for 2 hr. The color rapidly changed from purple to green. The solution was evaporated at 40° under reduced pressure to give brown solid residue. Chromatography from hexane–benzene on activity grade 4 neutral alumina gave 1.06 g of crude *trans*-cyano-*m*-fluorophenylbis(triethylphosphine)nickel-(II) which crystallized from hexane as yellow-brown crystals. mp 85–88°. The purity did not improve on further chromatography or crystallization (Table V). Later fractions from the chromatographic column proved to be dicyanobis(triethylphosphine)nickel-(II) which formed bright yellow crystals from hexane, ν_{CN} 2110 cm^{-1}.

Anal. Calcd for $C_{14}H_{30}N_2NiP_2$: C, 48.45; H, 8.71; N, 8.08. Found: C, 48.63; H, 8.79; N, 8.04.

Both the *m*- and *p*-cyanofluorophenylbis(triethylphosphine)-nickel complexes showed overlap of CH_2 and CH_3 signals in the ^{1}H nmr spectrum at 60 MHz, but the signals were well separated at 220 MHz in a 10% solution in C_6D_6 (Me_4Si internal standard). The CH_2 signal was a poorly resolved multiplet at δ 1.3 but the CH_3 signal was a clean quintet ($J_{apparent} = 7.5$ Hz) at δ 0.90. When 100 μl of triethylphosphine was added to the solution containing 101 mg of complex, the CH_2 signal became a sharp quartet ($J = 7$ Hz) and the CH_3 signal became a triplet ($J = 7$ Hz) at δ 1.27 and 0.95, respectively. The ^{19}F signal did not shift measurably.

trans-**Phenyl-*p*-fluorophenylbis(triethylphosphine)palladium(II).** The Grignard reagent solution prepared from 0.30 g of magnesium turnings and 2.10 g of *p*-bromofluorobenzene in 18 ml of ether was filtered under nitrogen and evaporated to a volume of *ca.* 3 ml. To this solution was added a solution of 5.0 g of *trans*-bromophenyl-bis(triethylphosphine)palladium(II)[2,7] in 50 ml of benzene. The mixture was stirred at room temperature for 5 min. The mixture was diluted with hexane and was filtered to remove magnesium bromide and unreacted starting materials. The filtrate was evaporated to dryness and was extracted with 200 ml of pentane. Chilling the extract to −35° gave 3.15 g of off-white crystalline *trans*-phenyl-*p*-fluorophenylbis(triethylphosphine)palladium(II). An additional 1.27 g was recovered by further chilling. The product was obtained as a pure white solid for analysis (Table IV) by recrystallization from hexane after treatment of the solution with activated carbon. The proton nmr spectrum at 220 MHz in acetone-d_6 solution showed aryl, CH_2, and CH_3 signals in a ratio of 9.2:12.3:18. The methyl signal was a pseudoquintet at δ 1.00 and the methylene absorption was a complex multiplet at δ 1.20.

The same product was obtained by reaction of phenylmagnesium bromide with the analogous *p*-fluorophenylpalladium bromide complex. The same reactions using *m*-fluorophenyl reagents gave *trans*-phenyl-*m*-fluorophenylbis(triethylphosphine)palladium(II).

trans-**Methyl-*m*-fluorophenylbis(triethylphosphine)palladium(II).** A 1.0-ml portion of 2.4 *M* methylmagnesium bromide solution in diethyl ether was added to a solution of 1.04 g of *trans*-bromo-*m*-fluorophenylbis(triethylphosphine)palladium in 20 ml of ether and 20 ml of benzene. After being stirred for 30 min at room temperature, the mixture was evaporated to dryness. The residue was extracted with pentane and the extract was chilled to crystallize the product. Recrystallization from pentane gave 0.6 g of the title compound as a pure white solid which was stored at −30° under nitrogen for analysis. The 220-MHz proton nmr spectrum (benzene-d_6, Me_4Si internal standard) showed four aryl resonances of equal intensity at τ 2.47, 2.62, 2.91, and 3.21. The lone methyl

group gave a triplet signal ($J_{PH} = 5.6$ Hz) at τ 10.17. The ethyl CH_3 signal was a pseudoquintet at τ 9.28 and the CH_2 gave a complex multiplet at τ 8.71. The ^{19}F nmr absorption (proton decoupled) was a triplet ($J_{PF} = 1.0$ Hz) at 3.90 ppm high field from internal fluorobenzene in cyclohexane solution.

The para isomer was obtained by the same procedure; the yield was 0.71 g.

trans-**Phenyl-*p*-fluorophenylbis(triethylphosphine)nickel(II).** Phenylmagnesium bromide solution prepared from 0.06 g of magnesium and 0.40 g of bromobenzene in 10 ml of ether was filtered and evaporated to half volume under nitrogen. A solution of 0.91 g of *trans*-bromo-*p*-fluorophenylbis(triethylphosphine)nickel-(II) in 15 ml of pentane was added at room temperature. The solution changed from red-brown to yellow and a solid precipitated. After 5 min, the mixture was filtered and the filtrate was evaporated to dryness. Recrystallization of the residue from pentane gave 0.64 g of yellow crystals of the title compound, mp 138–139° with color change to red. The proton nmr spectrum even at 220 MHz showed exact coincidence of the CH_2 and CH_3 signals at δ 0.48 ppm. The aryl:alkyl intensity ratio was 8.6:30. A trans configuration was indicated by a triplet ($J_{PF} = 2.0$ Hz) ^{19}F signal in the proton-decoupled spectrum. The meta isomer was prepared as yellow crystals in exactly the same way.

trans-**Methyl-*p*-fluorophenylbis(triethylphosphine)nickel(II).** A 1.0-ml portion of 2.2 *M* methyllithium solution in pentane was added to a solution of 0.94 g of *trans*-bromo-*p*-fluorophenylbis-(triethylphosphine)nickel(II) in 50 ml of hexane and 25 ml of diethyl ether. After 15 min of stirring at room temperature, the mixture was evaporated and the residue was extracted with warm (30–35°) hexane. After treatment with decolorizing charcoal, cooling gave the title compound as an amber solid, yield 0.23 g, mp 73–75° with decomposition to a deep red-orange substance. The 220-MHz proton nmr spectrum (in benzene-d_6, Me_4Si internal standard) showed a triplet CH_3 signal ($J_{PH} = 8.5$ Hz) at τ 10.73. The proton-decoupled ^{19}F signal was also a triplet ($J_{PF} = 3.0$ Hz) indicative of a trans configuration.

The meta isomer was obtained similarly in 0.20 g yield. It melted at 62–63° and the melt discolored to deep red at 71–72°.

Solution Stability. The stabilities of the methyl and phenyl nickel and palladium compounds were determined by preparing *ca.* 10% solutions in benzene-d_6. The 60-MHz ^{1}H nmr spectra were determined promptly and at twice-weekly intervals during storage of the solutions in a nitrogen atmosphere at 25 ± 2° for 5 weeks.

The decomposition of the methyl complexes was monitored by disappearance of the triplet $M–CH_3$ signal at δ 0 to −1 and appearance of a fluorotoluene methyl signal at *ca.* δ 2. With the phenyl-*p*-fluorophenyl complexes, the change was followed by disappearance of aryl absorptions at δ 6.5 and 7.1 and appearance of peaks assignable to *p*-fluorobiphenyl at δ 6.1 and 6.5. The latter peaks were identical in form with those produced by a solution of the authentic compound.

Spectral Measurements. The ^{19}F nmr spectra were measured on a Varian HA-100 spectrometer at 94.1 MHz with proton decoupling on cyclohexane and acetone solutions containing fluorobenzene as an internal standard. The measurements in cyclohexane solution are reported because they are relatively insensitive to concentration and to the amount of fluorobenzene added to the solution. The data on the acetone solutions vary somewhat more with concentration. These results are available in Tables VI and VII. (See paragraph at end of paper regarding supplementary material.) Spectral measurements on the *m*- and *p*-fluorophenyl isomers of each compound were carried out in the same solution as well as separately in order to give a more accurate value for the chemical shift between the two isomers. Substantial amounts (10–20%) of fluorobenzene were used in order to swamp any interactions between aromatic rings and the metal atoms of the complexes.

Supplementary Material Available. A listing of ligand effects (Table VI) and ^{19}F shielding parameters (Table VII) will appear

Effect of Ligand Constraints on the Geometry of Two Sulfur-Bridged Binuclear Iron(II) Complexes. The Structures of Bis{μ-[*N*,*N'*-dimethyl-*N*,*N'*-bis(β-mercaptoethyl)ethylenediamine]}-diiron(II) and Bis{μ-[*N*,*N'*-dimethyl-*N*,*N'*-bis(β-mercaptoethyl)-1,3-propanediamine]}-diiron(II)

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Abstract: The crystal and molecular structures of two high-spin ferrous complexes, bis{μ-[*N*,*N'*-dimethyl-*N*,*N'*-bis(β-mercaptoethyl)ethylenediamine]}-diiron(II), (FeL)₂, and bis{μ-[*N*,*N'*-dimethyl-*N*,*N'*-bis(β-mercaptoethyl)-1,3-propanediamine]}-diiron(II), (FeL')₂, are reported. (FeL')₂ crystallizes as red-brown parallelepipeds in space group $P2_1/c$. The cell parameters are a = 9.538 (1) Å, b = 11.636 (1) Å, c = 12.248 (1) Å, and β = 115.54 (1)°. The measured density is 1.497 (2) g/cm³ in agreement with the calculated value of 1.496 (1) g/cm³ for four Fe-(C₉H₂₀N₂S₂) formulas in the unit cell. The structure has been refined to R_1 = 0.059 and R_2 = 0.085 based on 1532 independent observed reflections. The molecule is a dimercapto-bridged dimer with an iron–iron distance of 3.371 (2) Å. The coordination geometry about each of the iron atoms is a slightly distorted trigonal bipyramid. (FeL)₂ has the same space group with cell constants a = 9.202 (4) Å, b = 11.080 (7) Å, c = 12.418 (6) Å, and β = 112.62 (2)°. The measured density is 1.495 (5) g/cm³ and the calculated density is 1.490 (3) g/cm³ for four Fe(C₈H₁₈N₂S₂) formulas per unit cell. Its structure was solved based on 738 independent reflections and refined to R values of 0.074 and 0.083. With the same N₂S₃ donor atom set as (FeL')₂, the coordination geometry of (FeL)₂ is much more distorted from that of a trigonal bipyramid. Elimination of one methylene group between the two nitrogen donor atoms has caused a 15° decrease of the axial–metal–axial angle and deformation of the Fe₂S₂ rhombus. The iron–iron nonbonded distance is shortened significantly from 3.371 (2) Å in (FeL')₂ to 3.206 (5) Å in (FeL)₂, accompanied by a decrease in the bridging angle Fe–S1–Fe' from 86.91 (8)° in (FeL')₂ to 82.7 (2)° in (FeL)₂. These results demonstrate that external ligand constraints can influence the geometry of a binuclear Fe₂S₂ system.

The variation of metal–metal distance with electronic configuration has previously been established for low-spin sulfur-bridged iron dimers where strong metal–metal bonding can occur.[1-3] Here we report that the metal–metal distance in binuclear Fe₂(SR)₂ complexes can also be influenced by geometric constraints when the bridging sulfur atom is part of a tetradentate chelating ligand. This work is part of a continuing investigation of iron–sulfur coordination compounds and proteins.[4]

A tetradentate ligand system with an N₂S₂ donor atom set was employed. Two ligands, *N*,*N'*-dimethyl-*N*,*N'*-bis(β-mercaptoethyl)ethylenediamine (LH₂) and *N*,*N'*-dimethyl-*N*,*N'*-bis(β-mercaptoethyl)-1,3-propanediamine (L'H₂), were synthesized.[5] As anticipated from

LH₂   L'H₂
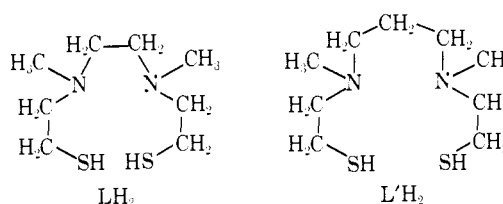
a careful examination of molecular models and subsequently demonstrated by the structural analysis of a zinc derivative,[6] [Zn₂LCl₂]₂·2H₂O, complexes of the former ligand are sterically strained. The strain may be judged by anomalously small bond angles imposed by the chelate rings and by other geometric criteria discussed in detail below. In complexes of L', the strain was expected to be relieved by the presence of the additional methylene group in the N,N chelate ring.

The synthesis and chemical and physical properties of the iron derivatives [Fe(C₈H₁₈N₂S₂)]₂,(Fe L)₂, and [Fe(C₉H₂₀N₂S₂)]₂, (FeL')₂, will be the subject of future communications.[7] Here we report the molecular

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