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Tricarbonylrhenium(I) Complexes of Pentafluorophenyl-Substituted Indenyl Ligands[1]

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Depending on ratios of starting materials and reaction conditions, treatment of sodium indenide (NaInd) with C_6F_6 and NaH in THF afforded 3-(pentafluorophenyl)indene (**1**) or 1,3-bis(pentafluorophenyl)indene (**2**) in 65% and 80% yields, respectively, after aqueous workup and recrystallization from methanol. Both **1** and **2** reacted quantitatively with NaH to afford the corresponding mono- and diarylated sodium indenides (**3** and **4**), respectively. The monoarylated ligand (**3**) reacted with $Re(CO)_5Br$ in THF at 65 °C for 2 h to afford pentacarbonyl(η^1-3-(pentafluorophenyl)-1-indenyl]rhenium(I) (**5**, 57%), which was thermally decarbonylated in decane to afford tricarbonyl[η^5-1-(pentafluorophenyl)indenyl]rhenium(I) (**6**, 85%). An analogous reaction of the diarylated ligand (**4**) with $Re(CO)_5Br$ in THF at 65 °C directly gave tricarbonyl[η^5-1,3-bis(pentafluorophenyl)indenyl]rhenium(I) (**7**) in 67% yield. All three rhenium carbonyl complexes were characterized by IR, NMR, elemental analysis, and single-crystal X-ray diffraction. Infrared spectroscopic measurements showed that each C_6F_5 substituent increases ν_{CO} of η^5-indenylrhenium tricarbonyl complexes by 4 cm^{-1} relative to the unsubstituted parent, demonstrating the strong electron-withdrawing capabilities of the C_6F_5 group. Distinct, intermolecular C−H···F−C interactions were identified in the crystal packing diagrams of **5**−**7**.

Introduction

Replacing a η^5-cyclopentadienyl ligand (Cp) with η^5-indenyl (Ind) often significantly changes the structure, reactivity, and physical properties of a transition metal complex.[2] The increased electron-richness,[3] greater “ring-slip” tendency,[4] and unsymmetrical steric bulk resulting from the rigidly fused six-membered ring are all important considerations in the design of indenyl complexes for use in catalysis.[5]

For several reasons, *electronic* substituent effects in Ind complexes are often neglected in the design of new metallocene catalysts.[6,8] First, ring substitution complicates the optimization of critical steric/geometric features. Second, substituting any position other than the 2-carbon desymmetrizes the indenyl anion from C_{2v} to C_s, raising issues of enantioselection in metal complexation of a single ligand and of diastereoselection in metallocene synthesis.[7] Third, relatively few substituents with strong electronic effects, either donating or withdrawing, are functionally compatible with many of the highly electrophilic transition metal species under investigation as catalysts. All these difficulties are rarely overcome at the same time,[8] justifying further development of general synthetic methods leading to indenyl ligands bearing highly electron-donating or electron-withdrawing substituents.

We previously reported a general method for the synthesis of Cp ligands bearing pentafluorophenyl

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Table 1. Crystallographic Data

	5	**6**	**7**
empirical formula	$C_{20}H_6F_5O_5Re$	$C_{18}H_6F_5O_3Re$	$C_{24}H_5F_{10}O_3Re$
fw	607.45	551.44	717.49
diffractometer	Siemens P4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
cryst dimens (mm)	0.4 × 0.4 × 0.08	0.33 × 0.30 × 0.22	0.32 × 0.30 × 0.15
cryst syst	triclinic	monoclinic	triclinic
a (Å)	7.4686(12)	17.272(1)	9.9740(6)
b (Å)	10.768(8)	7.353(5)	10.6664(7)
c (Å)	12.496(2)	13.813(1)	12.171(1)
α (deg)	82.69(4)		86.837(6)
β (deg)	75.567(7)	113.183(3)	68.086(6)
γ (deg)	74.89(3)		64.486(5)
V (Å)^3	937.5(7)	1612.6(4)	1075.5
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Z	2	4	2
D_{calc} (Mg m^{-3})	2.152	2.271	2.22
abs coeff (mm^{-1})	6.561	7.706	5.836
F_{000}	572	1032	676
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
temp (K)	298(2)	298(2)	298(2)
θ range for collection	1.96−25.00	2.5−29.97	2.5−29.97
no. of reflns colld	4118	6172	6585
no. of indep reflns	3293	4519	6252
abs corr method	ψ scans	ψ scans	ψ scans
max, min transm	0.848, 0.408	1.000, 0.523	1.000, 0.6316
no. of data/restrts/params	3234/0/305	3597/0/245	5306/0/364
R [$I > 2\sigma(I)$]	0.040	0.031	0.030
R_w [$I > 2\sigma(I)$]	0.096	0.029	0.029
GoF on F^2	1.123	1.168	1.234
largest diff peak and hole (e Å^{-3})	1.478, −1.569	1.235, −0.202	1.52, −0.34

(C_6F_5) substituents.[9] Cyclic voltammetric analysis of C_6F_5−substituted ferrocenes and infrared spectroscopic analysis of substituted $CpRe(CO)_3$ complexes confirmed that the C_6F_5 group is highly electron-withdrawing.[9a] The facile synthesis of group 4 metallocenes bearing C_6F_5 substituents showed that the C_6F_5 group, when compared to acetyl or trifluoromethyl, is much more compatible with electrophilic early transition metal reagents.[10]

We now report the synthesis of 3-(pentafluorophenyl)indene (**1**), 1,3-bis(pentafluorophenyl)indene (**2**), and their respective sodium indenides (**3**, **4**). The latter, thermally stable salts serve as precursors to the corresponding C_6F_5-substituted tricarbonyl(η^5-indenyl)rhenium(I) complexes (**6**, **7**). Crystallographic analysis confirms the assignment of pentahapticity in the rhenium tricarbonyl complexes (**6**, **7**) and suggests a preferred conformational angle of about 45° between the indenyl and pentafluorophenyl groups in the crystalline state; ^{19}F NMR shows that Cp−C_6F_5 bond rotation is facile at room temperature. Infrared spectroscopic analysis shows that the electronic effects of the C_6F_5 groups on the $Re(CO)_3$ moiety are similar to the analogous effects in substituted Cp complexes.

Experimental Section

General Considerations. All reactions were carried out using routine inert-atmosphere techniques.[11] NMR spectra were recorded on either a Varian U-400 or a Bruker AM-360 instrument. Elemental microanalysis was performed by Oneida Research Services (Whitesboro, NY) or Galbraith Laboratories (Knoxville, TN). Melting points were obtained in open capillaries and are uncorrected. $Re(CO)_5Br$, NaH, and indene were used as received from Aldrich. Hexafluorobenzene was used as received from PCR (now Lancaster). THF and hexanes were purified by published methods.[11a]

Crystallographic Studies. All crystals analyzed in this work by X-ray diffraction were obtained as colorless prisms by cooling concentrated hexanes solutions to −20 °C. Relevant data-collection and structure-refinement information is summarized in Table 1.

Infrared Spectroscopic Measurements. Carbonyl stretching frequencies for rhenium carbonyl complexes were measured using a Midac M-series FT-IR operating at 1 cm^{-1} resolution using dilute *n*-octane solutions injected into an NaCl-windowed cell.

3-(Pentafluorophenyl)indene (1). A mixture of indene (5.8 g, 0.050 mol), NaH (3.3 g, 0.14 mol), and THF (100 mL) was refluxed under nitrogen for 3 h. The resulting deep violet mixture was cooled to 0 °C. C_6F_6 (9.0 g, 0.048 mol) was then added in small portions over 1 h while maintaining the reaction at 0 °C with stirring. The resulting mixture was stirred for an additional 2 h while warming to 25 °C. The solvent and unreacted C_6F_6 were then removed under vacuum, and hexanes (100 mL) was added. The solid residue was triturated and dispersed with a spatula under a nitrogen counterstream. Water (50 mL) was added, and the mixture was stirred for 0.5 h to hydrolyze unreacted sodium hydride. The biphasic mixture was filtered through Celite, and the dark filter cake was extracted further with additional hexanes (2 × 50 mL). The filtrate was separated into an orange aqueous layer and a dark brown organic layer. The aqueous layer was extracted with 50 mL of hexanes. The combined organic layers were dried over $MgSO_4$ and treated with decolorizing carbon. The resulting black mixture was filtered through a bed of neutral alumina (10 cm × 5 cm), eluting with additional hexanes. The pale orange eluent was evaporated to afford 12.3 g (90%) of an orange solid, which was shown by ^1H and ^{19}F NMR to contain about 10% of **2**. Recrystallization from 100 mL of CH_3OH afforded 8.5 g (0.030 mol, 60%) of a pale crystalline solid: mp 107−108 °C. ^1H NMR ($CDCl_3$): δ 7.58 (d, J = 7.2 Hz, 1 H), 7.34 (td, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H), 7.31 (td, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H), 7.21 (m, 1 H), 6.78 (t, J = 1.8 Hz, 1 H), 3.64 (d, J = 2.0 Hz, 1 H). ^{19}F NMR ($CDCl_3$): δ −139.91 (m, 2 F), −156.16 (t, J = 22 Hz, 1 F), −163.1 (m, 2 F). ^{13}C NMR ($CDCl_3$): δ 144.4 (d, $^1J_{CF}$ = 220 Hz, *C*F), 143.2

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(*C*), 142.7 (*C*) 141.5 (d, $^1J_{CF}$ = 230 Hz, *C*F), 137.9 (d, $^1J_{CF}$ = 225 Hz, *C*F), 137.7 (dt, $^1J_{CH}$ = 170 Hz, $^2J_{CH}$ = 6 Hz, *C*H), 130.1 (*C*), 126.4 (dd, $^1J_{CH}$ = 159 Hz, $^3J_{CH}$ = 7 Hz, *C*H), 125.5 (dd, $^1J_{CH}$ = 159 Hz, $^3J_{CH}$ = 7 Hz, *C*H), 124.0 (dd, $^1J_{CH}$ = 157 Hz, $^3J_{CH}$ = 7 Hz, *C*H), 120.1 (ddt, $^1J_{CH}$ = 159 Hz, $^3J_{CH}$ = 7 Hz, $^5J_{CF}$ = 2 Hz, *C*H), 110.4 (td, $^2J_{CF}$ = 17 Hz, $^4J_{CF}$ = 5 Hz, C_6F_5 ipso), 39.1 (tdd, $^1J_{CH}$ = 129 Hz, $^2J_{CH}$ = 7 Hz, $^3J_{CH}$ = 3 Hz, *C*H_2). ($C_{15}H_7F_5$HRMS (EI): *m/z* calcd for $C_{15}H_7F_5$ 282.0468, found 282.0476. Anal. Calcd for $C_{15}H_7F_5$: C, 63.84; H, 2.50. Found: C, 63.65; H, 2.61.

1,3-Bis(pentafluorophenyl)indene (2). A mixture of indene (3.48 g, 30.0 mmol), NaH (2.4 g, 0.10 mol), C_6F_6 (12.1 g, 0.065 mol), and THF (100 mL) was refluxed under nitrogen for 15 h and then cooled. Following the same workup as for **1**, the desired product was isolated as fine white needles (10.8 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.38 (m, 1 H), 7.30 (m, 2 H), 7.22 (m, 1 H), 6.68 (d, ^3J = 2.0 Hz, 1 H), 5.18 (m, 1 H). ^{19}F NMR ($CDCl_3$): δ −139.65 (m, 2 F), −142.97 (m, 2 F), −155.01, (tt, ^3J = 21 Hz, ^4J = 2 Hz, 1 F), −156.47 (tt, ^3J = 21 Hz, ^4J = 1 Hz, 1 F), −162.59 (m, 2 F), −162.70 (m, 2 F). ^{13}C NMR ($CDCl_3$): δ 145.3 (dm, $^1J_{CF}$ = 249 Hz, *C*F), 144.5 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 144.1 (*C*), 141.8 (*C*), 141.0 (dm, $^1J_{CF}$ = 255 Hz, *C*F), 138.5 (dm, $^1J_{CF}$ = 240 Hz, *C*F), 137.8 (*C*H), 137.7 (dm, $^1J_{CF}$ = 245 Hz, *C*F), 137.1 (dm, $^1J_{CF}$ = 242 Hz, *C*F), 131.5 (*C*), 127.8 (*C*H), 126.7 (*C*H), 123.3 (*C*H), 120.8 (*C*H), 112.0 (td, $^2J_{CF}$ = 16 Hz, $^4J_{CF}$ = 4 Hz, C_6F_5 ipso *C*), 109.5 (td, $^2J_{CF}$ = 18 Hz, $^4J_{CF}$ = 5 Hz, C_6F_5 ipso *C*), 44.4 (*C*H). Anal. Calcd for $C_{21}H_6F_{10}$: C, 56.27; H, 1.35. Found: C, 56.71; H, 1.44.

Sodium 1-(Pentafluorophenyl)indenide (3). To a suspension of NaH (120 mg, 5.00 mmol) in THF (50 mL) was added **1** (1.00 g, 3.55 mmol) in one portion under a nitrogen counterstream. After stirring for 1 h at 25 °C, the mixture was filtered to remove unreacted NaH, and the bright orange filtrate was evaporated. Trituration of the dark residue with pentane (3 × 50 mL) afforded 1.1 g of a dark green solid. ^{1}H NMR analysis in THF-d_8 indicated the presence of residual THF. ^{1}H NMR (THF-d_8): δ 7.36 (ddd, *J* = 8.0 Hz, 1.2 Hz, 0.8 Hz, 1 H), 7.25 (m, 1 H), 6.87 (m, 1 H), 6.64 (ddd, *J* = 8.4 Hz, 6.4 Hz, 1.2 Hz, 1 H), 6.58 (ddd, *J* = 8.4 Hz, 6.4 Hz, 1.2 Hz, 1 H), 6.22 (dd, *J* = 4.0 Hz, 0.8 Hz, 1 H). ^{19}F NMR (THF-d_8): δ −142.42 (d, ^3J = 25 Hz, 2 F), −165.75 (m, 2 F), −170.46 (tt, $^3J_{FF}$ = 21 Hz, ^4J = 5 Hz, 1 F). ^{13}C NMR (THF-d_8): δ 143.6 (d, $^1J_{CF}$ = 233 Hz, *C*F), 139.0 (d, $^1J_{CF}$ = 242 Hz, *C*F), 138.8 (d, $^1J_{CF}$ = 240 Hz, *C*F), 132.6 (*C*), 128.8 (*C*), 122.2 (m, *C*), (121.2 (*C*H), 119.6 (*C*H), 118.8 (t, J_{CF} = 5 Hz, *C*H), 115.8 (*C*H), 114.8 (*C*H), 98.9 (*C*H), 90.4 (t, J_{CF} = 3 Hz, *C*).

Sodium 1,3-Bis(pentafluorophenyl)indenide (4). A procedure similar to that for the preparation of **3** was employed, using instead **2** as the starting material. A dark green solid was isolated, which was shown by ^{1}H NMR analysis to contain some residual THF. ^{1}H NMR (THF-d_8): δ 7.21 (m, 2 H), 7.07 (pentet, $^5J_{HF}$ = 2.2 Hz, 1 H), 6.65 (m, 2 H). ^{19}F NMR (THF-d_8): δ −141.04 (d, ^3J = 24 Hz, 4 F), −165.80 (m, 4 F), −169.33 (tt, ^3J = 21 Hz, ^4J = 5 Hz, 2 F). ^{13}C NMR (THF-d_8): δ 144.1 (d, $^1J_{CF}$ = 241 Hz, *C*F), 138.9 (d, ^1J = 236 Hz, *C*F), 136.1 (d, ^1J = 240 Hz, *C*F), 132.02 (*C*), 125.8 (pentet, $^4J_{CF}$ = 2 Hz, *C*H), 118.9 (*C*), 118.6 (t, $^5J_{CF}$ = 5 Hz, *C*H), 115.8 (*C*H), 96.1 (br, *C*).

Pentacarbonyl(η^1-3-(pentafluorophenyl)-1-indenyl]rhenium(I) (5). A solution of $Re(CO)_5Br$ (202 mg, 0.500 mmol) and **3** (170 mg, 0.560 mmol) in THF (40 mL) was refluxed for 2 h under nitrogen and then cooled. The solvent was then evaporated under reduced pressure, and the resulting yellow-orange residue was triturated with hexanes and transferred to a 2 cm bed of neutral alumina. A small portion of **1** was eluted with 100 mL of hexane, and then 40 mL of benzene was used to elute the product. Evaporation of the benzene fraction afforded 180 mg (0.28 mmol, 57%) of a yellow-orange solid. An analytical sample was obtained by recrystallization from hexanes. Mp: 130−135 °C (d). IR (*n*-octane): ν_{CO} = 2027, 2022, 1991 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.50 (dd, ^3J = 7.6 Hz, ^4J = 0.5 Hz, 1 H), 7.26−7.20 (m, 3 H), 7.13 (td, ^3J = 7.2 Hz, ^4J = 0.7 Hz, 1 H), 4.38 (d, ^3J = 1.9 Hz, 1 H). ^{19}F NMR ($CDCl_3$): δ −140.83 (m, 2 F), −158.24 (t, ^3J = 22 Hz, 1 F), −164.05 (m, 2 F). ^{13}C NMR ($CDCl_3$): δ 182.6 (4 equatorial *C*O) 178.3 (axial *C*O), 157.0 (*C*), 151.7 (*C*H), 144.8 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 140.1 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 137.8 (dm, $^1J_{CF}$ = 250 Hz, *C*F), 137.1 (*C*), 123.4 (*C*H), 123.2 (*C*H), 121.8 (*C*H), 120.4 (*C*H), 115.4 (*C*), 111.2 (td, $^2J_{CF}$ = 17 Hz, $^4J_{CF}$ = 5 Hz, C_6F_5 ipso *C*), 25.7 (*C*H). Anal. Calcd for $C_{20}H_6F_5O_5Re$: C, 39.55; H, 1.00. Found: C, 39.78; H, 0.80.

Tricarbonyl[η^5-1-(pentafluorophenyl)indenyl]rhenium(I) (6). A solution of **5** (120 mg, 0.20 mmol) in decane (2 mL) was prepared in a 10 mL test tube. The tube was placed in a preheated 120 °C oil bath. Gas evolution commenced within 5 s and continued for 2 min (*Caution: carbon monoxide is poisonous. Conduct this procedure in a well-ventilated fume hood.*) After 10 min, the mixture was cooled, the solvent was evaporated in a nitrogen stream, and the residue was dried under vacuum to afford 98 mg (0.17 mmol, 85%) of a pale solid, which was recrystallized from hexanes to afford pale yellow prisms. IR (octane): ν_{CO} = 2034, 1952, 1941 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.98 (dm, ^3J = 8.2 Hz, 1 H), 6.90 (dt, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 1 H), 6.66 (ddd, ^3J = 8.6 Hz, ^3J = 6.8 Hz, ^4J = 1.0 Hz, 1 H), 6.56 (ddd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.0 Hz, 1 H), 5.25 (dt, $^3J_{HH}$ = 3.0 Hz, $^5J_{HF}$ = 1.6 Hz, 1 H), 5.05 (dd, ^3J = 2.8 Hz, ^4J = 0.8 Hz, 1 H). In $CDCl_3$, the corresponding ^{1}H chemical shifts are 7.39, 7.60, 7.24, 7.17, 5.99, and 5.98. ^{19}F NMR ($CDCl_3$): δ −135.29 (d, ^3J = 20 Hz, 2 F), −155.20 (tt, ^3J = 21 Hz, ^4J = 2 Hz, 1 F), −162.03 (m, 2 F). Anal. Calcd for $C_{18}H_6F_5O_3Re$: C, 39.21; H, 1.10. Found: C, 39.52; H, 0.89.

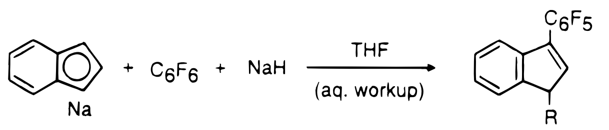
Tricarbonyl[η^5-1,3-bis(pentafluorophenyl)indenyl]rhenium(I) (7). A mixture of **4** (150 mg, 0.32 mmol), Re(CO)$_5$Br (101 mg, 0.25 mmol), and THF was stirred at reflux under nitrogen for 3 h and then cooled. After evaporation of the solvent, the resulting orange residue was transferred to a 5 cm column of neutral alumina with 25 mL of CH_2Cl_2 and eluted with additional dichloromethane (75 mL). The combined filtrate was evaporated to afford 200 mg of a white solid. Analysis of this crude product by ^{1}H and ^{19}F NMR ($CDCl_3$ solution) as well as IR (dichloromethane solution) showed only the pentahapto diarylated indenylrhenium complex (**7**) and a small amount of **2**. Signals corresponding to neither $Re(CO)_5Br$ nor the putative monohapto diarylated indenylrhenium intermediate were observed. The white solid was then subjected to chromatography on neutral alumina. Elution with hexanes followed by evaporation of the solvent gave 60 mg of **2**. Subsequent elution with dichloromethane afforded, after evaporation of the solvent, 121 mg (0.167 mmol, 67%) of a white solid. Recrystallization from hexanes afforded an analytical sample, mp 182−184 °C. IR (octane): ν_{CO} = 2038, 1957, 1948 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.51 (m, 2 H), 7.31 (m, 2 H), 6.29 (pentet, $^5J_{CF}$ = 1.5 Hz, 1 H). ^{19}F NMR ($CDCl_3$): δ −134.72 (d, ^3J = 21 Hz, 4 F), −153.96 (tt, ^3J = 21 Hz, ^4J = 2 Hz, 2 F), −161.44 (m, 4 F). ^{13}C NMR ($CDCl_3$): δ 190.6 (*C*O), 144.2 (d, $^1J_{CF}$ = 251 Hz, *C*F), 141.8 (dm, $^1J_{CF}$ = 255 Hz, *C*F), 138.1 (dm, $^1J_{CF}$ = 251 Hz, *C*F), 127.3 (*C*(5,6)H), 123.1 (t, $^5J_{CF}$ = 4 Hz, *C*(4,7)H), 107.9 (t, $^2J_{CF}$ = 13 Hz, C_6F_5 ipso *C*), 106.6 (*C*(3a,-7a)), 96.0 (pentet, $^4J_{CF}$ = 4 Hz, *C*(2)H), 75.7 (m, *C*(2)). Anal. Calcd for $C_{24}H_5F_{10}O_3Re$: C, 40.18; H, 0.70. Found: C, 40.57; H, 0.56.

Results and Discussion

Ligand Synthesis. Sodium indenide reacts with hexafluorobenzene in tetrahydrofuran to afford either the monoarylated (**1**) or diarylated indene (**2**) in 60% or 80% isolated yield, respectively, depending on the temperature and ratio of reactants (Scheme 1). In the synthesis of the monoarylated indene (**1**), the crude product is contaminated with about 10% of **2**, as determined by ^{1}H and ^{19}F NMR, but the purity can be improved to 95% by a single recrystallization from methanol. The diarylated indene (**2**) is formed regioselectively.

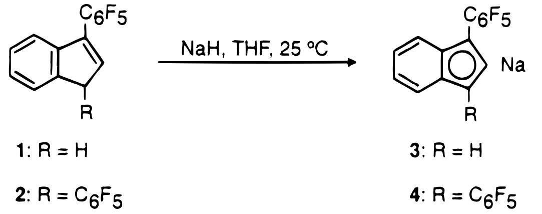
Both of the C_6F_5-substituted indenes (**1** and **2**) react with sodium hydride in THF to afford the corresponding

Scheme 1

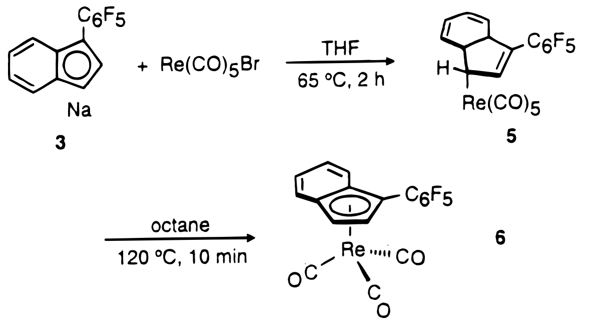


mol ratios	conditions	isolated yields
1.0 : 1.0 : 2.8	0 °C, 3 h	**1**: R = H; 60 %
1.0 : 2.2 : 3.3	65 °C, 15 h	**2**: R = C_6F_5; 80 %

Scheme 2



Scheme 3

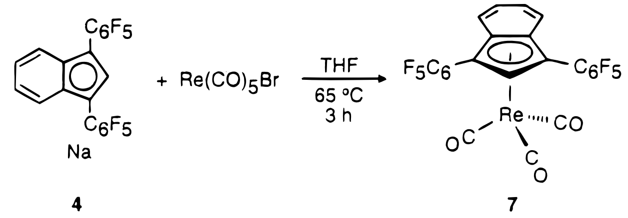


sodium indenides (**3** and **4**, respectively, Scheme 2). Crude products contain variable amounts of THF, which can be mostly removed by heating under high vacuum (80 °C, 2 × 10^{-5} Torr, 4 h). The salts, which vary in color from dark green to brown, depending on the amount of residual THF, can be stored indefinitely at 25 °C under nitrogen.

Synthesis of Indenylrhenium Carbonyl Complexes. The monoarylated ligand (**3**) reacts with rhenium pentacarbonyl bromide in THF at 65 °C to afford the η^1-indenylrhenium complex (**5**, Scheme 3). The pseudo-C_{4v} symmetry of the $Re(CO)_5$ group of **5** is characterized by three strong absorbances in the infrared spectrum (octane solution) corresponding to symmetry-adapted carbonyl stretching coordinates ($2A_1 + B_1 + E$, where B_1 is inactive) and by two signals in the ^{13}C NMR at 182.6 and 178.3 ppm in an approximate integrated intensity ratio of 4:1, respectively. Thermolytic decarbonylation[4b] of the monohapto monoarylated complex (**5**) at 120 °C in decane solution (Scheme 3) affords the pentahapto analogue (**6**). Three strong, well-resolved absorbances corresponding to carbonyl stretching suggest significant distortion from ideal C_{3v} symmetry ($A_1 + E$).

In contrast, the diarylated ligand (**4**) reacts with $Re(CO)_5Br$ in THF (Scheme 4) to afford directly the corresponding pentahapto rhenium complex (**7**) in 67% yield. A diarylated monohapto intermediate analogous to **5** was neither isolated nor identified spectroscopically (IR, ^1H NMR, ^{19}F NMR) in the crude product mixture of this reaction. The infrared spectrum of the purified diarylated rhenium complex (**7**) shows three strong absorbances in the carbonyl stretching region, confirming the assignment of an unsymmetrical "piano stool" complex similar to the monoarylated analogue (**6**).

Scheme 4



Structural Characterization. This section presents the analysis of **5**, **6**, and **7** by single-crystal X-ray diffraction. Details of the data collection and structure solution and refinement are provided in Table 1. Complete tables of interatomic distances and intramolecular angles are archived in the Supporting Information.

Molecular Structure of 5. A thermal ellipsoid plot of **5** (Figure 1) confirms the assigned 1,3-substitution of the C_6F_5 and $Re(CO)_5$ groups. The indenyl 1-hydrogen (H6, located and isotropically refined) in **5** is positioned directly between two carbonyl ligands with an H(6)−C(6)−Re(1)−C(4) torsion angle of 46.0°. A similar feature was observed in both $(\eta^1\text{-}7\text{-}C_7H_7)Re(CO)_5$[12] and *fac*-$(\eta^1\text{-}5\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$.[13b] The $Re(CO)_5$ fragment adopts a nearly ideal square-pyramidal configuration with OC−Re−CO angles ranging from 87.6° to 92.9°, Re−CO distances ranging from 1.937 to 2.043 Å and five equal C−O distances of 1.14 ± 0.01 Å. The carbonyl ligand trans to the η^1-indenyl group (strong donor) has the shortest Re−CO distance.

Table 2. Slip-Fold Distortions of Some η-Indenyl Complexes

entry no.	compound	slip (Δ, Å)[a]	hinge (deg)[a]	fold (deg)[a]
1	$[\eta^5\text{-}1\text{-}(C_6F_5)Ind]Re(CO)_3$ (**6**)	0.071	2.4	3.4
2	$[\eta^5\text{-}1,3\text{-}(C_6F_5)_2Ind]Re(CO)_3$ (**7**)	0.060	2.7	3.8
3	$[\eta^5\text{-}Ind]_2Fe$[b]	0.043	2.2	0.8
4	$[\eta^3\text{-}Ind]_2Ni$[b]	0.418	13.9	13.1

[a] Slip-fold parameters defined in ref 14a. [b] Average values for the two indenyl ligands. Data from ref 14b.

Structures of 6 and 7. Thermal ellipsoid plots for the rhenium complexes (**6** and **7**) are provided in Figure 2 and Figure 3. Both **6** and **7** exhibit "slip-fold" distortions from ideal pentahapto coordination of the $Re(CO)_3$ fragment (Table 2, entries 1, 2).[14] These variations are typical of η^5-bonded indenyl ligands, as the comparison with canonical pentahapto and trihapto complexes attests (Table 2, entries 3, 4). The *ipso* carbons of the C_6F_5 groups are displaced *away* from the coordinated side of the indenyl five-membered ring least-squares plane: in the monoarylated complex (**6**), C(9) is displaced 0.14 Å, and in the diarylated complex (**7**), C(9)

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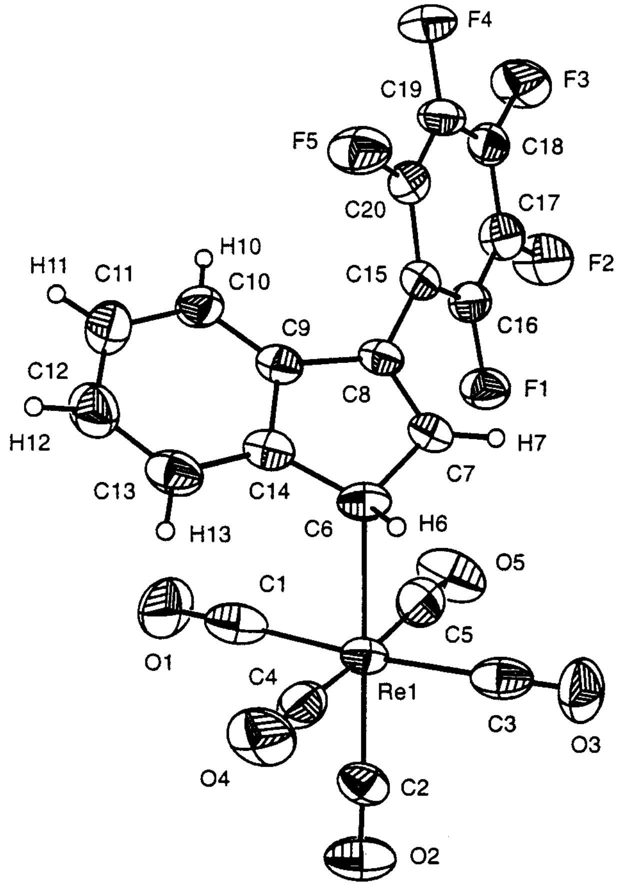

Figure 1. Solid-state molecular structure of **5** showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms were located and isotropically refined. Selected interatomic distances (Å) and intramolecular angles (deg): Re–C(1), 2.029(10); Re–C(2), 1.937(8); Re–C(3), 2.043(10); Re–C(4), 1.971(10); Re–C(5), 1.993(10); Re–C(6), 2.320(7); C(6)–C(7), 1.494(9); C(7)–C(8), 1.332(9), C(8)–C(9), 1.478(8); C(9)–C(14), 1.409(9); C(6)–C(14), 1.473(10); C(9)–C(10), 1.392(9); C(10)–C(11), 1.379(10); C(11)–C(12), 1.397(12); C(12)–C(13), 1.380(12); C(13)–C(14), 1.390(10); C(7)–C(6)–Re, 111.5(5); C(14)–C(6)–Re, 115.5(5); C(7)–C(6)–C(14), 103.9; C(6)–C(7)–C(8), 110.3(6); C(7)–C(8)–C(9), 109.6(6); C(7)–C(8)–C(15), 125.8(6); C(9)–C(8)–C(15), 124.5(6).

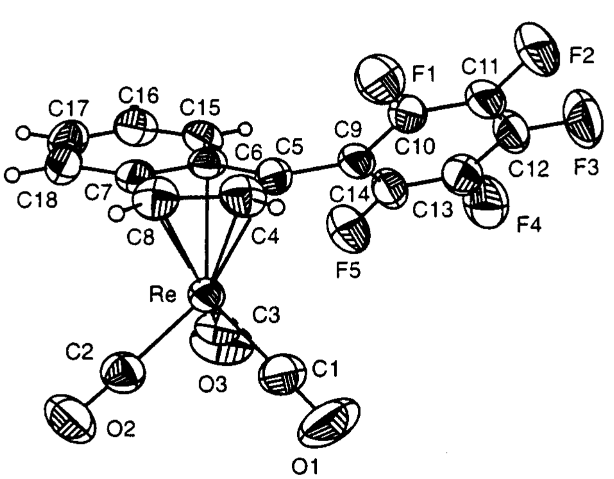

Figure 2. Solid-state molecular structure of **6** showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms were placed in idealized positions. Selected interatomic distances (Å) and intramolecular angles (deg): Re–C(4), 2.287(5); Re–C(5), 2.323(4), Re–C(6), 2.379(4); Re–C(7), 2.353(4); Re–C(8), 2.289(5); C(4)–C(5), 1.427(6); C(5)–C(6), 1.441(6); C(6)–C(7), 1.451(5); C(7)–C(8), 1.439(7); C(8)–C(4), 1.397(6); C(6)–C(15), 1.427(7); C(10)–C(9)–C(14), 115.2(4); C(5)–C(4)–C(8), 110.4(8); C(1)–Re–C(2), 88.6(2); C(2)–Re–C(3), 90.9(2); C(3)–Re–C(1), 87.8(2); C(6)–C(5)–C(9), 127.8(4); C(4)–C(5)–C(9), 124.9(4).

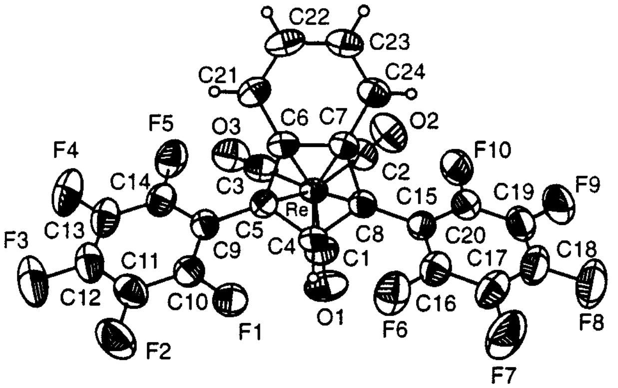

Figure 3. Solid-state molecular structure of **7** showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms were located and isotropically refined. Selected interatomic distances (Å) and intramolecular angles (deg): Re–C(1), 1.877(3); Re–C(2), 1.9009(4); Re–C(3), 1.914(5); Re–C(4), 2.287(3); Re–C(5), 2.316(3); Re–C(6), 2.391(3); Re–C(7), 2.376(3); Re–C(8), 2.308(3); C(4)–C(5), 1.430(6); C(5)–C(6), 1.453(4); C(6)–C(7), 1.435(6); C(7)–C(8), 1.444(5); C(8)–C(4), 1.420(5); C(6)–C(21), 1.412(6); C(21)–C(22), 1.363(6); C(22)–C(23), 1.402(8); C(23)–C(24), 1.349(6); C(24)–C(7), 1.422(5); C(14)–C(9)–C(10), 115.4(2); C(20)–C(15)–C(16), 115.5(4); C(5)–C(4)–C(8), 109.6(3); C(1)–Re–C(2), 89.3(2); C(2)–Re–C(3), 87.2(2); C(3)–Re–C(1), 88.1(2).

and C(15) are displaced 0.18 and 0.23 Å, respectively. Electron-withdrawing substitutents attached to carbocyclic ligands are usually displaced away from coordinated tricarbonylmetal groups.

C_6F_5–Indenyl Conformations. The C_6F_5 group adopts an orientation of about 45° relative to the five-membered ring of the indenyl ligand. C_6F_5–indenyl interplanar angles are 47.7° in the monoarylated complex (**6**) and 42.5° and 48.0° in the diarylated complex (**7**). In the η^1-indenyl complex (**5**), the indenyl–C_6F_5 interplanar angle is nearly the same (51.6°), suggesting that a change in ligand hapticity has little effect on this conformational parameter. The potential energy surface for indenyl–C_6F_5 torsion could also simply be shallow enough for the electronic effects on the interplanar angle to be overcome by lattice-packing forces.

Intermolecular C–H···F–C Interactions. Packing diagrams for **5**–**7** are shown in Figure 4. The shortest intermolecular contacts in crystalline **5** are C–H···F–C interactions in which H(7) interacts with the corresponding F(2) and F(4) of two distinct neighbors (2.600 and 2.596 Å, respectively), forming an acute F···H···F angle of 73.2° and a C–H···F angle of 145.6°. The next shortest C–H···F contact (H···F distance = 2.667 Å, C–H···F angle = 138.6°) involves F(1) and a neighboring H(11). The shortest C–H···F distances in **6** are 2.530 Å, between F(3) and a neighboring H(15), and 2.794 Å, between F(5) and a neighboring H(4), with respective C–H···F angles of 139.7° and 143.1°. The shortest C–H···F contacts in **7** are 2.478 Å, between F(4) and a neighboring H(21), and 2.803 Å, between F(2) and a

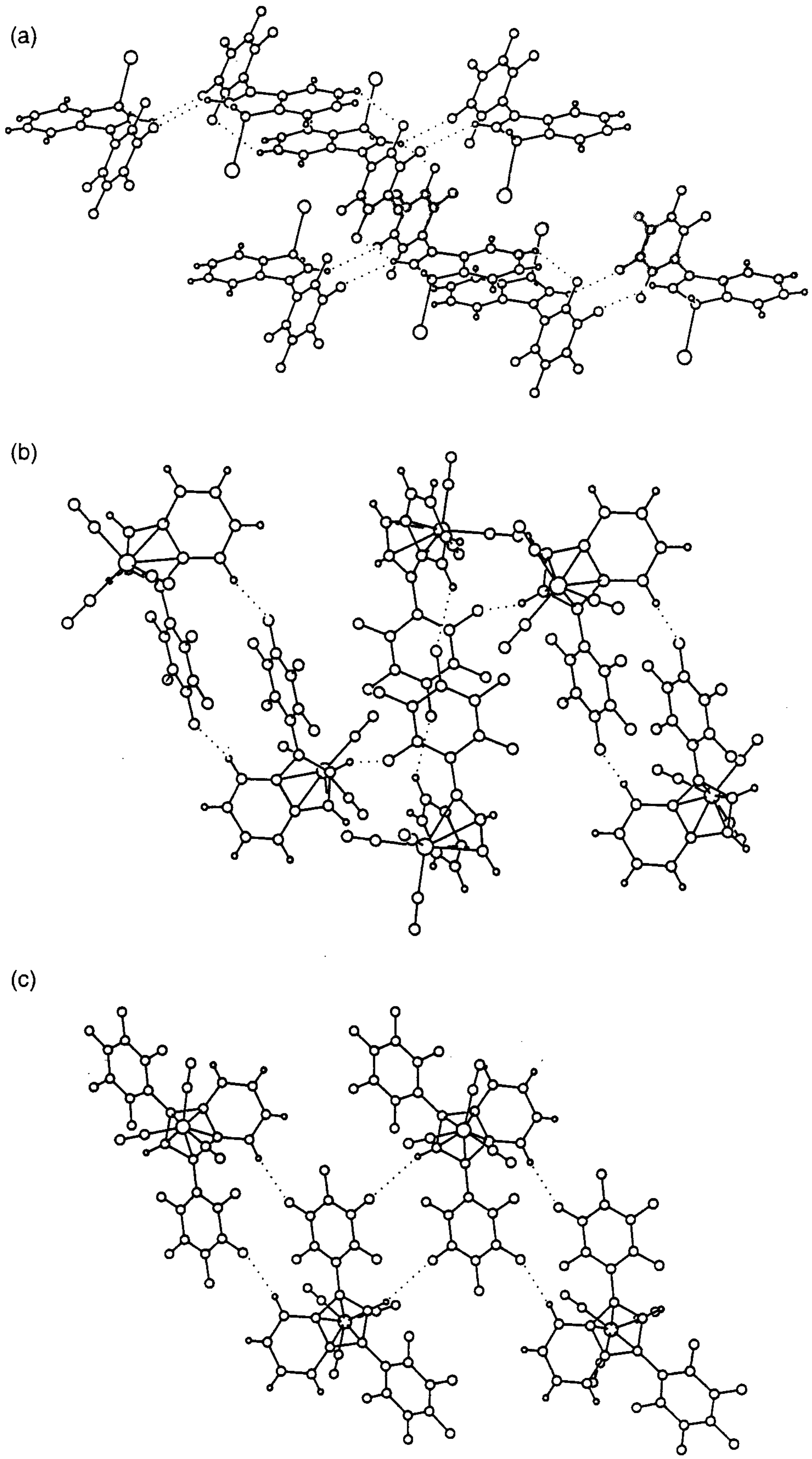

Figure 4. Crystal packing diagrams showing intermolecular C−H···F−C interactions as dotted lines. (a) Packing diagrams of **5** with carbonyl ligands omitted for clarity. (b) Packing diagram of **6**. (c) Packing diagram of **7**.

neighboring H(4), with respective C−H···F angles of 128.9° and 139.7°.

These C−H···F angles are typical for single C−H···F interactions,[15] and we considered the possibility that these complexes exhibit weak "hydrogen bonding". Several criteria have been used to define "close" C−H···F−C contacts. Dunitz and Taylor[15] suggested that an H···F distance less than 2.3 Å is an appropriate criterion, because the sum of the van der Waals radii of hydrogen and fluorine is in the range 2.5−2.7 Å,[16] and because H···N and H···O hydrogen bonds generally exhibit H···X distances that are significantly shorter than the sum of their respective van der Waals radii. They concluded that C−F bonds are poor hydrogen-bond acceptors and that donors such as O−H, N−H, and C−H will interact with stronger acceptors if available. Howard et al.[17] observed that C−H interactions do not contribute much toward lattice stabilization,[18] even though 39 compounds having such interactions with H···F distances of less than 2.35 Å were found among 360 compounds containing sp^2-hybridized C−F bonds. Others have suggested that C−H···F−C interactions may arise from interactions among permanent dipoles, which should diminish more slowly with increasing H···F distance and could remain important at longer distances than corresponding van der Waals interactions.[19] Desiraju and co-workers, however, suggested that the strong, inverse correlation between H···F distance and C−H···F angle in a series of fluorinated benzenes "is very characteristic of hydrogen bonding".[20] The bond lengths and angles reported here for **5**−**7** do not exhibit an inverse relationship.

In this context, it is noteworthy that our tricarbonylindenylrhenium(I) complexes did not exhibit significant C−H···O≡C−M interactions, even though arene and Cp C−H bonds commonly serve as "donors" toward CO ligands.[21] Another striking observation is that all three complexes involve the hydrogen at the 2-position of the indenyl ligand for these interactions. Also, both η^5-indenyl complexes involve the same two hydrogens (2- and 7-positions) in these intermolecular contacts, even though **6** uses the *ortho* and *para* fluorines of its C_6F_5, while **7** uses the two *meta* fluorines. We believe further trends in crystal packing may arise from detailed investigation of other C_6F_5-substituted cyclopentadienyl and indenyl complexes, especially when more electrophilic metal fragments are coordinated, and work is underway to explore these trends in greater detail.

Infrared Spectroscopic Studies. Table 3 presents carbonyl stretching frequencies for several C_6F_5-substituted $CpRe(CO)_3$ and $IndRe(CO)_3$ complexes. Entries 1, 3, and 4 show that pentafluorophenyl substitution of $CpRe(CO)_3$ complexes results in a linear increase in ν_{CO} (A_1) of 4 cm^{-1} per C_6F_5 substituent relative to the respective unsubstituted complex, indicating substantial electron withdrawl by the C_6F_5 group,[9] comparable to that of the acetyl group (entry 3).[22] The substituted η^5-indenylrhenium complexes (entries 5−7) show the same quantitative effect of the C_6F_5 group. Noteworthy is the lack of an observable difference in electronic effects on the $Re(CO)_3$ moiety for Cp vs Ind complexes (entry 1 vs 5, entry 3 vs 7, and entry 4 vs 7).[23,24] The corresponding effect in $LMn(CO)_3$ complexes is substantial (entry 8 vs 9).[23,24] According to King and Efraty, this could reflect a "synergistic" weakening of both donor (σ, π) and acceptor (δ) interactions leading to an overall retention of the metal-centered electron density upon fusion of the benzene ring in $IndMn(CO)_3$ compared to $CpMn(CO)_3$.[24] This "synergistic" effect is apparently insensitive to the presence of C_6F_5 ring substituents. A lack of theoretical support for this hypothesis suggests an area of further investigation.

Table 3. Carbonyl Stretching Frequencies of Several Pentafluorophenyl-Substituted $CpM(CO)_3$ and $IndM(CO)_3$ Complexes (M = Mn, Re)

entry no.	compound	ν_{CO} (cm^{-1})
1	(η^5-Cp)$Re(CO)_3$	2030, 1943[a]
2	(η^5-CH_3COCp)$Re(CO)_3$	2033, 1945[a]
3	(η^5-C_6F_5Cp)$Re(CO)_3$	2034, 1947[b]
4	[η^5-1,3-$(C_6F_5)_2$Cp]$Re(CO)_3$	2038, 1953[b]
5	(η^5-Ind)$Re(CO)_3$	2030, 1942, 1936[a]
6	[η^5-1-(C_6F_5)Ind]$Re(CO)_3$ (**6**)	2034, 1952, 1941
7	[η^5-1,3-$(C_6F_5)_2$Ind]$Re(CO)_3$ (**7**)	2038, 1957, 1948
8	(η^5-Cp)$Mn(CO)_3$	2025, 1942[c]
9	(η^5-Ind)$Mn(CO)_3$	2030, 1949, 1940[d]

[a] Data from ref 22. [b] Data from ref 9. [c] Data from ref 23. [d] Data from ref 24.

Conclusions. Nucleophilic substitution of hexafluorobenzene with indenyl anions provides a convenient route to new pentafluorophenyl-substituted indenyl ligands for use in synthetic organometallic chemistry. Substitution in the 1- and 3-positions is complementary to existing methods for attachment of C_6F_5 at the 2-position.[8] The C_6F_5 substituent exhibits the same electron-withdrawing influences on the $Re(CO)_3$ fragments whether attached to either Cp or Ind. C_6F_5-substituted indenyl rhenium carbonyl complexes show C−H···F packing interactions that tend to involve hydrogens at the 2- and 7-positions of the indenyl ligands. Research is underway to explore the synthesis and reactivity of additional fluoroarylated indenyl complexes.

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Supporting Information Available: Tables of crystal and intensity data, atomic coordinates, distances and angles, thermal displacement parameters, and hydrogen bond distances for **5**, **6**, and **7**. ^{1}H and ^{19}F NMR data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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