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Organometallic Polymer and Linear Mono-, Bi-, and Trimetallic Octafluoro-*p*,*p*′-biphenylene-Bridged Complexes of Bis(methyldiphenylphosphine)nickel: X-ray Crystal Structures of $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$ and $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$[1,2]

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Metathesis reactions between organolithium reagents and nickel bromide complexes are used to prepare a series of five linear mono-, bi- and trimetallic oligomers of $Ni(PMePh_2)_2$ having the octafluoro-*p*,*p*′-biphenylene bridging unit (i.e. $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$, $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$, $[Ni(PMePh_2)_2]_2(\mu-4,4'-C_{12}F_8)Br_2$, $[Ni(PMePh_2)_2]_2(\mu-4,4'-C_{12}F_8)(4,4'-C_{12}F_8H)_2$, and $[Ni(PMePh_2)_2]_3(\mu-4,4'-C_{12}F_8)_2Br_2$). These complexes have been characterized by conventional analytical and spectroscopic means, and two representative examples have had their structures confirmed by X-ray crystallography: $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$ ($C_{38}H_{27}BrF_8NiP_2$; $a = 15.952$ (5), Å, $b = 17.080$ (4), Å, $c = 14.048$ (4), Å, $\beta = 116.42$ (3)°, $V = 3427$ Å^3; monoclinic; $C2/c$, $Z = 4$) and $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$ ($C_{50}H_{28}F_{16}NiP_2$; $a = 10.718$ (11) Å, $b = 16.424$ (7), Å, $c = 13.202$ (6), Å, $\beta = 110.41$ (6)°, $V = 2178.1$ Å^3; monoclinic; $P2_1/c$, $Z = 2$). The ^1H, ^{19}F, and ^{31}P NMR data for these complexes suggest that, in contrast to the analogous tetrafluoro-*p*-phenylene-bridged species, there is no significant electronic interaction between adjacent metal centers in the octafluoro-*p*,*p*′-biphenylene-bridged complexes. This suggestion is consistent with the large twist angles (52.2 and 53.1°) observed between rings of the octafluorobiphenyl groups. The related reaction between $4,4'-C_{12}F_8Li_2$ and $Ni(PMePh_2)_2Br_2$ produces the first example of an arene-bridged organometallic polymer (i.e. $-[Ni(PMePh_2)_2(\mu-4,4'-C_{12}F_8)]_n-$). Its spectroscopic properties suggest that its repeating units have the same structures (i.e. 4,4′-disubstituted $C_{12}F_8$ bridging units and para-substituted $Ni(PMePh_2)_2(aryl)_2$ fragments) as do the discrete oligomers.

Introduction

Recently, there has been growing interest in polymeric materials that incorporate transition-metal moieties into the polymer backbone due, in part, to the enormous potential of such materials for applications in areas such as one-dimensional conductivity and nonlinear optics.[4-6] By analogy with their conjugated organic analogues,[6] materials in which transition-metal centers are joined by organic ligands having delocalized π-systems are expected to be particularly interesting in this regard. However, for any new material to be viable in an industrial process, its stability characteristics, physical properties, and processing characteristics must also meet specific requirements. Our model studies on iron and nickel complexes indicate that organometallic materials having aromatic bridging groups can display excellent thermal, oxidative, and chemical stabilities.[2,7] We are currently attempting to evaluate whether their physical properties and processing characteristics can be varied systematically by changes to the natures of the bridging groups, the metal centers, the ancillary ligands,[8] the average chain length, the molecular weight distribution, and the end group identity of the nickel-containing organometallic complexes and polymers. In this paper, we report the effects of changing the identity

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Table I. Analytical and Melting Point Data for the Complexes

complex	analytical data, % C calcd	C found	H calcd	H found	Br calcd	Br found	mp dec^a
$Ni(PMePh_2)_2(C_{12}F_8H)Br$ (1)	54.58	54.25	3.25	3.21	9.56	9.77	209–210
$Ni(PMePh_2)_2(C_{12}F_8H)_2$ (2)	57.01	56.68	2.68	2.81			212–215
$[Ni(PMePh_2)_2]_2(\mu\text{-}C_{12}F_8)Br_2$ (3)	55.94	55.67	3.81	3.67	11.63	11.64	220–225
$[Ni(PMePh_2)_2]_2(\mu\text{-}C_{12}F_8)(C_{12}F_8H)_2$ (4)	58.44	58.74	3.01	3.05			210–215
$[Ni(PMePh_2)_2]_3(\mu\text{-}C_{12}F_8)_2Br_2$ (5)	57.53	57.25	3.69	3.66	7.50	7.43	210–215
$-[Ni(PMePh_2)_2(\mu\text{-}C_{12}F_8)]_n-$ (6)^b	59.63	59.39	3.44	3.39	1.31	1.26	220–245

[a] These are decomposition points *in air* and were ascertained by visual methods in unsealed capillaries (in °C). [b] Bulk polymer; elemental analysis data calculated for $n = 8$.

Table II. ^1H, ^{19}F, and ^{31}P NMR Data (CD_2Cl_2) for the Complexes^a

complex	^1H NMR	^{19}F NMR	$^{31}P\{^1H\}$ NMR
1	7.54 (m, 8 H), 7.29 (m, 12 H), 7.12 (m, 1 H), 2.19 (t, 6 H, J_{H-P} = 7.8)	−117.94 (m, 2 F), −138.22 (m, 2 F), −139.83 (m, 2 F), −142.59 (m, 2 F)	9.40 (s)
2	7.52 (m, 8 H), 7.31 (m, 12 H), 7.16 (m, 2 H), 1.75 (t, 2 H, J_{H-P} = 7.3)	−116.34 (m, 4 F), −138.94 (m, 4 F), −139.75 (m, 4 F), −142.57 (m, 4 F)	9.82 (s)
3	7.53 (m, 16 H), 7.28 (m, 24 H), 2.16 (t, 12 H, J_{H-P} = 7.5)	−119.51 (m, 4 F), −141.35 (m, 4 F)	9.38 (s)
4	7.49 (m, 16 H), 7.29 (m, 24 H), 7.15 (m, 2 H), 1.70 (t, 12 H, J_{H-P} = 7.1)	−116.35 (m, 4 F), −117.51 (m, 4 F), −138.91 (m, 4 F), −139.72 (m, 4 F), −142.17 (m, 4 F), −142.70 (m, 4 F)	9.91 (s)
5	7.57 (m, 16 H), 7.45 (m, 8 H), 7.27 (m, 36 H), 2.12 (t, 12 H, J_{H-P} = 7.6), 1.67 (t, 6 H, J_{H-P} = 7.3)	−117.78 (m, 4 F), −119.23 (m, 4 F), −141.50 (m, 4 F), −142.09 (m, 4 F)	9.92 (s, 1 P), 9.15 (s, 2 P)

[a] The ^1H, ^{19}F, and ^{31}P NMR spectra were measured at 400.135, 376.503, and 161.978 MHz, respectively, and are reported in ppm; J_{H-P} coupling constants are reported in Hz.

of the bridging units. In particular, we have substituted 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl for the 1,2,4,5-tetrafluorobenzene used previously[2] in these synthesis and we compare the physical and spectroscopic (especially the ^1H, ^{19}F, and ^{31}P NMR chemical shifts) properties of the resultant materials. X-ray crystallographic structures of two representative octafluorobiphenyl complexes, $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)Br$ and $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)_2$, are presented, and the observed differences in the degree of intermetallic conjugation of these two classes of arene-bridged materials are rationalized. In addition, the synthesis and characterization of a novel octafluoro-*p*,*p*′-biphenylene-bridged organometallic polymer whose repeating units have structures similar to those of the discrete complexes are reported.

Experimental Section

Unless otherwise noted, all reactions and subsequent manipulations were performed using conventional techniques for the manipulation of air-sensitive compounds as described previously.[7a,b,9] Thus anaerobic and anhydrous conditions were maintained by using a prepurified argon or nitrogen atmosphere employing conventional vacuum line techniques.[10a] 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.[10] Thus, $Ni(PMePh_2)_2Br_2$ was prepared via reaction of $NiBr_2$ with $PMePh_2$ in 1-butanol[11] and the nominally 2.5 or 1.6 M ^nBuLi/hexanes solutions were standardized regularly.[12] Solvents used were dried and deaerated by standard procedures and stored under N_2 or Ar.[10,13] Unless specified otherwise, the reactions and any subsequent manipulations described below were effected at ambient temperatures (≈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 from external Me_4Si, $CFCl_3$, and 85% H_3PO_4, respectively. Melting points were ascertained by visual methods in unsealed capillaries. Analytical, melting point, and NMR data are presented in Tables I and II.

Preparation of $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)Br$ (1). 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl (0.482 g, 1.62 mmol) was dissolved in THF (10 mL), and the solution was deaerated with N_2(g) and cooled in a dry ice/acetone bath to ≈−78 °C. To this solution was added 0.65 mL (1.6 mmol) of ^nBuLi (2.5 M solution in hexanes) dropwise[12] via syringe. The resulting faint white slurry was stirred at ≈−78 °C for 15 min and then transferred via cannula to a purple, deaerated suspension of 1.000 g (1.616 mmol) of $Ni(PMePh_2)_2Br_2$ in THF (10 mL), and the mixture was cooled in an ice/water bath to 0 °C. Upon addition of the lithium reagent the dark orange-brown solution that formed was stirred at 0 °C for ≈1 h and then at room temperature for 21 h, after which the volume was reduced under vacuum to ≈5 mL. This was followed by the addition of methanol (30 mL) via syringe. The resulting yellow precipitate was cooled to 0 °C, stirred for 1 h, and then suction-filtered in air. The solid was washed with methanol (2 × 30 mL) and hexanes (2 × 20 mL) and air-dried. Finally, recrystallization from CH_2Cl_2/hexanes and drying under vacuum yielded 0.818 g (0.978 mmol, 61%) of $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)Br$ as a yellow powder.

Preparation of $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)_2$ (2). 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl (3.200 g, 10.73 mmol) was dissolved in THF (30 mL), and the solution was deaerated with dinitrogen and cooled in a dry ice/acetone bath to ≈−78 °C. To this solution was added 6.66 mL (10.7 mmol) of ^nBuLi (1.6 M solution in hexanes) dropwise via syringe with vigorous stirring. The resulting white slurry was stirred at ≈−78 °C for 30 min, at which point 3.000 g (4.847 mmol) of $Ni(PMePh_2)_2Br_2$ was added under a positive pressure of N_2. This purple suspension was slowly warmed to room temperature over a period of 1 h and was stirred for an additional 17 h, after which the orange-red solution was concentrated under vacuum to ≈5 mL producing a yellow precipitate. Methanol (50 mL) was then added to complete precipitation, and this mixture was stirred for 24 h. The yellow solid was then allowed to settle, the supernatant drawn off via cannula, and the solid washed with methanol (2 × 30 mL) and then dried

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under a stream of N_2, followed by vacuum to give 4.83 g (4.59 mmol, 95%) of $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$.

Preparation of $[Ni(PMePh_2)_2]_2(\mu-4,4'-C_{12}F_8)Br_2$ (3). 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl (0.482 g, 1.62 mmol) was dissolved in THF (20 mL), and the solution was deaerated with N_2 and cooled to dry ice/acetone bath to ≈–78 °C. To this solution was added 2.08 mL (3.24 mmol) of ^nBuLi (1.56 M solution in hexanes) dropwise via syringe. The resulting white slurry was stirred at ≈–78 °C for 30 min and then transferred via cannula to a purple, deaerated suspension of 2.000 g (3.231 mmol) of $Ni(PMePh_2)_2Br_2$ in THF (20 mL) cooled in an ice/water bath to 0 °C. An immediate lightening of the slurry to orange-brown was noted, and the mixture was stirred at 0 °C for ≈2 h and then at room temperature for an additional 19 h. The solution was then concentrated under vacuum to ≈10 mL followed by addition of methanol (50 mL), which produced an orange precipitate. This mixture was cooled to 0 °C, stirred for 30 min, and allowed to settle. The supernatant was removed via cannula and the solid washed with methanol (2 × 30 mL) and dried under vacuum. To remove any occluded methanol the solid was dissolved in CH_2Cl_2 (10 mL) and reprecipitated with diethyl ether (50 mL), followed by drying under vacuum to yield 1.46 g (1.06 mmol, 66%) of $[Ni(PMePh_2)_2]_2(\mu-4,4'-C_{12}F_8)Br_2$ as an orange powder.

Preparation of $[Ni(PMePh_2)_2]_2(\mu-4,4'-C_{12}F_8)(4,4'-C_{12}F_8H)_2$ (4). Method A. 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl (0.723 g, 2.43 mmol) was dissolved in THF (10 mL), and the solution was deaerated with N_2 and cooled in a dry ice/acetone bath to ≈–78 °C. To this solution was added 1.29 mL (3.23 mmoL) of ^nBuLi (2.5 M solution in hexanes) dropwise via syringe. The resulting white slurry was stirred at ≈–78 °C for 20 min and then transferred via cannula to a purple, deaerated suspension of 1.000 g (1.616 mmol) of $Ni(PMePh_2)_2Br_2$ in THF (10 mL), cooled in an ice/water bath to 0 °C. At this point a dark orange solution formed that was stirred at 0 °C for ≈1 h and at room temperature for 21 h. The solution was then concentrated to ≈5 mL under vacuum followed by addition of methanol (40 mL) producing a yellow precipitate. This precipitate was stirred at 0 °C for 30 min and suction filtered in air; the solid was then washed with methanol (2 × 30 mL), ether (2 × 20 mL), and hexanes (1 × 20 mL) and then dried under vacuum. This procedure yielded 0.76 g (0.42 mmol, 52%) of $[Ni(PMePh_2)_2]_2(\mu-4,4'-C_{12}F_8)(4,4'-C_{12}F_8H)_2$ as a yellow powder containing trace quantities (i.e. 1–2% by NMR) of complex 2 that could subsequently be removed by recrystallization from CH_2Cl_2/Et_2O.

Method B. 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl (0.166 g, 0.557 mmol) was dissolved in THF (10 mL), and the solution was deaerated with N_2 and cooled in a dry ice/acetone bath to ≈–78 °C. To this solution was added 0.44 mL (1.1 mmol) of ^nBuLi (2.5 M solution in hexanes) dropwise via syringe. The resulting white slurry was stirred at ≈–78 °C for 15 min and then transferred via cannula to a yellow, deaerated suspension of 0.930 g (1.11 mmol) of $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$ in THF (10 mL), cooled in an ice/water bath to 0 °C. Upon addition of the lithium reagent, the light orange solution that formed was stirred at 0 °C for ≈1 h and then at room temperature for 45 h. The solution was then concentrated under vacuum to ≈5 mL, and methanol (30 mL) was added to produce a yellow precipitate. The mixture was stirred for 4 h and allowed to settle. The supernatant was removed via cannula and the solid washed with methanol (2 × 30 mL) and dried under a stream of N_2 followed by vacuum to give 0.71 g (0.39 mmol, 71%) of $[Ni(PMePh_2)_2]_2(\mu-4,4'-C_{12}F_8)(4,4'-C_{12}F_8H)_2$ as a yellow powder.

Preparation of $[Ni(PMePh_2)_2]_3(\mu-4,4'-C_{12}F_8)_2Br_2$ (5). $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$ (0.587 g, 0.557 mmol) was dissolved in THF (20 mL), and the solution was deaerated with $N_2(g)$ and cooled in a dry ice/acetone bath to ≈–78 °C. To this solution was added 0.45 mL (1.1 mmol) of ^nBuLi (2.45 M solution in hexanes) dropwise via syringe. The resulting yellow solution was stirred at ≈–78 °C for 15 min and then transferred via cannula to a purple, deaerated suspension of 0.759 g (1.23 mmol) of $Ni(PMePh_2)_2Br_2$ in THF (10 mL), cooled in an ice/water bath to 0 °C. This orange-brown solution was stirred at 0 °C for ≈1 h and then at room temperature for 21 h, after which the volume was reduced under vacuum to ≈5 mL. At this point methanol (50 mL) was added, producing a yellow precipitate that was suction filtered in air, washed with methanol (2 × 30 mL) and hexanes (2 × 30 mL), and dried under vacuum to give 0.758 g (0.356 mmol, 64%) of $[Ni(PMePh_2)_2]_3(\mu-4,4'-C_{12}F_8)_2Br_2$, which was collected as a yellow powder.

Synthesis of the Polymer $-[Ni(PMePh_2)_2(\mu-4,4'-C_{12}F_8)]_n-$. 2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl (1.193 g, 4.000 mmol) was dissolved in THF (40 mL), and the solution was deaerated with N_2 and cooled in a dry ice/acetone bath to ≈–78 °C. To this solution was added 5.13 mL (8.00 mmol) of ^nBuLi (2.5 M solution in hexanes) dropwise via syringe. The resulting white slurry was stirred at ≈–78 °C for 30 min and then transferred via cannula to a purple, deaerated suspension of 2.476 g (4.000 mmol) of $Ni(PMePh_2)_2Br_2$ in THF (30 mL), cooled in an ice/water bath to 0 °C. Upon addition of the lithium reagent, a lightening of the solution to orange-brown was noted, and the mixture was stirred at 0 °C for ≈1 h and then allowed to warm to room temperature. After the mixture was stirred for ≈3 h, an orange precipitate formed, and this slurry became increasingly viscous as it was stirred for a total of 24 h, at which point the solvent was removed under vacuum. The resulting orange solid was stirred with methanol (50 mL) for 30 min and suction filtered in air. The solid was washed with methanol (2 × 30 mL) and dried under vacuum to yield 2.37 g (80%) of a yellow powder ($-[Ni(PMePh_2)_2(\mu-4,4'-C_{12}F_8)]_n-$).

This solid was only partially soluble in organic solvents. For example, only 30% by weight would dissolve in THF when 0.25 g was stirred for 2 h in 30 mL of THF. The complex ^{19}F NMR spectrum of the soluble portion of this polymeric material (CD_2Cl_2) displayed four multiplets at low field (–116.34, –117.53, –117.82, –119.31 ppm) and five multiplets at high field (–138.95, –139.80, –142.29, –142.76, –144.03 ppm), while the ^{31}P NMR spectrum (CD_2Cl_2) displayed two signals at 9.69 (s, 12 P) and 9.07 (s, 1 P) ppm.

Gel Permeation Chromatography. A 10-mg sample of this yellow powder was partially dissolved in 1 mL of THF (≈30% dissolves). A sample of the supernatant solution (100 μL) was injected into a Waters Model 600E gel permeation chromatograph operating at 30.0 °C. THF was used as the eluting solvent at a flow rate of 1.0 mL/min through a 2-μm filter and two Water HT μ-Styragel GPC columns (10^3 Å and 10 μm linear) connected in series. The eluted materials were detected on Waters Model 991 photodiode array (UV–visible) and 410 refractive index detectors. The most abundant oligomer present in the organometallic polymer has the same GPC retention time as does a polystyrene standard having a number average molecular weight, $\bar{M}_n$, of approximately 5100. Organometallic oligomers having GPC retention times equivalent to those of polystyrene standards having $\bar{M}_n$ values of greater than 100 000 were also observed in the chromatograms of the THF soluble fractions. The UV–visible spectra of the GPC eluents (collected every 0.77/s) were similar for the discrete oligomers and the low and high molecular weight fractions. This is consistent with the high molecular weight species being composed of organometallic molecules.

X-ray Crystallographic Characterization of Complexes $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$ (1) and $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$ (2). Golden yellow crystals of the two title complexes were grown by slow evaporation of dichloromethane solutions and were mounted on glass fibers and optically centered in the X-ray beam on an Enraf-Nonius CAD4 automated diffractometer. Data collection and structure solution parameters are given in Table III. Data were corrected for Lorentz and polarization effects and also for absorption via the method of Walker and Stuart.[14] Details of the usual procedures used in our laboratories have been published elsewhere.[7b] Structure solution proceeded in a routine fashion for both compounds utilizing the SDP structure solution

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(14) (a) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications by Dr. R. G. Ball. (b) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. I. (c) The computer programs used in this analysis include the Enraf-Nonius *Structure Determination Package, Version 3*, 1985, Delft, The Netherlands, adapted for a SUN Microsystems 3/160 computer, and several locally written programs by Dr. R. G. Ball. (d) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. (Present distributor D. Reidel, Dordrecht, The Netherlands.) (e) *Ibid*, Table 2.3.1. (f) Walker, N.; Stuart D. *Acta Crystallogr.* 1983, *A39*, 158.

Table III. Summary of the Crystal Data and Intensity Collection for the Complexes

param	complex 1	complex 2
formula	$C_{38}H_{27}BrF_8NiP_2$	$C_{50}H_{28}F_{16}NiP_2$
fw	836.19	1053.41
cryst dimens, mm	0.62 × 0.16 × 0.04	0.6 × 0.4 × 0.1
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
cryst syst	monoclinic	monoclinic
a, Å	15.952 (5)	10.718 (11)
b, Å	17.080 (4)	16.424 (7)
c, Å	14.048 (4)	13.202 (6)
β, deg	116.42 (3)	110.41 (6)
V, Å^3	3427	2178.1
Z	4	2
calcd density, g cm^{-3}	1.602	1.606
abs coeff, cm^{-1}	18.84	6.21
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)
filter	Zr filter	Zr filter
take-off angle, deg	2.0	2.0
detector aperture, mm	2.40 × 4.0 vert	2.40 × 4.0 vert
crystal-to-detector dist, mm	173	173
scan type	θ–2θ	θ–2θ
scan width	$0.60 + .347 \tan \theta$	$0.65 + .347 \tan \theta$
scan rate, deg min^{-1}	6.7–1.5	1.0
2θ range, deg	$2.0 \leq 2\theta \leq 50.0$	$2.0 \leq 2\theta \leq 50.0$
data collcn index range	$h,k,\pm l$	$h,k,\pm l$
no. of reflcns	4597	3774
no. of significant reflcns	1661, $I > 3\sigma(I)$	1340, $I > 3\sigma(I)$
observns/variables ratio	1661/229	1340/188
agreement factors R_1, R_2, GOF	0.068, 0.078, 1.90	0.076, 0.080, 2.03
corrs appl	empirical abs corr	empirical abs corr

Table IV. Positional (×10^3) and Equivalent Isotropic Gaussian Displacement (Å^2 × 10^2) Parameters for $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)Br$ (1)

atom	x	y	z	U^a
Br	0	62.5 (1)	250	4.65 (7)
Ni	0	199.5 (1)	250	2.65 (7)
P	−138.2 (2)	200.6 (2)	253.0 (2)	2.9 (1)
F2	102.2 (4)	315.7 (4)	432.3 (5)	4.5 (3)
F3	108.1 (4)	472.2 (4)	431.6 (5)	5.2 (3)
F6	−40.0 (5)	570.2 (4)	392.4 (6)	6.9 (3)
F7	−38.6 (6)	725.8 (5)	393.3 (7)	10.2 (4)
C1	0	308.7 (9)	250	2.5 (5)
C2	50.4 (6)	353.6 (6)	341.0 (7)	2.1 (4)
C3	52.9 (7)	434.1 (7)	340.6 (8)	3.2 (4)
C4	0	477.8 (9)	250	2.5 (5)
C5	0	564.1 (9)	250	4.7 (7)
C6	−18.6 (8)	609.5 (6)	320 (1)	5.1 (5)
C7	−18.5 (8)	686.5 (7)	323 (1)	6.0 (5)
C8	0	729.2 (9)	250	5.8 (9)
C11	−222.5 (7)	139.4 (7)	147.5 (8)	4.2 (5)
C21	−195.3 (6)	294.2 (6)	238.0 (8)	3.2 (4)
C22	−265.1 (7)	319.7 (7)	139.3 (9)	4.2 (5)
C23	−299.6 (8)	396.2 (7)	126 (1)	5.7 (6)
C24	−266.5 (8)	447.3 (7)	209 (1)	5.6 (5)
C25	−199.0 (7)	423.3 (7)	309.1 (9)	4.4 (5)
C26	−163.3 (7)	348.3 (6)	322.0 (9)	4.4 (5)
C31	−140.0 (7)	162.7 (6)	370.6 (8)	2.7 (4)
C32	−63.6 (8)	125.6 (8)	449.7 (8)	5.0 (5)
C33	−67.0 (9)	95.3 (8)	540 (1)	6.5 (6)
C34	−146.4 (9)	97.7 (8)	553 (1)	6.5 (6)
C35	−222.8 (9)	135.7 (9)	479.1 (9)	7.5 (6)
C36	−219.8 (8)	169.0 (8)	389 (1)	5.9 (5)

[a] U is defined as $^1/_3\sum_{i=1}^{3} r_i^2$, where r_i values are the root-mean-square amplitudes of vibration. Those parameters without esd's were not refined.

Table V. Positional (×10^4) and Equivalent Isotropic Gaussian Displacement (Å^2 × 10^2) Parameters for $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)_2$ (2)

atom	x	y	z	U^a
Ni	0	0	0	3.63 (7)*
P	−669 (3)	−1226 (2)	247 (3)	4.2 (1)*
F2	−2550 (7)	691 (5)	339 (5)	5.8 (3)*
F3	−4926 (6)	1047 (5)	−1069 (6)	6.1 (3)*
F6	−3636 (6)	43 (5)	−3890 (5)	6.3 (3)*
F7	−1199 (6)	−248 (5)	−2503 (6)	6.1 (3)*
F8	−6678 (6)	−98 (5)	−2269 (5)	6.7 (3)*
F9	−9135 (6)	170 (5)	−3630 (6)	7.5 (4)*
F11	−7450 (8)	1738 (5)	−5833 (6)	7.9 (4)*
F12	−4972 (7)	1484 (5)	−4454 (6)	6.4 (3)*
C1	−1728 (11)	250 (8)	−998 (10)	5.1 (4)
C2	−2748 (11)	555 (8)	−708 (9)	4.0 (3)
C3	−4000 (11)	714 (8)	−1426 (10)	4.4 (4)
C4	−4368 (11)	551 (8)	−2527 (10)	4.1 (4)
C5	−5728 (11)	697 (8)	−3302 (10)	4.4 (4)
C6	−3369 (10)	227 (7)	−2841 (9)	4.0 (3)
C7	−2091 (10)	93 (9)	−2098 (9)	4.7 (3)
C8	−6816 (11)	399 (8)	−3130 (10)	4.5 (4)
C9	−8111 (11)	494 (9)	−3835 (10)	4.9 (4)
C10	−8330 (11)	968 (8)	−4748 (10)	4.7 (4)
C11	−7277 (11)	1283 (9)	−4926 (10)	4.9 (4)
C12	−6000 (11)	1150 (8)	−4248 (10)	4.5 (4)
C13	−905 (12)	−1203 (10)	1527 (10)	6.8 (5)
C21	505 (11)	−2059 (9)	324 (10)	5.1 (4)
C22	850 (12)	−2580 (9)	1200 (12)	6.4 (4)
C23	1775 (13)	−3229 (10)	1207 (12)	7.9 (5)
C24	2177 (14)	−3310 (10)	389 (12)	8.5 (6)
C25	1883 (14)	−2830 (10)	−480 (13)	8.2 (5)
C26	989 (12)	−2166 (9)	−493 (11)	6.3 (4)
C31	−2261 (11)	−1586 (8)	−704 (10)	4.2 (3)
C32	−2324 (12)	−2025 (8)	−1626 (10)	5.0 (4)
C33	−3551 (13)	−2281 (9)	−2361 (12)	6.8 (5)
C34	−4698 (12)	−2075 (9)	−2172 (10)	5.5 (4)
C35	−4678 (13)	−1660 (9)	−1287 (11)	5.9 (4)
C36	−3449 (12)	−1392 (9)	−518 (11)	5.8 (4)

[a] An asterisk indicates an atom refined anisotropically. The equivalent isotropic displacement parameter U is $^1/_3\sum_{i=1}^{3} r_i^2$, where r_i values are the root-mean-square amplitudes of vibration.

package.[14] All non-hydrogen atoms were treated with anisotropic thermal parameters except for the carbon atoms of complex 2, which were refined isotropically. All hydrogen atoms were geometrically generated and included in the model as "riding" on the attached atoms with isotropic displacement parameters constrained to be 1.2 times those of the attached atoms.[15] The parameters R_1, R_2, and goodness-of-fit were calculated as follows: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$.

Final fractional atomic coordinates and equivalent isotropic displacement parameters are given in Tables IV and V for compounds 1 and 2, respectively. Tables of structure factors are available from the authors.

Results and Discussion

To ascertain the effects of substituting octafluoro-p,p'-biphenylene for tetrafluoro-p-phenylene bridges in organometallic complexes, we have now prepared a series of such μ-4,4′-$C_{12}F_8$ bridged $Ni(PMePh_2)_2$ oligomers analogous to the 1,4-C_6F_4 bridged species we reported earlier.[2] These syntheses are generally similar to those of their 1,4-C_6F_4 counterparts, and produce the desired linear mono-, bi-, and trimetallic products in high yields (eqs 1–4). Interestingly, the "arene-rich" bimetallic complex (e.g. $[Ni(PMePh_2)_2]_2(\mu\text{-}4,4'\text{-}C_{12}F_8)(4,4'\text{-}C_{12}F_8H)_2$) can also be prepared in higher overall yield (52 vs 41%) in a one-step reaction using $Ni(PMePh_2)_2Br_2$ and a 1:2 ratio of di- and monolithiobiphenyl reagents (eqs 5 and 6). While this

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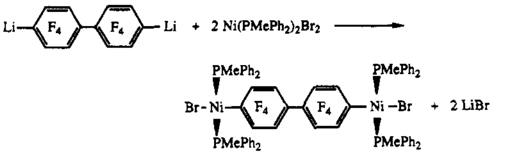
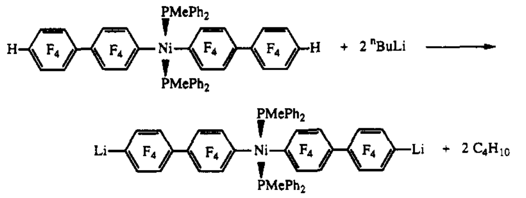
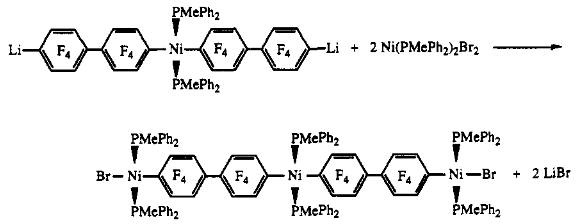
(15) (a) Enquiries concerning the crystallographic results for 1 should be directed to R.M. and quote SDL:ADH9201. (b) Enquiries concerning the crystallographic results for 2 should be directed to B.D.S. and quote SDL:ADH9111. (c) Enquiries concerning the attempted X-ray crystallographic characterization of 3 should be directed to R.M. and quote SDL:ADH9106.



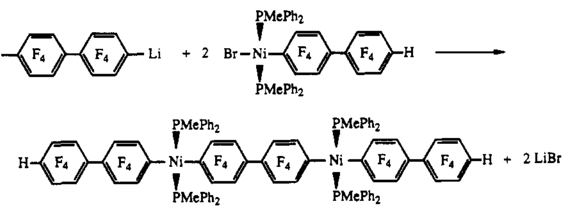
(1)



(2)



(3)



(4)

$$3\,4,4'\text{-}C_{12}F_8H_2 \xrightarrow{+4\text{BuLi (slow)}} 4,4'\text{-}C_{12}F_8Li_2 + 2\,4,4'\text{-}C_{12}F_8HLi + 4C_4H_{10} \tag{5}$$

$$2Ni(PMePh_2)_2Br_2 + 4,4'\text{-}C_{12}F_8Li_2 + 2\,4,4'\text{-}C_{12}F_8HLi \rightarrow [Ni(PMePh_2)_2]_2(\mu\text{-}4,4'\text{-}C_{12}F_8)(4,4'\text{-}C_{12}F_8H_2) \tag{6}$$

reaction proves to be advantageous in that it is a convenient one-step synthesis, it also serves to emphasize that special care must be taken during the preparation of $4,4'\text{-}C_{12}F_8HLi$ from the reaction of 1 equiv of BuLi with 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl. If the stoichiometry or rate of BuLi addition is not controlled adequately, mixtures of $4,4'\text{-}C_{12}F_8Li_2$, $4,4'\text{-}C_{12}F_8HLi$, and $4,4'\text{-}C_{12}F_8H_2$ may result and lead to complex mixtures of organometallic products, i.e.

$$4,4'\text{-}C_{12}F_8H_2 \xrightarrow{+\text{BuLi (slow)}} 4,4'\text{-}C_{12}F_8HLi + C_4H_{10} \tag{7}$$

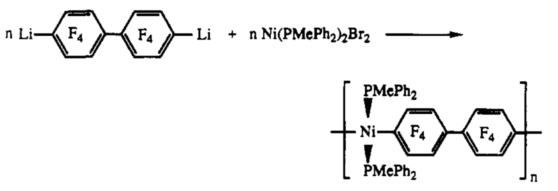
$$4,4'\text{-}C_{12}F_8H_2 \xrightarrow{+2\text{ BuLi}} 4,4'\text{-}C_{12}F_8Li_2 + 2\ C_4H_{10} \tag{8}$$

$$4,4'\text{-}C_{12}F_8H_2 \xrightarrow{+\text{BuLi (fast)}} x\,4,4'\text{-}C_{12}F_8H_2 + y\,4,4'\text{-}C_{12}F_8HLi + z\,4,4'\text{-}C_{12}F_8Li_2 + C_4H_{10} \tag{9}$$

This sensitivity to the rate of BuLi addition is much greater than it is for $1,2,4,5\text{-}C_6F_4H_2$,[2] reflecting the lower degree of electronic interaction observed between the ends of the aromatic rings in the biphenyl compounds.

The new octafluorobiphenyl complexes obtained from these reactions are analytically pure (Table I) microcrystalline yellow or orange solids. These materials displayed excellent air, water, and thermal stabilities (i.e. their decomposition temperatures were ≈210 °C *in air*), and they could therefore be handled in air for extended periods as solids or in solutions for short periods of time without the occurrence of noticeable decomposition. The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectral data for the isolated complexes (Table II) unambiguously establish that they have the expected 4,4′-substitution geometries about the $C_{12}F_8$ units and trans geometries about the nickel centers. No evidence for cis intermediates, such as those found for the related C_6F_4 complexes, was observed for the octafluorobiphenyl derivatives, perhaps because of the longer reaction times employed. The ^1H and ^{31}P NMR chemical shifts of the phosphine ligands are almost independent of oligomer chain length, which implies that, in contrast to the C_6F_4 complexes,[2] there is little intermetallic conjugation for the octafluoro-*p,p*′-biphenylene bridged species; see below. However, these chemical shifts are dependent on the nature of the nickel center. Thus, the methyl protons and phosphorus atoms of $Ni(PMePh_2)_2(aryl)_2$ units are observed from 1.70 to 1.75 ppm and from 9.82 to 9.92 ppm, respectively, while for $Ni(PMePh_2)_2(aryl)Br$ units they are observed from 2.12 to 2.19 ppm and from 9.15 to 9.40 ppm, respectively. In addition, the fluorine atoms of the octafluorobiphenyl ligands that are ortho-substituted to Ni give characteristic chemical shifts (−116.34 to −119.51 ppm) downfield of the other fluorine atoms (−138.22 to −142.70 ppm) in the ^{19}F NMR spectra. This ^1H, ^{19}F, and ^{31}P NMR chemical shift information, combined with the peak multiplicities and symmetries and the ^1H NMR signal attributable to the terminal aryl hydrogen atoms (i.e. $C_{12}F_8H$), allows one to unambiguously establish the chain length of each specific oligomer.

Condensation polymerization of $4,4'\text{-}C_{12}F_8Li_2$ and $Ni(PMePh_2)_2Br_2$, i.e.



(10)

gives a yellow solid in 80% isolated yield. This material displays air and moisture stabilities (220–245 °C dec *in air*) similar to those of the discrete oligomers. However, it is less soluble in common organic solvents such as THF and CH_2Cl_2 with only 30% being soluble in THF. The ^{19}F and ^{31}P NMR spectra of the soluble fraction are qualitatively similar to those of the discrete oligomers (Table II) and are consistent with the polymer repeating units having the same structural features (i.e. para-substituted Ni centers and $4,4'\text{-}C_{12}F_8$ bridges) as the discrete oligomers. The bulk solid gave analytical data consistent with average chain lengths of 8–13. The THF-soluble fraction gave GPC and spectroscopic data consistent with somewhat lower average molecular weights (i.e. 5–10 repeating units).

In addition to spectroscopic characterization, complexes **1**, $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)Br$, and **2**, $Ni(PMePh_2)_2(4,4'\text{-}C_{12}F_8H)_2$, were also characterized via X-ray crystallography (Figures 1 and 2; Tables VI and VII). The structural data for these complexes are unexceptional[16-19] and confirm that the Ni(II) centers and octafluorobiphenyl groups in these molecules have the structures predicted from the NMR data; see above. From these crystallo-

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(16) Churchill, M. R.; Kalra, K. L.; Veidis, M. V. *Inorg. Chem.* **1973**, *12*, 1656–1662.

(17) (a) Churchill, M. R.; Veidis, M. V. *J. Chem. Soc. A* **1971**, 3463–3468. (b) Chruchill, M. R.; Veidis, M. V. *J. Chem. Soc., Dalton Trans.* **1972**, 670–675.

(18) The five atoms Ni, P, P′, Cl, and Cl′ of complex **2** are constrained to be coplanar by crystallographic symmetry.

(19) (a) Foss, L. I.; Syed, A.; Stevens, E. D.; Klein, C. L. *Acta Crystallogr.* **1984**, *C40*, 272–274. (b) Naae, D. G. *Acta Crystallogr.* **1979**, *B35*, 2765–2768. (c) Neronova, N. N. *Z. Strukt. Khim.* **1968**, *9*, 147–148. (d) Gleason, W. B.; Britton, D. *Cryst. Struct. Commun.* **1976**, *5*, 483–488. (e) Lindeman, S. V.; Struchkov, Y. T.; Malichenko, B. F.; Shklover, V. E.; Vasnev, V. A.; Kameneva, T. M.; Sheludko, E. V. *Makromol. Chem.* **1985**, *186*, 2087–2101.

Table VI. Bond Lengths (Å) for 1 and 2

	$Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$ (1)		
Br–Ni	2.340 (2)	C6–C7	1.32 (1)
Ni–P	2.224 (2)	C7–C8	1.39 (1)
Ni–C1	1.86 (1)	C21–C22	1.40 (1)
P–C11	1.828 (9)	C21–C26	1.41 (1)
P–C21	1.802 (9)	C22–C23	1.40 (1)
P–C31	1.785 (9)	C23–C24	1.36 (1)
F2–C2	1.340 (9)	C24–C25	1.40 (1)
F3–C3	1.36 (1)	C25–C26	1.38 (1)
F6–C6	1.38 (1)	C31–C32	1.38 (1)
F7–C7	1.35 (1)	C31–C36	1.41 (1)
C1–C2	1.40 (1)	C32–C33	1.39 (1)
C2–C3	1.38 (1)	C33–C34	1.36 (1)
C3–C4	1.39 (1)	C34–C35	1.36 (1)
C4–C5	1.47 (2)	C35–C36	1.41 (1)
C5–C6	1.38 (1)		
	$Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$ (2)		
Ni–P	2.199 (3)	C5–C8	1.36 (1)
Ni–C1	1.906 (9)	C5–C12	1.39 (1)
P–C13	1.79 (1)	C6–C7	1.40 (1)
P–C21	1.84 (1)	C8–C9	1.38 (1)
P–C31	1.828 (9)	C9–C10	1.38 (1)
F2–C2	1.34 (1)	C10–C11	1.34 (1)
F3–C3	1.35 (1)	C11–C12	1.37 (1)
F6–C6	1.35 (1)	C21–C22	1.38 (1)
F7–C7	1.37 (1)	C21–C26	1.36 (1)
F8–C8	1.36 (1)	C22–C23	1.45 (1)
F9–C9	1.33 (1)	C23–C24	1.30 (1)
F11–C11	1.37 (1)	C24–C25	1.34 (2)
F12–C12	1.34 (1)	C25–C26	1.45 (1)
C1–C2	1.37 (1)	C31–C32	1.40 (1)
C1–C7	1.39 (1)	C31–C36	1.42 (1)
C2–C3	1.37 (1)	C32–C33	1.40 (1)
C3–C4	1.39 (1)	C33–C34	1.38 (1)
C4–C5	1.48 (1)	C34–C35	1.35 (1)
C4–C6	1.38 (1)	C35–C36	1.42 (1)

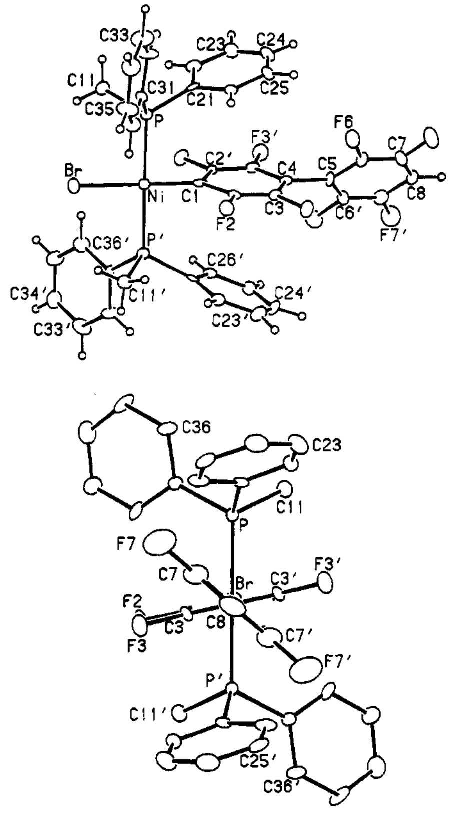

Figure 1. ORTEP plots of the complex $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$ (1): (a, top) perspective view; (b, bottom) view down the octafluorobiphenyl axis.

Table VII. Bond Angles (deg) for 1 and 2

	$Ni(PMePh_2)_2(4,4'-C_{12}F_8H)Br$ (1)		
Br–Ni–P	90.26 (9)	C4–C5–C6′	124.1 (6)
Br–Ni–P′	90.73 (9)	C6–C5–C6′	112 (1)
Br–Ni–C1	180.00	F6–C6–C5	116.8 (9)
P–Ni–P′	179.0 (2)	F6–C6–C7	117 (1)
P–Ni–C1	89.74 (9)	C5–C6–C7	126 (1)
P′–Ni–C1	89.27 (9)	F7–C7–C6	121 (1)
Ni–P–C11	111.1 (3)	F7–C7–C8	119 (1)
Ni–P–C21	117.1 (3)	C6–C7–C8	120 (1)
Ni–P–C31	116.1 (3)	C7–C8–C7′	117 (1)
C11–P–C21	105.3 (4)	P–C21–C22	121.5 (8)
C11–P–C31	103.5 (4)	P–C21–C26	120.7 (7)
C21–P–C31	102.2 (4)	C22–C21–C26	117.4 (9)
Ni–C1–C2	123.5 (6)	C21–C22–C23	120 (1)
Ni–C1–C2′	123.1 (6)	C22–C23–C24	121 (1)
C2–C1–C2′	113 (1)	C23–C24–C25	120 (1)
F2–C2–C1	117.9 (8)	C24–C25–C26	119 (1)
F2–C2–C3	118.4 (8)	C21–C26–C25	122 (1)
C1–C2–C3	123.6 (9)	P–C31–C32	122.4 (7)
F3–C3–C2	119.2 (8)	P–C31–C36	122.0 (7)
F3–C3–C4	118.8 (9)	C32–C31–C36	115.6 (9)
C2–C3–C4	122.1 (9)	C31–C32–C33	121 (1)
C3–C4–C3′	115 (1)	C32–C33–C34	122 (1)
C3–C4–C5	122.2 (6)	C33–C34–C35	118 (1)
C3′–C4–C5	122.7 (6)	C34–C35–C36	120 (1)
C4–C5–C6	124.2 (7)	C31–C36–C35	122 (1)
	$Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$ (2)		
P–Ni–C1	90.7 (3)	F8–C8–C9	115 (1)
Ni–P–C13	106.4 (4)	C5–C8–C9	125 (1)
Ni–P–C21	115.9 (3)	F9–C9–C8	122 (1)
Ni–P–C31	117.9 (3)	F9–C9–C10	120.1 (9)
C13–P–C21	106.4 (5)	C8–C9–C10	118 (1)
C13–P–C31	104.5 (5)	C9–C10–C11	118 (1)
C21–P–C31	104.7 (5)	F11–C11–C10	120.1 (9)
Ni–C1–C2	124.2 (8)	F11–C11–C12	117 (1)
Ni–C1–C7	122.2 (8)	C10–C11–C12	123 (1)
C2–C1–C7	113.5 (9)	F12–C12–C5	118.0 (9)
F2–C2–C1	119.5 (9)	F12–C12–C11	121 (1)
F2–C2–C3	116.4 (9)	C5–C12–C11	121 (1)
C1–C2–C3	124 (1)	P–C21–C22	119.0 (9)
F3–C3–C2	119.7 (9)	P–C21–C26	119.7 (9)
F3–C3–C4	117.7 (8)	C22–C21–C26	121 (1)
C2–C3–C4	123 (1)	C21–C22–C23	116 (1)
C3–C4–C5	122.9 (9)	C22–C23–C24	119 (1)
C3–C4–C6	114.8 (9)	C23–C24–C25	127 (1)
C5–C4–C6	122.3 (9)	C24–C25–C26	114 (1)
C4–C5–C8	122 (1)	C21–C26–C25	121 (1)
C4–C5–C12	123.7 (9)	P–C31–C32	121.1 (7)
C8–C5–C12	114.8 (9)	P–C31–C36	119.2 (8)
F6–C6–C4	119.1 (8)	C32–C31–C36	119.6 (9)
F6–C6–C7	119.4 (8)	C31–C32–C33	121 (1)
C4–C6–C7	121.5 (9)	C32–C33–C34	119 (1)
F7–C7–C1	120.4 (8)	C33–C34–C35	122 (1)
F7–C7–C6	116.0 (8)	C34–C35–C36	120 (1)
C1–C7–C6	123.6 (9)	C31–C36–C35	118 (1)
F8–C8–C5	120.4 (9)		

graphic data, one can calculate that the repeat distance, and thus the Ni–Ni distance, in the related polymers would be about 11.0 Å.[20] This large intermetallic distance in the oligomer/polymer backbones suggests that there will be no significant *intra*molecular steric interactions between the phosphine ligands on adjacent metal centers having $4,4'-C_{12}F_8$ bridges, even with phosphine ligands that are substantially more bulky[8] than is $PMePh_2$ (e.g. PPh_3).[21] This is in marked contrast to the tetrafluoro-*p*-

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(20) Complex 3 readily grows large single crystals from a variety of solvent systems. Unfortunately, all attempts to collect X-ray data suitable for a complete molecular structure determination have so far been unsuccessful due to rapid desolvation of the crystals used (even when they are sealed in capillaries under an atmosphere saturated in the crystallizing solvents). However, crystals grown from CH_2Cl_2/Et_2O were sufficiently stable that a unit cell could be determined having a *C*-centered monoclinic unit cell (a = 28.393 (7) Å, b = 14.582 (9) Å, c = 22.912 (6) Å, β = 130.43 (2)°, V = 7221 Å^3, Z = 4), which, on the basis of systematic absences, was assigned to either *Cc* or *C*2/*c*.

(21) This suggestion is confirmed by qualitative molecular modeling studies carried out for these species using the program Chem3D Plus (Cambridge Scientific Computing) and metrical parameters derived from the X-ray crystallographic data.

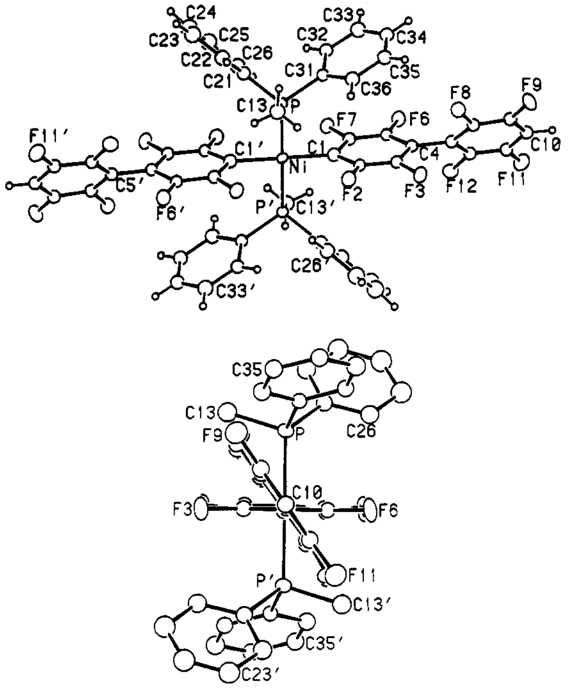

Figure 2. ORTEP plots of the complex $Ni(PMePh_2)_2(4,4'-C_{12}F_8H)_2$ (**2**): (a, top) perspective view; (b, bottom) view down the octafluorobiphenyl axis.

phenylene-bridged complexes, where unfavorable steric interactions between phosphine ligands on adjacent metal centers prevent the formation of such linkages for phosphine ligands significantly more bulky than $PMePh_2$.[2] The most interesting structural features are the large dihedral angles observed for the octafluorobiphenyl ligands (52.2 and 53.1°). Since inter-ring π-conjugation is proportional to the cosine of this angle, this suggests that little π-conjugation can be expected down the backbones of oligomers having octafluoro-*p*,*p*′-biphenylene groups; see above. Thus, it seems that octafluoro-*p*,*p*′-biphenylene linkages are poor candidates for applications requiring a high degree of conjugation down polymer backbones. However, these, and related rigid-rod organometallic polymers, might have other applications based on their high thermal and air stabilities and their chemical and mechanical properties (e.g. as components of engineering plastics and polymer blends).

Conclusions

The results of this study suggest that the effect of replacing tetrafluoro-*p*-phenylene bridges with octafluoro-*p*,*p*′-biphenylene bridges in a series of low molecular weight oligomers of the $Ni(PMePh_2)_2$ unit is to decrease the degree of electronic interaction between adjacent metal centers. Analysis of the X-ray crystallographic data for two representative examples having terminal octafluorobiphenyl ligands suggests a rationale for this decreased conjugation down the oligomer backbones; namely, the substantial twist angle observed between the adjacent aromatic rings. Finally, we have successfully prepared a novel organometallic polymer whose repeating units appear to have the same structures as do the linear oligomers. Efforts are currently underway to expand the range of such polymeric materials, to more fully evaluate their molecular weights and molecular weight distributions, and to evaluate their utilities for practical applications.

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Registry No. **1**, 142781-21-3; **2**, 142781-22-4; **3**, 142781-23-5; **4**, 142781-24-6; **5**, 142797-61-3; **6**, 142781-25-7; $4,4'-C_{12}F_8H_2$, 3883-86-1; $Ni(PMePh_2)_2Br_2$, 15683-34-8.

Supplementary Material Available: Figures containing the ^{19}F NMR spectra of representative complexes and the GPC chromatogram of the THF-soluble fraction of the polymer, complete textual descriptions of the X-ray crystal structure determinations, and tables of anisotropic Gaussian parameters, hydrogen atom coordinates and Gaussian parameters, least-squares planes, torsional angles, and root-mean-square amplitudes of vibration (19 pages). Ordering information is given on any current masthead page.

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