solid was formed. Yield: 223 mg of S=PMe$_3$ (2.06 mmol, 86%). ^{1}H NMR (C$_6$D$_6$): 1.0482 (d, J = 13 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 27.81 (s).

X-ray Structure of Cp*Rh(PMe$_3$)(SCH$_2$S). A single crystal of the complex (crystal dimensions 0.15 × 0.18 × 0.75 mm) was mounted, and cell constants were obtained from 25 centered reflections with values of χ between 0 and 70°. A quadrant of data was collected in accord with the parameters given in Table IV. The Molecular Structure Corporation TEXSAN analysis software package was used for data reduction and solution.[13] A standard Patterson map solution of the structure to locate the rhodium, followed by expansion of the structure with the program <<DIRDIF, revealed all non-hydrogen atoms. After isotropic refinement, an absorption correction was applied using the program DIFABS. Full-matrix least-squares anisotropic refinement of the non-hydrogen atoms with hydrogens attached to carbon in idealized positions was carried out to convergence. Selected distances and angles are given in Table III.

Acknowledgment. We thank the U.S. Department of Energy (Grant DE-FG02-86ER13569) for their support of this work.

Supplementary Material Available: Complete tables of final positional and thermal parameters, non-hydrogen bond distances and angles, and least-squares planes (7 pages); a listing of calculated and observed structure factors (18 pages). Ordering information is given on any current masthead page.

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[13] $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\{\sum wF_o^2\}$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Synthesis and Spectroscopic Characterization of Linear Mono-, Bi-, and Trimetallic Bis(methyldiphenylphosphine)nickel Complexes Having 1,4-Tetrafluorophenylene Bridges[1,2]

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The synthesis and spectroscopic characterization of a series of linear mono-, bi-, and trimetallic complexes containing (MePh$_2$P)$_2$Ni units and bridging and/or terminal fluoroaryl groups is reported. The mononickel complexes (MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$X)Br and (MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$X)$_2$ (X = H, F, Br) may be prepared via reaction of (MePh$_2$P)$_2$NiBr$_2$ with 1 or 2 equiv, respectively, of 1,4-C$_6$F$_4$XLi. The "arene-poor" di- and trinickel complexes [(MePh$_2$P)$_2$NiBr]$_2$(μ-1,4-C$_6$F$_4$) and [(MePh$_2$P)$_2$Ni]$_3$(μ-1,4-C$_6$F$_4$)$_2$Br$_2$ are obtained via reaction of 1 equiv of 1,4-C$_6$F$_4$Li$_2$ or (MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$Li)$_2$, respectively, with 2 equiv of (MePh$_2$P)$_2$NiBr$_2$, while [(MePh$_2$P)$_2$Ni]$_3$(μ-1,4-C$_6$F$_4$)$_2$Cl$_2$ is obtained in an analogous reaction from (MePh$_2$P)$_2$NiCl$_2$. The "arene-rich" di- and trinickel compounds [(MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$H)]$_2$(μ-1,4-C$_6$F$_4$) and [(MePh$_2$P)$_2$Ni]$_3$(μ-1,4-C$_6$F$_4$)$_2$(1,4-C$_6$F$_4$H)$_2$ may then be prepared from the reaction of their respective "arene-poor" precursors with 2 equiv of 1,4-C$_6$F$_4$HLi. The ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectroscopic data for each oligomer unambiguously establishes its chain length and repeat unit structure (trans geometry about nickel and 1,4-substitution about C$_6$F$_4$) and suggests that there is significant electronic communication down the oligomer backbones in the polymetallic complexes. Evidence is also presented which suggests that *cis*-(MePh$_2$P)$_2$Ni(1,4-C$_6$F$_4$Br)$_2$ is a kinetic intermediate in the synthesis of the trans isomer.

Introduction

Over the last several years there has been growing interest in the preparation and characterization of organometallic polymers having transition metals in the polymer backbone. Such materials are of interest because of their substantial potential for practical applications in the areas of one-dimensional conductivity[3] and nonlinear optical behavior.[4] Complexes in which the transition-metal centers are joined by organic fragments capable of π conjugation (e.g. -C≡CC$_6$H$_4$C≡C-, -NC$_4$H$_4$N-, -CNC$_6$H$_4$NC-)[5,6] are expected to display these useful properties due to conjugation of the π-symmetry orbitals on the metal centers and the organic ligands. These ma-

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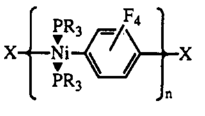
terials offer a number of potential advantages over more conventional π-conjugated organic polymers (e.g. polyacetylene, poly(*p*-phenylene) and polythiophene) owing to the introduction of the metal centers and their ancillary ligands into the polymer backbones. For example, it should prove possible to fine tune the physical properties of these materials which are related to polymer processability (e.g. melting point, solubility) independently of the properties of interest, which are derived from the π conjugation (e.g. nonlinear optical coefficients, *intra*chain conductivity), by the judicious choice of ancillary ligands (e.g. PBu_3 vs PPh_3).[7] This is generally not possible, or is expected to be much more difficult, for the analogous organic polymers.

Since polymeric materials are generally more difficult to prepare and, especially, to structurally characterize than are discrete complexes, a common approach to developing transition-metal-containing polymers has involved the initial syntheses and characterization of low molecular weight species having the same structures as the repeat units in the target polymers.[5,6,8] One theme of current research in this area has been directed toward the study of polymers in which the bridging groups have aromatic cores. The subclass of such materials that we have chosen to investigate is that in which the metal centers are bridged by aromatic ligands via direct metal–arene σ bonds. Our initial studies in this area have focused on bi- and trimetallic complexes of iron and manganese (e.g. 1,4-$C_6F_4Fp_2$ and 1,3,5-$C_6H_3(Mn(CO)_5)_3$, where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$)[9] including those in which the arene bridge is π bound to chromium-, molybdenum-, and tungsten-containing fragments (e.g. $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3$).[10] These studies have demonstrated that such aromatic linkages produce relatively strong electronic interactions between the adjacent metal centers and have suggested that they occur primarily via π-symmetry overlap between filled metal-centered orbitals and the arene π^* orbitals.[9,10]

More recently, we have begun to prepare a series of model oligomers of fluorinated arene-bridged $Ni(PR_3)_2$ units, i.e.



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These studies have four goals, namely, to optimize synthetic routes for the preparation of such polymetallic linkages, to ascertain how such materials are best characterized (particularly, how ^1H, ^{19}F, and ^{31}P NMR spectroscopy can be used to establish oligmer/polymer repeat unit structure and chain length), to estimate the degree of conjugation down the backbones of these materials, and to prepare "monomers" for eventual polymer syntheses. In this paper, we present the complete results of these initial studies, including the preparation of a series of mono-, bi-, and trimetallic nickel complexes having *p*-tetrafluorophenylene bridging groups and methyldiphenylphosphine ($PMePh_2$) as the ancillary phosphine ligands on nickel.

Experimental Section

Unless otherwise noted, all reactions and subsequent manipulations were performed by conventional techniques for the manipulation of air-sensitive compounds as described previously.[9a,b] Thus, anaerobic and anhydrous conditions were maintained by using a prepurified argon or dinitrogen atmosphere using vacuum-line and inert-atmosphere glovebox techniques.[11a] The reagents used were purchased from commercial suppliers or were prepared according to the published procedures. The chemicals used were of reagent grade or comparable purity, and where necessary, they were purified before use and their purity ascertained by elemental analyses and/or other suitable methods.[11b] Thus, $(Ph_3P)_2NiBr_2$, $(MePh_2P)_2NiBr_2$, and $(MePh_2P)_2NiCl_2$ were prepared via reaction of $NiBr_2$ or $NiCl_2{\cdot}6H_2O$ with PPh_3 or $PMePh_2$ in 1-butanol,[12] and the nominally 2.5 M *n*-BuLi/hexanes solution was standardized regularly.[13] Solvents used were dried and deaerated by standard procedures and stored under N_2 or Ar.[11b] Thus, THF and Et_2O were distilled from sodium–benzophenone ketal under an inert atmosphere. Unless specified otherwise, the reactions and any subsequent manipulations described below were effected at ambient temperatures ($\approx$23 °C).

Nuclear magnetic resonance spectra were recorded using a Bruker AM-400 spectrometer on CD_2Cl_2 solutions and employing a deuterated solvent lock. The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR chemical shifts are reported in parts per million downfield from external Me_4Si, $CFCl_3$, and 85% H_3PO_4, respectively. Elemental analyses were performed by D. Mahlow and A. Dunn of this department.

Preparation of Compounds. (a) $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)Br$. To a solution of 1,2,4,5-tetrafluorobenzene (0.25 mL, 0.34 g, 2.2 mmol) in THF (10 mL) that had been cooled in a dry ice/acetone bath to $\approx$−78 °C was added *n*-butyllithium (0.65 mL, 2.5 M *n*-BuLi/hexanes; 1.6 mmol *n*-BuLi).[13] The colorless suspension of 1,4-C_6F_4HLi thus formed[14] was stirred at $\approx$−78 °C for

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Table I. NMR Data for the Complexes (δ in ppm)[a]

complex	NMR data		
	$^{31}P\{^1H\}$	^{19}F	^1H
$(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)Br$	9.17 (s)	−119.41 (m, 2 F), −142.28 (m, 2 F) (AA′MM′X)	7.58 (m, 8 H), 7.35 (t, 4 H), 7.29 (t, 8 H), 5.92 (m, 1 H, H_X), 2.00 (t, 6 H, $^3J_{H-P} = 7.6$ Hz)[b]
$(MePh_2P)_2Ni(C_6F_5)Br$	8.91 (s)	−117.47 (m, 2 F), −162.80 (m, 1 F), −163.96 (m, 2 F) (AA′MXX′)	7.56 (m, 8 H), 7.36 (t, 4 H), 7.29 (t, 8 H), 2.06 (t, 6 H, $^3J_{H-P} = 7.6$ Hz)[b]
$(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)Br$	8.74 (s)	−116.15 (m, 2 F), −136.95 (m, 2 F) (AA′XX′)	7.56 (d, 8 H), 7.35 (t, 4 H), 7.28 (t, 8 H), 2.06 (t, 6 H, $^3J_{H-P} = 7.6$ Hz)[b]
$(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$	10.51 (s)	−117.64 (m, 4F), −142.50 (m, 4 F) (AA′MM′X)	7.46 (m, 8 H), 7.32 (t, 4 H), 7.24 (t, 8 H), 6.16 (m, 2 H, H_X), 1.61 (t, 6 H, $^3J_{H-P} = 7.2$ Hz)[b]
$(MePh_2P)_2Ni(C_6F_5)_2$	9.63 (s)	−115.77 (m, 4 F), −161.93 (m, 2 F), −163.95 (m, 4 F), (AA′MXX′)	7.46 (m, 8 H), 7.38 (m, 4 H), 7.26 (m, 8 H), 1.65 (t, 6 H, $^3J_{H-P} = 7.2$ Hz)[b]
$(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$	9.40 (s)	−114.38 (m, 4 F), −137.12 (m, 4 F) (AA′XX′)	7.46 (m, 8 H), 7.33 (m, 4 H), 7.26 (m, 8 H), 1.66 (t, 6 H, $^3J_{H-P} = 7.2$ Hz)[b]
$[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$	5.52 (s)	−118.96 (s)	7.72 (m, 16 H), 7.48 (m, 8 H), 7.38 (m, 16 H), 1.07 (t, 12 H, $^3J_{H-P} \approx 8$ Hz)[b]
$[(MePh_2P)_2NiBr](\mu\text{-}1,4\text{-}C_6F_4)\text{-}[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]$	10.28 (s), 6.42 (s)	−115.95 (m, 2 F), −118.39 (m, 2 F), −120.82 (m, 2 F), −143.09 (m, 2 F) (AA′EE′MM′RR′X)	7.70–7.17 (m, br, 40 H), 1.56 (t, 6 H, $^3J_{H-P} = 20$ Hz),[b] 0.82 (t, 6 H, $^3J_{H-P} \approx 18$ Hz)[b]
$[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]_2\text{-}(\mu\text{-}1,4\text{-}C_6F_4)$	10.38 (s)	−117.98 (s, 4 F), −118.14 (m, 4 F), −143.25 (m, 4 F) (AA′MM′X)	7.36 (m, 16 H), 7.23 (t, 8 H), 7.15 (t, 16 H), 5.87 (m, 2 H, H_X), 1.30 (t, 12 H, $^3J_{H-P} \approx 8$ Hz)[b]
$[(MePh_2P)_2Ni]_3\text{-}(\mu\text{-}1,4\text{-}C_6F_4)_2Cl_2$	8.78 (s, 2 P), 4.93 (s, 4 P)	−116.34 (m, 4 F), −120.59 (m, 4 F) (AA′XX′)	7.67 (d, 16 H), 7.44 (t, 8 H), 7.39 (d, 8 H), 7.35 (m, 16 H), 7.24 (t, 4 H), 7.14 (t, 8 H), 1.02 (t, 6 H, $^3J_{H-P} \approx 8$ Hz),[b] 0.69 (t, 12 H, $^3J_{H-P} \approx 8$ Hz)[b]
$[(MePh_2P)_2Ni]_3\text{-}(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$	8.64 (s, 2 P), 6.11 (s, 4 P)	−116.11 (m, 4 F), −120.86 (m, 4 F) (AA′XX′)	7.67 (d, 16 H), 7.47 (d, 8 H), 7.41 (m, 8 H), 7.37 (m, 16 H), 7.24 (m, 4 H), 7.14 (t, 8 H), 1.07 (t, 6 H, $^3J_{H-P} \approx 8$ Hz),[b] 0.70 (t, 12 H, $^3J_{P-H} \approx 8$ Hz)[b]
$[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2\text{-}(1,4\text{-}C_6F_4H)_2$	11.09 (s, 4 P), 9.28 (s, 2 P)	−118.0 (m, 6 F), −143.36 (m, 2 F) (AA′EE′MM′RR′X)	7.34 (m, 16 H), 7.24 (m, 16 H), 7.15 (m, 16 H), 7.08 (t, 4 H), 6.94 (t, 8 H), 5.80 (m, 2 H), 1.20 (t, 12 H, $^3J_{H-P} \approx 7$ Hz),[b] 0.74 (t, 6 H, $^3H_{-P} \approx 7$ Hz)[b]

[a] NMR data were recorded as CD_2Cl_2 solutions, at 161.978 MHz for $^{31}P\{^1H\}$, at 376.503 MHz for ^{19}F, and at 400.135 MHz for ^1H spectra. [b] The $^3J_{H-P}$ coupling constants are approximated by the difference between the chemical shifts of the two *external* lines of these virtual triplets; see ref 19 in text.

15 min and then transferred via cannula into a solution of $(MePh_2P)_2NiBr_2$[12] (1.00 g, 1.62 mmol) in THF (10 mL) that had been cooled in an ice water bath to ≈0 °C, resulting in a color change of the solution from brown-purple to deep orange. The mixture was stirred at ≈0 °C for 1 h and then at room temperature for 3 h, after which the volume was reduced under vacuum to ≈5 mL. Degassed methanol (15 mL) was added, resulting in the formation of an orange-brown precipitate. The resulting mixture was stirred in ice for 15 min and allowed to settle, and the supernatant liquid was drawn off by cannulation. The solid was then washed with methanol (2 × 10 mL) and then dried under a stream of N_2. After further drying in vacuo, $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)Br$ was obtained as an orange-brown powder (0.84 g, 1.22 mmol) in 76% yield. Anal. Calcd for $C_{32}H_{27}BrF_4NiP_2$: C, 55.86; H, 3.95; Br, 11.61. Found: C, 55.72; H, 3.88; 11.58.

The compounds $(MePh_2P)_2Ni(C_6F_5)Br$[15] and $(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)Br$[16] were prepared using a procedure similar to that described above (substituting C_6F_5Br or $1,4\text{-}C_6F_4Br_2$, respectively, for $1,2,4,5\text{-}C_6F_4H_2$) and were isolated in 39% and 85% yields, respectively. The $^{31}P\{^1H\}$, ^{19}F, and ^1H NMR spectroscopic data for these compounds and those reported subsequently are found in Table I. Anal. Calcd for $C_{32}H_{26}Br_2F_4NiP_2$: C, 50.11; H, 3.42; Br, 20.84. Found: C, 48.71; H, 3.40; Br, 20.83.

(b) $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$. To a solution of 1,2,4,5-tetrafluorobenzene (0.90 mL, 1.21 g, 8.06 mmol) in THF (25 mL) that had been cooled in a dry ice/acetone bath to ≈−78 °C was added *n*-butyllithium (2.60 mL, 2.5 M *n*-BuLi/hexanes; 6.50 mmol *n*-BuLi). The colorless suspension of $1,4\text{-}C_6F_4HLi$ thus formed[14] was stirred at ≈−78 °C for 20 min and then transferred via cannula to a solution of $(MePh_2P)_2NiBr_2$ (2.00 g, 3.23 mmol) in THF (15 mL) that had been cooled in an ice water bath to ≈0 °C, causing the solution to change from deep brown-purple to deep orange. The resulting mixture was stirred at ≈0 °C for 1 h, during which time it lightened to yellow and a flocculent pale yellow precipitate was formed. An additional 15 mL of THF was added and the mixture stirred at room temperature for 2 days, after which the volume was reduced under vacuum to ≈10 mL, followed by addition of deaerated methanol (50 mL) to complete precipitation. The solid was allowed to settle, and the supernatant liquid was drawn off by cannulation. The solid was then washed with methanol (2 × 15 mL) and dried under a stream of N_2 followed by vacuum. The pale yellow solid thus obtained was recrystallized from THF/hexanes (40 mL/50 mL) to give 2.14 g (2.82 mmol, 88% yield) of $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$ as a pale yellow powder. Anal. Calcd for $C_{38}H_{28}F_8NiP_2$: C, 60.27; H, 3.73. Found: C, 59.90; H, 3.66.

The compounds $(MePh_2P)_2Ni(C_6F_5)_2$[15] and $(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$ were prepared in a similar manner (substituting C_6F_5Br or $1,4\text{-}C_6F_4Br_2$, respectively, for $1,2,4,5\text{-}C_6F_4H_2$) and were obtained in 27% and 72% yields, respectively. Anal. Calcd for $C_{38}H_{26}Br_2F_8NiP_2$: C, 49.88; H, 2.86; Br, 17.46. Found: C, 49.88; H, 2.82; Br, 17.22.

(c) $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$. To a solution of 1,4-dibromotetrafluorobenzene (0.497 g, 1.61 mmol) in THF (30 mL) that had been cooled in a dry ice/acetone bath to ≈−78 °C was added *n*-butyllithium (1.30 mL, 2.5 M *n*-BuLi/hexanes; 3.25 mmol *n*-BuLi).[13] The colorless suspension of $1,4\text{-}C_6F_4Li_2$ thus formed[14] was stirred at ≈−78 °C for 20 min and then transferred via cannula to a solution of $(MePh_2P)_2NiBr_2$ (2.00 g, 3.23 mmol) in THF (15 mL) that had been cooled in an ice water bath to ≈0 °C. This caused a change in color from deep brown-purple to deep orange-brown. The resulting solution was stirred at ≈0 °C for 2 h, during which time a yellow-orange precipitate formed. The mixture was then stirred at room temperature overnight and

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(14) (a) Cohen, S. C. *J. Chem. Soc., Dalton Trans.* **1973**, 553–555. (b) Chivers, T. *J. Organomet. Chem.* **1969**, *19*, 75–80. (c) Cohen, S. C.; Reddy, M. L. N.; Roe, D. M.; Tomlinson, A. J.; Massey, A. G. *J. Organomet. Chem.* **1968**, *14*, 241–251. (d) De Pasquale, R. J.; Tamborski, C. *J. Organomet. Chem.* **1968**, *13*, 273–282. (e) Cohen, S. C.; Moore, D.; Price, R.; Massey, A. G. *J. Organomet. Chem.* **1968**, *12*, P37–P38. (f) Fearon, F. W. G.; Gilman, H. *J. Organomet. Chem.* **1967**, *10*, 535–537. (g) Cohen, S. C.; Massey, A. G. *J. Organomet. Chem.* **1967**, *10*, 471–481. (h) Tamborski, C.; Burton, W. H.; Breed, L. W. *J. Org. Chem.* **1966**, *31*, 4229–4230. (i) Tamborski, C.; Soloski, E. J. *J. Org. Chem.* **1966**, *31*, 746–749. (j) Tamborski, C.; Soloski, E. J. *J. Org. Chem.* **1966**, *31*, 743–745. (k) Holland, D. G.; Tamborski, C. *J. Org. Chem.* **1966**, *31*, 280–283. (l) Cohen, S. C.; Fenton, D. E.; Tomlinson, A. J.; Massey, A. G. *J. Organomet. Chem.* **1966**, *6*, 301–305. (m) Cohen, S. C.; Massey, A. G. *Tetrahedron Lett.* **1966**, 4393–4394. (n) Harper, R. J., Jr.; Soloski, E. J.; Tamborski, C. *J. Org. Chem.* **1964**, *29*, 2385–2389. (o) Skancke, A. In *Fluorine-Containing Molecules: Structure, Reactivity, Synthesis, and Applications*; Liebman, J. F.; Greenberg, A.; Dolbier, W. R., Jr., Eds.; VCH Publishers: New York, 1988; pp 43–64.

(15) (a) Rausch, M. D.; Tibbetts, F. E. *Inorg. Chem.* **1970**, *9*, 512–516. (b) Churchill, M. R.; Kalra, K. L.; Veidis, M. V. *Inorg. Chem.* **1973**, *12*, 1656–1662.

(16) This complex was not obtained in an analytically pure form but was characterized in detail by ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopy. These studies indicated that the isolated materials contained only the single organometallic species described.

reduced in volume to ≈10 mL. Deaerated methanol (50 mL) was slowly added to the resulting thick brown suspension producing an orange precipitate that was then cooled in an ice water bath to ≈0 °C and stirred for 30 min. The solid was then filtered out in air, washed with methanol (2 × 20 mL) and diethyl ether (2 × 20 mL), and dried under vacuum to yield $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$ as an orange powder (1.26 g, 1.03 mmol) in 64% yield. Anal. Calcd for $C_{58}H_{52}Br_2F_4Ni_2P_4$: C, 56.82; H, 4.27; Br, 13.03. Found: C, 56.42; H, 4.09; Br, 12.85.

(d) $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$. To a suspension of $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$ (1.00 g, 1.32 mmol) in THF (20 mL) that had been cooled in an ice water bath to ≈0 °C was added *n*-butyllithium (1.30 mL, 2.5 M *n*-BuLi/hexanes; 3.25 mmol *n*-BuLi),[13] causing a slight darkening of the mixture to yellow-orange. The resulting slurry was stirred at ≈0 °C for 15 min and then tranferred via cannula to a solution of $(MePh_2P)_2NiBr_2$ (2.00 g, 3.23 mmol) in THF (15 mL) that had been cooled in an ice water bath to ≈0 °C. This resulted in a change of color from deep brown-purple to deep orange. The mixture was stirred at ≈0 °C for 1 h, during which time an orange solid was formed, and then at room temperature for 3 h. The volume was reduced in vacuo to ≈10 mL, and precipitation was completed by the addition of degassed methanol (40 mL). The mixture was stirred at ≈0 °C for 15 min and then allowed to settle, after which the supernatant liquid was drawn off and the solid was washed with methanol (20 mL) and then dried under a stream of N_2 followed by vacuum. The product was recrystallized from THF/hexanes (30 mL/50 mL) to give an 83% yield (2.01 g, 1.10 mmol) of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ as a medium orange powder. Anal. Calcd $C_{90}H_{78}Br_2F_8Ni_3P_6$: C, 58.96; H, 4.29; Br, 8.72. Found: C, 58.72; H, 4.50; Br, 8.35.

The compound $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Cl_2$ was prepared using a procedure analogous to that above (using $(MePh_2P)_2NiCl_2$ in place of $(MePh_2P)_2NiBr_2$) and was obtained in 47% yield.[16] Anal. Calcd for $C_{90}H_{78}Cl_2F_8Ni_3P_6$: C, 61.97; H, 4.51; Cl, 4.06. Found: C, 60.82; H, 4.55; Cl, 4.27.

(e) $[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]_2(\mu\text{-}1,4\text{-}C_6F_4)$. To a solution of 1,2,4,5-tetrafluorobenzene (0.20 mL, 0.27 g, 1.8 mmol) in THF (10 mL) that had been cooled in a dry ice/acetone bath to ≈−78 °C was added *n*-butyllithium (0.40 mL, 2.5 M *n*-BuLi/hexanes; 1.00 mmol *n*-BuLi).[13] The resulting colorless suspension of $1,4\text{-}C_6F_4HLi$ thus formed[14] was stirred at ≈−78 °C for 15 min and then was transferred via cannula to a suspension of $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$ (0.500 g, 0.408 mmol) in THF (5 mL) that had been cooled to ≈0 °C in an ice water bath. The mixture was stirred at ≈0 °C for 1 h, during which time the suspension changed from light orange to medium yellow, and then at room temperature for 3 h. The volume was reduced to ≈5 mL in vacuo and degassed methanol (15 mL) was added, resulting in formation of a light orange solid. This mixture was stirred at ≈0 °C for 15 min and allowed to settle, and then the supernatant liquid was drawn off by cannula. The remaining solid was washed with methanol (10 mL) and then dried under a stream of N_2 and then in vacuo. The product, $[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]_2(\mu\text{-}1,4\text{-}C_6F_4)$, was thus obtained as a pale orange powder (0.13 g, 0.095 mmol) in 23% yield. Anal. Calcd for $C_{70}H_{54}F_{12}Ni_2P_4$: C, 61.62; H, 3.99. Found: C, 61.80; H, 4.00.

The compound $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2(1,4\text{-}C_6F_4H)_2$ was prepared using a procedure analogous to that above (substituting $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ for $[(MePh_2P)_2NiBr](\mu\text{-}1,4\text{-}C_6F_4)$) and was obtained in 24% yield.[16]

Preparation of Cis/Trans Isomer Mixtures of $(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$. The same method was used as was employed to synthesize pure *trans*-$(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$ (see part b above) with the exception that the total reaction time (i.e. starting with the addition of C_6F_4BrLi to the $(MePh_2P)_2NiBr_2$ solution and terminating with the addition of methanol to the product mixture) was limited to ca. 4 h. The yellow solids obtained were shown via $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy to consist of 20–50% of *cis*-$(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$, with the balance being the trans isomer.

Preparation of $[(MePh_2P)_2NiBr](\mu\text{-}1,4\text{-}C_6F_4)[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]/[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ Mixture. When the preparation of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ was attempted as described in part d, above, using a sample of $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$ which had not been recrystallized (i.e. the material isolated as in part b, above, after precipitation by the addition of methanol), the reaction product was found to be somewhat lighter in color than pure $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ and was shown via $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy to contain a significant proportion (20–80%) of $[(MePh_2P)_2NiBr](\mu\text{-}1,4\text{-}C_6F_4)[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]$. Although this material was never entirely separated from $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$, its $^{31}P\{^1H\}$, ^{19}F, and some of its ^1H NMR spectroscopic resonances could be discerned and are reported in Table I.

Results and Discussion

As was stated in the Introduction, we are interested in the preparation of polymeric materials containing repeating units composed of square-planar *trans*-bis(phosphine)nickel centers bridged by fluoroaryl groups. Initial investigations within this laboratory were concerned with the chemistry of triphenylphosphine-containing complexes (the best studied, least costly, and easiest to handle phosphine). A series of mononuclear mono- and diaryl complexes was prepared, either via oxidative-addition reactions with $Ni(PPh_3)_4$, e.g.

$$Ni(PPh_3)_4 + 1,4\text{-}C_6F_4Br_2 \rightarrow (Ph_3P)_2Ni(1,4\text{-}C_6F_4Br)Br + 2PPh_3 \quad (1)$$

or via metathesis reactions between $(Ph_3P)_2NiBr_2$ and aryllithium reagents, e.g.

$$(Ph_3P)_2NiBr_2 + C_6F_5Li \rightarrow (Ph_3P)_2Ni(C_6F_5)Br + LiBr \quad (2)$$

$$(Ph_3P)_2NiBr_2 + 2C_6F_5Li \rightarrow (Ph_3P)_2Ni(C_6F_5)_2 + 2LiBr \quad (3)$$

However, the syntheses of complexes of higher nuclearity were unsuccessful. Thus, the reactions of 2 equiv of $Ni(PPh_3)_4$ with 1 equiv of various *p*-dibromobenzenes, in which we were attempting to produce arene-bridged complexes, e.g.

$$2Ni(PPh_3)_4 + 1,4\text{-}C_6F_4Br_2 \nrightarrow [(Ph_3P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4) + 4PPh_3 \quad (4)$$

yielded only mixtures of starting material and monometallic monoaryl complexes, e.g.

$$2Ni(PPh_3)_4 + 1,4\text{-}C_6F_4Br_2 \rightarrow (Ph_3P)_2Ni(1,4\text{-}C_6F_4Br)Br + Ni(PPh_3)_4 + 2PPh_3 \quad (5)$$

Qualitative simulations of the molecular geometries of the desired polynuclear complexes containing *p*-phenylene-bridged $(Ph_3P)_2Ni$ units[17] were carried out using the program Chem3D Plus (Cambridge Scientific Computing) and showed significant steric interactions to be present between the phenyl rings of Ph_3P groups attached to adjacent nickel centers. This interaction was the result of the relatively short Ni–Ni distances in these species (≈6.6 Å) and the relatively large cone angle of PPh_3 (≈145°).[7] These qualitative models suggested that these adverse interferences could be decreased if the bridging *p*-phenylene rings were replaced by other aromatic groups, which would produce larger Ni–Ni separations (e.g. 4,4′-biphenyl), or if the cone angle of the phosphine ligand were reduced. Consequently, we redirected our efforts toward the synthesis of the $PMePh_2$-containing nickel monomers and oligomers, since this phosphine ligand has a sufficiently small cone angle (≈136°)[7] that no inter-phosphine steric interactions were observed in our molecular modeling

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(17) Metrical parameters for the individual $(R_3P)_2NiAr_2$ and $\mu\text{-}1,4\text{-}C_6F_4$ fragments were approximated from those reported for the related monometallic complexes.[15b,18]

(18) Churchill, M. R.; Veidis, M. V. *J. Chem. Soc., Dalton Trans.* **1972**, 670–675.

studies and because its methyl group is useful for establishing the geometry around the nickel center as either cis or trans (by NMR spectroscopy).[19]

As can be seen from the results presented in the Experimental Section, the preparations of these complexes are, in principle, relatively straightforward. However, particular care must be taken in controlling the rate of addition of *n*-butyllithium during the generation of the aryllithium reagents,[14] especially in the case of 1,4-C_6F_4HLi, where formation of unwanted 1,4-$C_6F_4Li_2$ can occur, i.e.[14,20]

$$1,4\text{-}C_6F_4H_2 + n\text{-BuLi} \rightarrow (1-2n)1,4\text{-}C_6F_4HLi + n\,1,4\text{-}C_6F_4Li_2 + C_4H_{10} \quad (6)$$

$$1,4\text{-}C_6F_4Br_2 + n\text{-BuLi} \rightarrow (1-2n)1,4\text{-}C_6F_4BrLi + n\,1,4\text{-}C_6F_4Li_2 + n\text{-BuBr} \quad (7)$$

The amount of 1,4-$C_6F_4Li_2$ formed as a byproduct in these reactions can be minimized through use of an excess of the parent fluoroaryl compound and by slow addition of *n*-BuLi at low temperatures (≈−78 °C).[21] In the synthesis of $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$, i.e.

$$2(MePh_2P)_2NiBr_2 + 1,4\text{-}C_6F_4Li_2 \rightarrow [(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4) + 2LiBr \quad (8)$$

where 1,4-$C_6F_4Li_2$ *is* the desired reagent, i.e.[21]

$$1,4\text{-}C_6F_4Br_2 + 2n\text{-BuLi} \rightarrow 1,4\text{-}C_6F_4Li_2 + 2n\text{-BuBr} \quad (9)$$

it is important to avoid the presence of excess *n*-butyllithium in the reaction mixture, since formation and decomposition of unstable alkylnickel species can result,[22] e.g.

$$(MePh_2P)_2NiBr_2 + n\text{-BuLi} \rightarrow (MePh_2P)_2Ni(n\text{-Bu})Br + LiBr \quad (10)$$

$$(MePh_2P)_2Ni(n\text{-Bu})Br \rightarrow \text{decomposition} \quad (11)$$

No special efforts were made to optimize the yields of the organometallic products described below. However, NMR spectroscopic monitoring of the reactions indicated that they proceed essentially quantitatively and that any particularly low *isolated* yields may be due to the relative inefficiency of the particular isolation procedures employed.

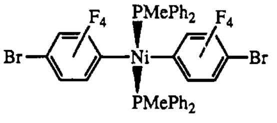
The reaction of $(MePh_2P)_2NiBr_2$ with 1 or 2 equiv of 1,4-C_6F_4XLi (X = H, F, Br) yields the respective monoaryl $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)Br$ and diaryl $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)_2$ nickel complexes, i.e.

$$(MePh_2P)_2NiBr_2 + 1,4\text{-}C_6F_4XLi \rightarrow (MePh_2P)_2Ni(1,4\text{-}C_6F_4X)Br + LiBr \quad (12)$$

$$(MePh_2P)_2NiBr_2 + 2\,1,4\text{-}C_6F_4XLi \rightarrow (MePh_2P)_2Ni(1,4\text{-}C_6F_4X)_2 + 2LiBr \quad (13)$$

Although the mono- and bis(pentafluorophenyl) compounds had been previously prepared[15] and have been structurally characterized,[15b,18] we were interested in the NMR spectroscopic parameters of the series of complexes, including the effects of substitution at the 4-position of the coordinated fluoraryl group. Within the series of monoaryl complexes it can be seen (Table I) that a change of substituent at the 4-position from H to F to Br results in increased shielding of the coordinated phosphorus nuclei, as observed in the shift to higher field of the $^{31}P\{^1H\}$ NMR signals for the respective compounds. The opposite trend is seen for the fluorine nuclei in the ortho positions relative to the nickel center, which for the full series of compounds discussed in this paper are characteristically observed in the ^{19}F NMR spectra at shifts between −114 and −121 ppm, while the fluorine atoms at the positions meta- or para-substituted to Ni occur at chemical shifts closer to those for the free fluoraryl precursors (i.e. −136 to −164 ppm).[23] The ^1H NMR chemical shifts of the protons of the $PMePh_2$ ligands appear to be relatively insensitive to such changes in substituents on the fluoroaryl ring. The $^1H\{^{31}P\}$ NMR spectra of these compounds indicate that the phosphine phenyl protons ortho-substituted to the phosphorus nuclei resonate at lower field than the para- and meta-substituted protons and that the phosphine methyl protons show no other couplings than those to the phosphorus atoms. The appearance of the phosphine methyl resonances in the ^1H NMR spectra indicates that the phosphorus atoms and methyl protons are behaving as an $AA'X_3X_3'$ spin system with a strong virtual coupling[19] between the methyl protons of one phosphine ligand and the phosphorus nucleus of the other. Such coupling gives these methyl resonances of each of the products isolated the *appearance* of a 1:2:1 triplet in the ^1H NMR spectrum, typically occurring between 1.5 and 2.1 ppm.

Although the $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)_2$ (X = H, F, Br) complexes are synthesized in a manner similar to that used for the monoaryl species, significantly longer reaction times are required to produce spectroscopically pure products. If, for example, the reaction of $(MePh_2P)_2NiBr_2$ with 2 equiv of 1,4-C_6F_4BrLi is stopped after only 4 h, the isolated material is a mixture of the trans and cis isomers of $(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$, with the latter being present in varying but substantial proportions (10–50%), i.e.



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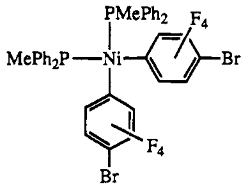

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Thus, the $^{31}P\{^1H\}$ NMR chemical shift of the cis complex (6.98 ppm) is significantly upfield of that for the trans species. The ^{19}F NMR resonances for the cis compounds are similar in chemical shift (but not overlapping) and appearance to those of the trans isomers, indicating that the coordinated aryl rings retain their para-substitution geometries. The strongest indicator of the coordination geometry of the cis complexes is the appearance of the phosphine methyl protons' resonances in the ^1H NMR spectra, which, for the cis isomers, are shielded by approximately 0.24 ppm compared to their trans analogues. For *cis*-$(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$, this signal is again a pseudotriplet characteristic of an $AA'X_3X_3'$ spin system, but the central line is of lower intensity and broader than the two external lines. The appearance of this resonance suggests that the $^2J_{P-P}$ coupling is significantly smaller than in the related complex that contains trans-phosphine ligands and is consistent with a cis disposition of the $PMePh_2$

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(19) (a) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275–2281. (b) Hunter, A. D.; Legzdins, P. *Inorg. Chem.* **1984**, *23*, 4198–4204. (c) Hunter, A. D.; Legzdins, P. *Organmetallics* **1986**, *5*, 1001–1009.

(20) It is therefore particularly important to regularly standardize the solutions of *n*-BuLi to be used.[13]

(21) Care must also be taken to avoid allowing solutions of these reagents to warm to ambient temperature in the absence of suitable reactants, since LiF elimination and consequent benzyne formation can result.[14]

(22) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel* (*Volume I: Organonickel Complexes*); Academic: New York, 1974; p 151.

(23) For the fluorinated arenes 1,2,4,5-$C_6F_4H_2$ and 1,4-$C_6F_4Br_2$, the ^{19}F NMR chemical shifts are −140.07 and −132.00 ppm, respectively, in CD_2Cl_2 solution; for C_6F_5Br the shifts are −133.02 (F_{ortho}), −154.87 (F_{para}), and −160.91 ppm (F_{meta}).

groups.[19] Although the cis isomers appear to be stable in the solid state, we find that for *cis*-$(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$ complete conversion to the trans isomer occurs over several days in THF solution, i.e.

$$cis\text{-}(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2 \rightarrow trans\text{-}(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2 \quad (14)$$

The trends in chemical shifts in the $^{31}P\{^1H\}$, ^{19}F, and ^1H NMR spectra within the series of diarylnickel complexes mirror those for the monoaryl series, but the differences between the $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)_2$ and $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)Br$ complexes containing the same aryl group are also worthy of note. In all cases the $^{31}P\{^1H\}$ NMR resonances for the diaryl complexes are shifted downfield (by at least 0.66 ppm) from the positions of their monoaryl counterparts (e.g. 8.74 ppm for $(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)Br$, 9.40 ppm for $(MePh_2P)_2Ni(1,4\text{-}C_6F_4Br)_2$). The ^{19}F NMR signals for the fluorine nuclei ortho-substituted to the nickel center are, in each diaryl complex, shifted downfield by approximately 1.75 ppm compared to the same peaks for the monoaryl compounds (e.g. −119.41 ppm for $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)Br$, −117.64 for $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$), while the fluorine atoms meta-substituted to Ni are not as significantly affected, showing at most an upfield shift of 0.22 ppm. The signal due to the fluorine atoms para-substituted to Ni in $(MePh_2P)_2Ni(C_6F_5)_2$ is moderately shifted, occurring 0.87 ppm downfield of the corresponding resonance for $(MePh_2P)_2Ni(C_6F_5)Br$. Of the ^1H NMR resonances for the phosphine phenyl protons of the diaryl complexes, only those due to the protons ortho-substituted to phosphorus are affected, being shifted approximately 0.1 ppm upfield. A more noticeable change occurs in the position of the phosphine methyl protons' signals, which resonate between 2.06 and 2.00 ppm for the monoaryl complexes and between 1.66 and 1.61 ppm for the diaryl species. The protons on the fluoroaryl ring which are para-substituted to Ni give rise to a signal in $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$ that is 0.24 ppm upfield of that due to the corresponding proton in $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)Br$.

As stated earlier, we anticipated that an advantage of using the methyldiphenylphosphine ligand in these compounds instead of triphenylphosphine would be that the decreased spatial requirements of $PMePh_2$ would allow extended linear chains of arene-bridged nickel centers to be constructed. Our initial results indicate that this should be possible, as we have successfully synthesized several linear bi- and trimetallic complexes of the formula $[(MePh_2P)_2Ni]_x(\mu\text{-}1,4\text{-}C_6F_4)_yX_2$ ($x = 2$, $y = 1$, X = Br, $1,4\text{-}C_6F_4H$; $x = 3$, $y = 2$, X = Cl, Br, $1,4\text{-}C_6F_4H$; Figure 1). The synthetic routes to the bimetallic monoaryl $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$ and the trimetallic diaryl $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ complexes are quite similar, involving reactions of 2 equiv of $(MePh_2P)_2NiBr_2$ with 1 equiv of $1,4\text{-}C_6F_4Li_2$ or $(MePh_2P)_2Ni(1,4\text{-}C_6F_4Li)_2$, respectively, i.e.

$$2(MePh_2P)_2NiBr_2 + 1,4\text{-}C_6F_4Li_2 \rightarrow [(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4) + 2LiBr \quad (15)$$

$$2(MePh_2P)_2NiBr_2 + (MePh_2P)_2Ni(1,4\text{-}C_6F_4Li)_2 \rightarrow [(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2 + 2LiBr \quad (16)$$

with the latter reagent being prepared from the reaction of $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$ with *n*-butyllithium, i.e.

$$(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2 + 2n\text{-}BuLi \rightarrow (MePh_2P)_2Ni(1,4\text{-}C_6F_4Li)_2 + 2C_4H_{10} \quad (17)$$

In turn, the bimetallic triaryl $[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2]_2(\mu\text{-}1,4\text{-}C_6F_4)$ and trimetallic tetraaryl $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2(1,4\text{-}C_6F_4H)_2$ species may be obtained via reaction of the "arene-poor" compounds with 2 equiv of $1,4\text{-}C_6F_4HLi$, i.e.

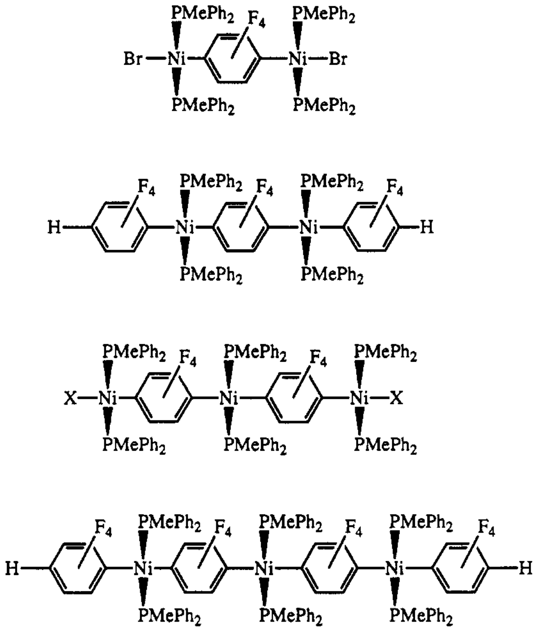

Figure 1. Structures of the linear bi- and trimetallic complexes (X = Br, Cl).

$$[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4) + 2\,1,4\text{-}C_6F_4HLi \rightarrow [(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]_2(\mu\text{-}1,4\text{-}C_6F_4) + 2LiBr \quad (18)$$

$$[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2 + 2\,1,4\text{-}C_6F_4HLi \rightarrow [(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2(1,4\text{-}C_6F_4H)_2 + 2LiBr \quad (19)$$

The structures of each of these new air- and thermally-stable bi- and trimetallic complexes (see Figure 1) were unambiguously established by their $^{31}P\{^1H\}$, ^{19}F, and ^1H NMR spectra (Table I), which were found to vary significantly as a function of oligomer chain length and end group.

For the bimetallic complexes, the NMR data are all consistent with the proposed linear structures having a single type of $(MePh_2P)_2Ni$ center (Figure 1 and Table I). However, it is found that the $^{31}P\{^1H\}$ NMR resonance for $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$ is shifted to higher field by ≈3.2–3.7 ppm compared to the monoaryl complexes (Table I) even though all contain $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)Br$ units. Similarly, the phosphine phenyl protons' ^1H NMR resonances on this bimetallic complex occur at ≈0.1–0.2 ppm lower field, while their methyl resonances occur at ≈1.0 ppm higher field than do the corresponding peaks for $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)Br$ compounds. Substitution of the Br ligands in $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$ by $1,4\text{-}C_6F_4H$ produces an even more dramatic downfield shift of the $^{31}P\{^1H\}$ NMR resonance (i.e. ≈5 ppm) than when the analogous replacement is done for the $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)Br$ complexes (i.e. 0.7–1.3 ppm). Similarly, the addition of the $1,4\text{-}C_6F_4H$ groups causes the ^{19}F resonance due to the $\mu\text{-}1,4\text{-}C_6F_4$ fluorine nuclei to be deshielded by 0.98 ppm and ^1H resonances of the phosphine ligands to be shielded for the phenyl protons and to be deshielded by 0.23 ppm for the methyl protons.

For the trimetallic complexes, the NMR data are all consistent with the proposed linear structures having two different types of $(MePh_2P)_2Ni$ centers (Figure 1 and Table I). For example, the $^{31}P\{^1H\}$ NMR spectrum of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ (Figure 2) shows two signals in 2:1 relative intensity, corresponding to the phosphorus atoms coordinated to the terminal and central nickel nuclei, respectively. The chemical shift for the

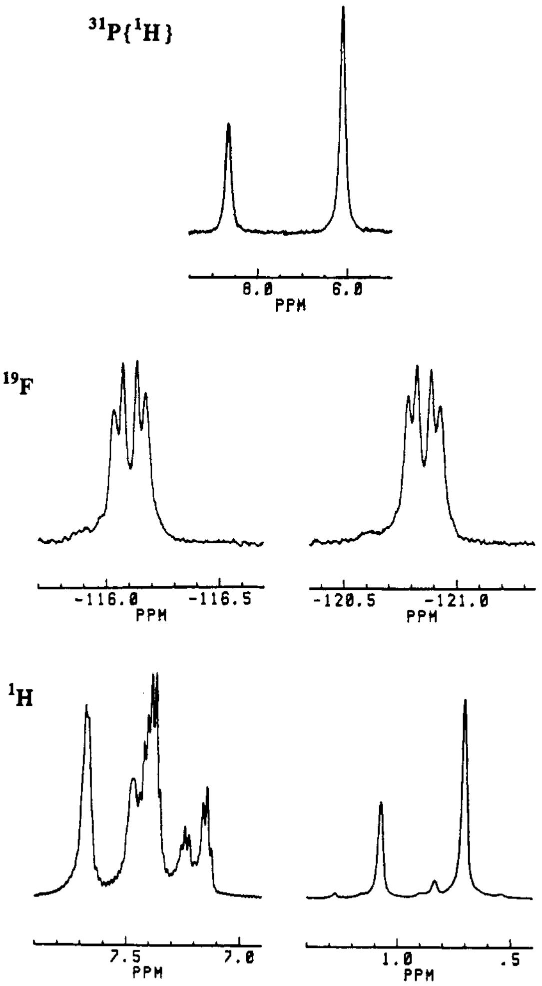

Figure 2. ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$.

terminal nickels' phosphine nuclei is deshielded by ≈0.6 ppm compared to those in $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$, while the resonance due to the central nickel's phosphines is shielded by ≈0.8–1.9 ppm compared to the $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)_2$ complexes. The ^1H NMR signals for the methyl protons of this "arene-poor" trimetallic oligomer are shielded by ≈0.4–0.6 ppm compared to the related mono- and bimetallic species (i.e. $(MePh_2P)_2Ni(1,4\text{-}C_6F_4X)_2$ and $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$, respectively) and are observed in the expected 2:1 ratio. Replacement of the terminal bromide ligands of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ by $1,4\text{-}C_6F_4H$ groups to give the "arene-rich" trimetallic results in a shift of the terminal phosphines' $^{31}P\{^1H\}$ NMR resonance to almost 5 ppm lower field, as is observed for the analogous substitution with the bimetallic species. In addition, the signal due to the central phosphine atoms of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2(1,4\text{-}C_6F_4H)_2$ is shifted by 0.64 ppm downfield of the corresponding resonance in the "arene-poor" trimetallic oligomer. A moderate shift in the ^1H NMR resonances of the phosphine phenyl H's to higher field is also observed on the addition of the terminal aryl groups, but more noticeable is the change in the relative positions of the phosphines' methyl protons. Thus, those located on the $PMePh_2$ groups coordinated to the terminal nickel centers undergo a downfield shift of 0.50 ppm upon replacement of Br by $1,4\text{-}C_6F_4H$ (a displacement in the same direction as, but of greater magnitude than, the shift for the bimetallic complexes), while the signal due to the Me protons of the central $(MePh_2P)_2Ni$ unit of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2(1,4\text{-}C_6F_4H)_2$ is observed at 0.33 ppm upfield of the analogous peak for the "arene-poor" trimetallic oligomer.

Occasionally during the synthesis of $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$, NMR evidence for the synthesis of an unsymmetrical bimetallic byproduct, which we have tentatively identified as $[(MePh_2P)_2NiBr](\mu\text{-}1,4\text{-}C_6F_4)[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)]$, was observed. The $^{31}P\{^1H\}$ NMR spectrum of this unsymmetrical complex shows resonances at 10.28 and 6.42 ppm; the former is close to that of $[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2]_2(\mu\text{-}1,4\text{-}C_6F_4)$, while the latter is similar to that for $[(MePh_2P)_2NiBr]_2(\mu\text{-}1,4\text{-}C_6F_4)$ and $[(MePh_2P)_2Ni]_3(\mu\text{-}1,4\text{-}C_6F_4)_2Br_2$ (Table I). The ^{19}F NMR spectrum shows four resonances due to this complex, three of which are at chemical shifts characteristic of fluorine nuclei that are ortho-substituted to nickel (i.e. −115.95, −118.39, and −120.82 ppm) and one of which is consistent with the fluorine atoms that are meta-substituted to nickel on a terminal $1,4\text{-}C_6F_4H$ group (i.e. −143.09 ppm). Finally, the phosphines' methyl protons give rise to two virtual triplets at 1.56 and 0.82 ppm, which can be tentatively assigned to the $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)(\mu\text{-}1,4\text{-}C_6F_4)$ and $(MePh_2P)_2NiBr(\mu\text{-}1,4\text{-}C_6F_4)$ fragments, respectively. Although the origin of this novel species is not entirely certain, it seems to arise from incomplete deprotonation of the monometallic starting material, i.e.

$$(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2 + n\text{-BuLi} \rightarrow (MePh_2P)_2Ni(1,4\text{-}C_6F_4H)(1,4\text{-}C_6F_4Li) \quad (20)$$

$$(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)(1,4\text{-}C_6F_4Li) + (MePh_2P)_2NiBr_2 \rightarrow [(MePh_2P)_2NiBr](\mu\text{-}1,4\text{-}C_6F_4)[(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)] \quad (21)$$

due to the consumption of some of the n-BuLi added by methanol and/or water occluded in the $(MePh_2P)_2Ni(1,4\text{-}C_6F_4H)_2$ used.

Our electrochemical studies of bimetallic complexes such as $1,4\text{-}C_6F_4Fp_2$ (where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) have unequivocally indicated that the 1,4-tetrafluorophenylene ligand is an excellent electronic bridging group between adjacent 18-electron iron centers.[9c] It is therefore not surprising that the ^1H, ^{19}F, and ^{31}P NMR data discussed above suggest that the same is true for the 16-electron nickel centers in these linear bi- and trimetallic complexes. In particular, the observation that the chemical shifts of the phosphine ligands and perfluorophenylene bridging groups show a substantial dependence on the identity of the oligomer end groups and on the oligomer chain lengths strongly suggests that there is significant conjugation down the oligomer backbones. This is very promising in terms of the potential utilities of these novel materials and their higher oligomers for practical applications which depend on their nonlinear optical and electrical properties.

Conclusions

In this study, we have developed a relatively simple methodology for synthesizing the requisite bimetallic linkages in a series of linear mono-, bi-, and trimetallic complexes containing $(MePh_2P)_2Ni$ units and bridging and/or terminal fluoroaryl groups. These oligomers have been found to be amenable to characterization via multinuclear ($^{31}P\{^1H\}$, ^{19}F, ^1H) NMR spectroscopy, such that the number of nickel centers present in the compounds and the coordination geometry around the nickel atoms can be easily determined. The NMR data also suggest that there is significant electronic interaction between the adjacent metal centers in the oligomers. The success of the synthetic studies indicates that the syntheses of oligomers

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and polymers of higher nuclearity might be expected to proceed analogously (i.e. via the stepwise methodology used to prepare the trimetallic derivatives or via convergent syntheses in which "arene-poor" complexes are reacted with dilithiated "arene-rich" reagents). Indeed, such studies are currently underway in our group.

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Palladium-Mediated Synthesis of Urethanes from Amines, Carbon Dioxide, and Cyclic Diolefins

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Addition of preformed carbamate anions $RR'NHCO_2^{-+}HBase$, generated from various primary and secondary amines and carbon dioxide, to (norbornadiene)palladium dichloride at −78 °C followed by addition of DIPHOS (bis(diphenylphosphino)ethane) and then reductive cleavage at 0 °C with sodium borohydride gave nortricyclo carbamate esters (**1a–d**) in good yields (75–100% by GC). Cleavage with anhydrous hydrogen chloride also gave nortricyclo carbamate esters. Addition of (dicyclopentadiene)palladium dichloride to the carbamate anion at 0 °C gave the corresponding carbamate esters (**2a–i**) in good yields (53–100% by GC) after reductive cleavage with either sodium borohydride or dihydrogen. Addition of $BuNHCO_2^{-+}H_3NBu$ to 1,4-(cyclooctadiene)palladium dichloride at −35 °C followed by reductive cleavage with sodium borohydride gave cyclooct-4-enyl-1 *N*-butylcarbamate (**3**) in 16% isolated yield. An indication of the nucleophilicity of the carbamate anion was obtained by direct competition studies with the acetate anion on attack on (dicyclopentadiene)palladium dichloride at 0 °C. The relative rate of reaction of $BuNHCO_2^{-+}H_3NBu$ vs $AcO^{-+}H_3NBu$ was determined to be 1:2.66.

Introduction

Urethane and polyurethane materials find many important applications. These materials are historically made by the addition of an alcohol to an isocyanate (eq 1).[1] The isocyanate in turn is constructed by the addition of

$$RN{=}C{=}O + R'OH \rightarrow RNHCO_2R' \qquad (1)$$

$$RNH_2 + COCl_2 \rightarrow RN{=}C{=}O + 2HCl \qquad (2)$$

phosgene to an amine with elimination of 2 equivalents of hydrogen chloride (eq 2). This method for the production of urethane compounds has the major drawback of using highly toxic raw materials, phosgene and isocyanates. Several publications and patents have dealt with either making isocyanates without the use of phosgene or constructing urethanes without the use of either phosgene or isocyanates.[2] These published results have found only limited success.

The utilization of carbon dioxide in the construction of useful moieties has drawn considerable attention.[3] One strategy for carbon dioxide activation is the addition of either a primary or secondary amine, as shown in eq 3, giving a carbamate salt.[4] Once carbon dioxide has been activated by the amine, the carbamate salt can then be used in further steps to give stable products.[5]

$$2RR'NH + CO_2 \rightleftharpoons RR'NCO_2^{-+}H_2NRR' \qquad (3)$$

The use of the carbamate anion as a nucleophile has been investigated, but with only limited success. The carbamate anion has been reported to give two major types of products when used as a nucleophilic agent. The desired product is that which results from oxygen attack on electrophiles giving urethane compounds while the other major reaction mode results from nitrogen attack giving amine products. It is not clear whether the nitrogen attack results from free amine (as a result of the equilibrium established from the reaction of the amine with carbon dioxide, eq 3) or directly from attack at the nitrogen of the carbamate anion.[6] An illustration of this multiple re-

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(1) For a discussion of urethane chemistry see: Oertel, G. *Polyurethane Handbood*; Hanser: Munich, 1985.

(2) One recent example appears in U.S. Patent 4713476 issued to Bayer which generates urethanes from amines, alcohols, and urea.

(3) See for example: Inoue, S.; Yamazaki, N. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha: Tokyo, 1982. Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. Aresta, A.; Forti, G. *Carbon Dioxide as a Source of Carbon*; NATO ASI Series C; Reidel: Dordrecht, The Netherlands, 1987; Vol. 206.

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