Organometallics **2001,** *20,* 2565−2569

Synthesis, Solution Dynamics, and X-ray Crystal Structure of Bis(2,4,6-tris(trifluoromethyl)phenyl)(1,2-dimethoxyethane)nickel

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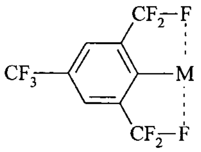
Received January 31, 2001

Reaction of dichloro(1,2-dimethoxyethane)nickel with 2 equiv of (tris(2,4,6-trifluoromethyl)phenyl)lithium, generated in situ, produced bis(2,4,6-tris(trifluoromethyl)phenyl)(1,2-dimethoxyethane)nickel. Significant nickel−fluorine interactions are revealed both in the solid state (X-ray crystal structure data) and in solution (variable-temperature ^{19}F NMR spectral data).

Introduction

The activation of halocarbons, in particular fluorocarbons, by metals has become increasingly of interest over the past decade.[4] A prelude to activation is thought to be, in many cases, coordination of the halocarbon to the metal center. A review of the coordination chemistry of fluorocarbons has been published recently.[5]

Complexes containing electron-withdrawing aryl ligands (i.e., those that are highly substituted with halogens) are known for many of the late transition metals, especially group 10. One subset of these types of ligands, 2,4,6-tris(trifluoromethyl)phenyl, is thought to exhibit an ideal combination of electronic and steric characteristics, since it can withdraw electrons from the metal inductively but can donate electron density to the metal from the fluorine atoms of the *o*-CF_3 substituents on the aryl ligand.[6]



A nickel complex has been synthesized and characterized as the homoleptic bis(2,4,6-tris(trifluoromethyl)phenyl)nickel.[7] This complex is noteworthy, since homoleptic diaryl derivatives of nickel are normally stable only in the presence of donor ligands. Given the apparent coordinative unsaturation of this complex (a formal 12-electron complex), one might expect electron donation from the fluorines of the *o*-trifluoromethyl substituents on the aryl ring. We report herein the synthesis, solution dynamics, and X-ray crystal structure of the bis(2,4,6-tris(trifluoromethyl)phenyl)nickel fragment containing the donor ligand 1,2-dimethoxyethane. This compound does exhibit significant interactions between the fluorines of the *o*-trifluoromethyl substituents and the nickel center despite being formally a 16-electron complex.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of prepurified nitrogen using standard Schlenk or drybox techniques. Solvents were dried and degassed with prepurified nitrogen. The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer operating at 500.14 and 470.53 MHz, respectively. Chemical shifts for ^{1}H NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. The ^{19}F NMR spectra were referenced to external $CFCl_3$. The mass spectra were recorded on a Finnigan MAT 95Q mass spectrometer. Elemental analysis was carried out by Robertson Microlit Laboratories, Madison, NJ.

Tris(trifluoromethyl)benzene was purchased from Aldrich and used as received. Dichloro(1,2-dimethoxyethane)nickel was obtained from Strem Chemicals and used without further purification.

Synthesis of Bis(2,4,6-tris(trifluoromethyl)phenyl)(1,2-dimethoxyethane)nickel (1). 1,3,5-Tris(trifluoromethyl)benzene (1.65 mL, 8.86 mmol) was dissolved in 20 mL of hexane and 20 mL of ether. The solution was cooled to −78 °C, and *n*-BuLi (5.80 mL of a 1.60 M solution in hexane, 9.28 mmol) was added. A yellow color developed. The solution was removed from the cooling bath and warmed to room temperature over 1 h. This solution was then transferred by cannula

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10.1021/om0100784 CCC: $20.00 © 2001 American Chemical Society
Publication on Web 05/09/2001

to a suspension of dichloro(1,2-dimethoxyethane)nickel (0.973 g, 4.43 mmol) in 20 mL of hexane and 20 mL of ether which had been cooled to −78 °C. No immediate change was noted. The mixture was warmed to room temperature. A brown color developed over time. Volatiles were removed under vacuum after 3 h. The resulting solid was extracted with 40 mL of toluene. The extract was filtered through Celite filtering aid to give a red solution. Hexane was added to the solution, resulting in the precipitation of purple microcrystals. The crystals were filtered and washed with hexane three times: yield 0.26 g (8%); mp 180−185 °C dec. Attempts to improve the yield by carrying out the reaction in the presence of 1,2-dimethoxyethane or THF were unsuccessful. ^{1}H NMR (C_6D_6): δ 7.75 (s, 2H), 2.17 (br s, 4H), 2.07 (s, 6H). ^{19}F NMR (C_6D_6): δ −58.2 (v br s, 6F), −63.2 (s, 3F). IR (Nujol): 1618 m, 1567 m, 1277 s, 1188 s, 1124 s, 1048 m, 1017 m, 912 s, 870 s, 831 s cm^{-1}. FI-MS: m/z 710 [M$^+$]. Anal. Found for $C_{22}H_{14}F_{18}O_2Ni$: C, 37.10; H, 1.90. Calcd: C, 37.16; H, 1.97.

X-ray Crystallographic study of 1. Crystal data for single crystals of bis(2,4,6-(tris(trifluoromethyl)phenyl)(1,2-dimethoxyethane)nickel (**1**), at 20.1 °C: monoclinic, space group $P2_1/n$ (an alternate setting of $P2_1/c$-C_{2h}^5 (No. 14)) with $a = 12.167(3)$ Å, $b = 16.373(4)$ Å, $c = 12.991(3)$ Å, $\beta = 91.18(2)°$, $V = 2587.4(11)$ Å^3, and $Z = 4$ ($d_{calcd} = 1.825$ g cm^{-3}; μ_a(Cu Kα) = 2.523 mm^{-1}). A total of 4035 reflections having 2θ(Cu Kα) < 120.3° (the equivalent of a 0.65 limiting Cu Kα sphere) were collected on a computer-controlled Nicolet autodiffractometer using 2.00° wide $\theta-2\theta$ scans and Ni-filtered Cu Kα radiation; 3849 of these reflections were unique. The Bruker SHELXTL-PC (version 5.0) software package was used to solve and refine the structure. "Direct methods" techniques were used to solve the structure, and the resulting structural parameters have been refined with F^2 data to convergence using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Final agreement factors are as follows: R1(unweighted, based on F) = 0.078 for 2032 independent absorption-corrected reflections having 2θ (Cu Kα) < 120.3° and $I > 2\sigma(I)$; R1(unweighted, based on F) = 0.131 and wR2-(weighted, based on F^2) = 0.215 for all 3849 independent absorption-corrected reflections having 2θ(Cu Kα) < 120.3°. A summary of crystallographic data can be found in Table 1.

Non-methyl hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2 or sp^3 hybridization of the carbon atoms and C−H bond lengths of 0.93−0.97 Å) "riding" on their respective carbon atoms. The two methyl groups (C_1, C_4, and their hydrogens) were refined as rigid rotors (using idealized sp^3-hybridized geometry and a C−H bond length of 0.96 Å) which were allowed to rotate about their C−C bonds in least-squares cycles. The isotropic thermal parameters of all hydrogen atoms were fixed at values 1.2 (non-methyl) or 1.5 times (methyl) the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded.

Two of the CF_3 groups (C_{18} and C_{28}) are disordered, with two alternate orientations about the C−C bond. Both have major orientations which are occupied 53% and 77% of the time, respectively, and minor orientations which are occupied 47% and 23% of the time, respectively. The major (53%) orientation for C_{18} is specified by fluorine atoms F_{181}, F_{182}, and F_{183}, and the major (77%) orientation for C_{28} is specified by fluorine atoms F_{281}, F_{282}, and F_{283}. The minor (47%) orientation for C_{18} is specified by fluorine atoms F_{184}, F_{185}, and F_{186}, and the minor (23%) orientation for C_{28} is specified by fluorine atoms F_{284}, F_{285}, and F_{286}.

Selected bond lengths and angles can be found in Table 2. Listings of anisotropic thermal parameters, atomic coordinates, and all bond lengths and angles can be found in the Supporting Information.

Table 1. Summary of Crystallographic Data for 1

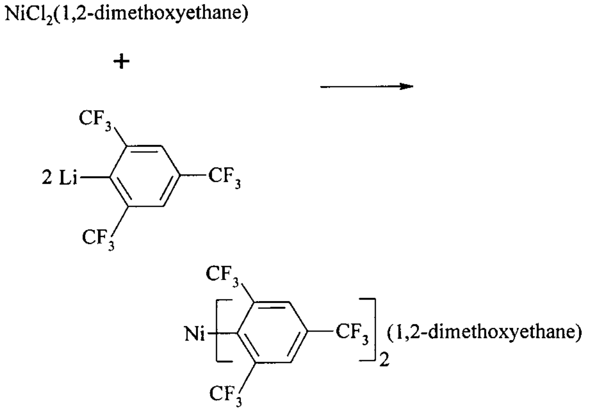
chem formula	$NiC_{22}H_{14}F_{18}O_2$
fw	711.04
temp	293(2) K
wavelength	1.541 84 Å
crystal syst	monoclinic
space group	$P2_1/n$
a	12.167(3) Å
b	16.373(4) Å
c	12.991(3) Å
α	90.00°
β	91.18(2)°
γ	90.00°
V, Å^3	2587.4(11) Å^3
Z	4
D_{calcd}	1.825 g cm^{-3}
abs coeff	2.523 mm^{-1}
F(000)	1408
cryst size	0.40 × 0.25 × 0.20 mm
θ range for collection	4.35−60.14°
limiting indices	$-13 \le h \le 13$, $0 \le k \le 18$, $0 \le l \le 14$
no. of rflns collected	4035
no. of indep rflns	3849 ($R_{int} = 0.0569$)
abs cor	integration
refinement method	full-matrix least squares on F^2
max and min transmissn	0.6641 and 0.4254
no. of data/restraints/params	3849/0/453
goodness of fit on F^2	0.957
final R indices ($I > 2\sigma(I)$)	R1 = 0.0778, wR2 = 0.1870
R indices (all data)	R1 = 0.1307, wR2 = 0.2153
extinction coeff	0.0017(3)
largest diff peak and hole	0.518 and −0.693 e Å^{-3}

Table 2. Selected Bond Distances and Angles in 1

type	distance (Å) or angle (deg)	type	distance (Å) or angle (deg)
Ni−O_1	2.013(6)	O_1−Ni−C_{11}	92.8(3)
Ni−O_2	2.017(6)	C_{11}−Ni−C_{21}	97.2(3)
Ni−C_{11}	1.873(8)	O_2−Ni−C_{21}	92.8(3)
Ni−C_{21}	1.886(6)	O_2−Ni−C_{11}	163.0(3)
Ni···F_{191}	2.592(5)	O_1−Ni−C_{21}	163.7(3)
Ni···F_{291}	2.595(5)	F_{191}···Ni···F_{291}	152.3(2)
O_1−Ni−O_2	80.7(3)		

Results and Discussion

Synthesis and Characterization. We chose dichloro(1,2-dimethoxyethane)nickel as the starting material (Edelmann used $NiCl_2$) for the reaction with (tris(2,4,6-trifluoromethyl)phenyl)lithium generated in situ (see eq 1). After appropriate workup, a low yield of a purple, microcrystalline compound was obtained. The complex exhibited a rather simple ^{1}H NMR spectral signature at room temperature. One peak is observed at 7.75 ppm due to equivalent protons at the 3- and 5-positions on



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(1)

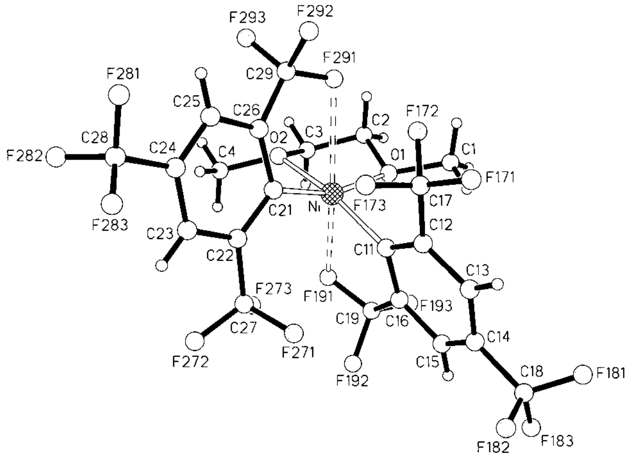

Figure 1. Perspective drawing of **1**.

the aryl ring. Edelmann reports a similar peak at 7.65 ppm for the brown nickel bis(tris(2,4,6-trifluoromethyl)-phenyl)nickel complex in the same solvent. However, the purple complex isolated herein exhibits additional peaks, one sharp at 2.07 ppm and one broad at 2.17 ppm, in the ^1H NMR spectrum. The position and intensity of these peaks are in agreement with the methyl and methylene protons, respectively, for a 1,2-dimethoxyethane adduct of bis(tris(2,4,6-trifluoromethyl)phenyl)nickel. Indeed, analytical data (both elemental and MS) support the formulation of the purple complex as bis(2,4,6-tris(trifluoromethyl)phenyl)(1,2-dimethoxyethane)nickel (**1**).

Two peaks are observed in the ^{19}F NMR spectrum of **1** at room temperature. The intensities observed are in agreement with two equivalent *o*-CF_3 (−58.2 ppm) and one *p*-CF_3 (−63.2 ppm) substituent on the aryl ring. However, the *o*-CF_3 resonance is extremely broad (ca. 800 Hz at half-height) and the *p*-CF_3 resonance is very sharp, indicating some sort of dynamic behavior (see below).

X-ray Crystal Structure. Crystals of **1** were grown from cold toluene solution. The results of the crystallographic study are given in Figure 1, which shows a perspective drawing of **1**. A listing of selected bond distances and angles for **1** can be found in Table 2.

The oxygens of the complexed 1,2-dimethoxyethane and the *ipso* carbons of the tris(2,4,6-trifluoromethyl)-phenyl ligands form the inner coordination sphere of **1**. The geometry around nickel in **1** can be described as distorted square planar. The sum of the four "square" bond angles around Ni is 3.5° larger than the idealized value of 360°. The "square" is S_4-ruffled with displacements of 0.23−0.25 Å from the five-atom mean plane for the Ni and coordinated oxygen and carbon atoms. As can be seen from Figure 1, however, the *ipso* carbons of the aryl ligands, C_{11} and C_{21}, reside above and below (0.51 and 0.49 Å, respectively) the plane defined by the Ni and two oxygens of the 1,2-dimethoxyethane ligand. A similar distorted-square-planar geometry has been reported for the homologous complex bis(2,4,6-tris-(trifluoromethyl)phenyl)(2,2′-bipyridine)palladium.[8]

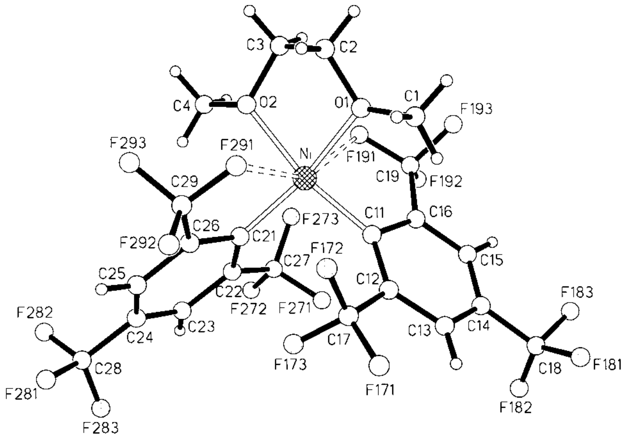

Figure 2. Perspective drawing of **1** along the F191···Ni···F291 axis.

The Ni−O distances of 2.013(6) and 2.017(6) Å in **1** are identical within experimental error, as are the Ni−C distances of 1.873(6) and 1.886(6) Å. Cis coordination of two *σ*-bonded aryl ligands which each contain a pair of *o*-CF_3 substituents introduces steric congestion above and below the "square" NiO_2C_2 coordination plane. Nonbonded repulsions between a given pair of these *o*-CF_3 groups on the same side of the "square" are minimized by tilting the Ni−C bonds for the two phenyl rings in opposite directions perpendicular to the "square". This motion allows one *o*-CF_3 group from each aryl ligand to move to an "axial" octahedral coordination site of the Ni and leaves two fluorines of the remaining *o*-CF_3 group on that side of the "square" in close contact with the cis aryl ligand. Even with this movement, several interligand nonbonded F···C and F···F contacts have values less than or equal to the sum of the appropriate van der Waals radii (2.94 Å for F···F and 3.17 Å for C···F[9]): $F_{172}\cdots F_{291}$, 2.68 Å; $F_{172}\cdots C_{29}$, 3.16 Å; $F_{173}\cdots C_{21}$, 2.92 Å; $F_{173}\cdots C_{26}$, 3.01 Å; $F_{271}\cdots C_{11}$, 2.93 Å; $F_{271}\cdots C_{16}$, 3.08 Å; $F_{273}\cdots F_{191}$, 2.60 Å; $F_{273}\cdots C_{19}$, 3.09 Å. The observed arrangement for the two *cis*-bonded tris(2,4,6-trifluoromethyl)phenyl ligands therefore represents one of two preferred conformations for this portion of the molecule; the other is related to the observed one by a C_2 axis passing through the Ni atom and the midpoint of the $C_{11}\rightarrow C_{21}$ vector. In some ways, the cis-bonded bis(aryl) unit in **1** can therefore be viewed as a tetradentate ligand with rigid planar halves whose relative orientations are determined by nonbonded contacts between these halves. More specifically, these nonbonded contacts determine the relative orientations of the four atoms interacting directly with the metal. This, in turn, determines the extent to which the geometrical requirements of square-planar and/or octahedral coordination can be satisfied. These interligand nonbonded contacts therefore determine the extent to which C_{11} and C_{12} can be coplanar with the Ni, O_1, and O_2 atoms. The "bite" of the "chelating" ligands defined by $C_{11}\rightarrow F_{191}$ and $C_{21}\rightarrow F_{291}$ then determine how close the interacting fluorines can approach idealized "axial" octahedral sites once the carbons are bonded to Ni. The steric constraints of this cis-aryl grouping in **1** causes the interacting *o*-CF_3 group for each aryl ligand to move slightly (approximately 0.6 Å) off its idealized trans octahedral site to a position above or below the coordinated 1,2-dimethoxyethane ligand; this reduces the $F_{191}\cdots Ni\cdots F_{291}$

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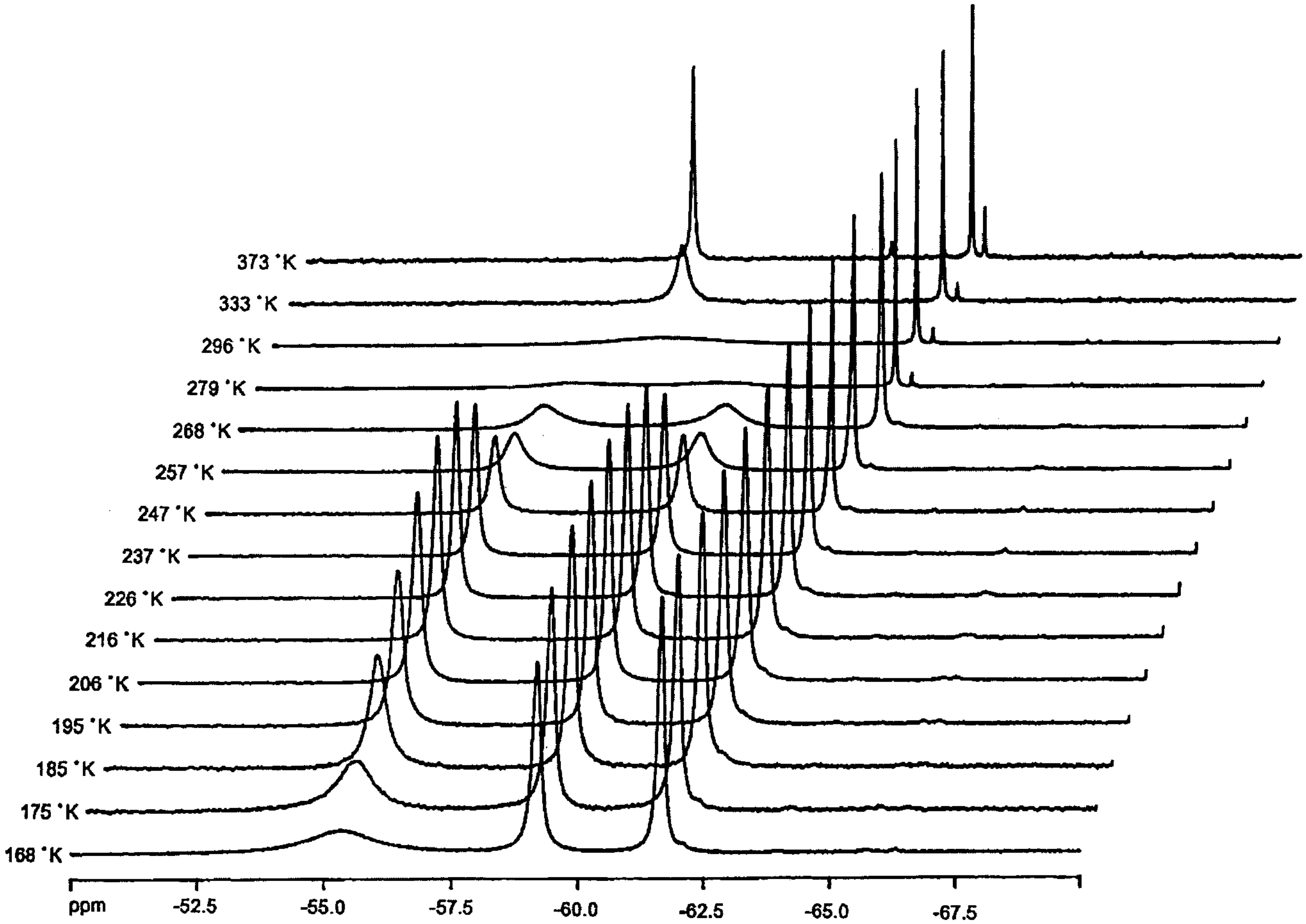

Figure 3. Stacked plot of variable-temperature ^{19}F NMR spectra of **1** in toluene-d_8.

angle from 180° to 152.3(2)°. The aryl ligands are also rotated by approximately 25° about their Ni−C bonds from an orientation perpendicular to the "square". Figure 2 shows these effects clearly. In contrast to the *o*-CF_3 groups, the *p*-CF_3 groups of both aryl ligands are not sterically locked into a specific conformation and are rotationally disordered about their C−C bonds.

While the two "axial" Ni−F interactions, with nearly identical lengths of 2.592(5) and 2.595(5) Å, are nonbonding (the sum of the covalent radii for Ni and F is 1.87 Å[10]), they are considerably shorter than the 3.10 Å[11] sum of the respective van der Waals radii for Ni and F. These separations are therefore consistent with a significant interaction between Ni and F. Similar close contacts between metal and fluorine have been documented for the palladium bipyridine complex cited above and in (2,4,6-tris(trifluoromethyl)phenyl)lithium, -tin, -lead, -vanadium, and -zinc complexes.[12]

The inclusion of fluorine from two *o*-CF_3 substituents on different aryl ligands in the coordination sphere of nickel serves to reduce the symmetry of **1** from an approximate C_{2v} to C_2. The consequence of this reduction in symmetry is observed in the solution structure of **1** at low temperatures, as monitored by ^{19}F NMR (see below).

Solution Dynamics. Variable-temperature ^{19}F NMR spectra were recorded for **1** from 168 to 373 K (see Figure 3). At the high temperature limit, two relatively sharp peaks in a 2:1 ratio are observed due to two equivalent *o*-CF_3 (ca. -57.1 ppm) and one *p*-CF_3 group (*ca.* -61.5 ppm), respectively. As the sample is cooled, the *o*-CF_3 resonance broadens considerably. Coalescence occurs at about 280 K. Below this temperature, this peak splits into two resonances at about −55.2 and −59.0 ppm. As the sample is cooled further, the most downfield resonance begins to broaden further while the peak at −59.0 ppm remains sharp. The *p*-CF_3 peak remains relatively sharp throughout the explored temperature regime.

The low-temperature solution NMR spectra are consistent with the X-ray crystal structure results. In this region of slow exchange, three distinct CF_3 groups per aryl ligand are observed. They are the *o*-CF_3 group that interacts with the Ni center, the noninteracting *o*-CF_3 group, and the *p*-CF_3 group. As the temperature is raised, the two *o*-CF_3 groups participate in a two-site exchange process that makes all four *o*-CF_3 groups equivalent. A simple fluxional process that is consistent with this behavior is a "windshield wiper" motion in which the two *o*-CF_3 substituents that are in close contact with nickel are replaced by the remaining two

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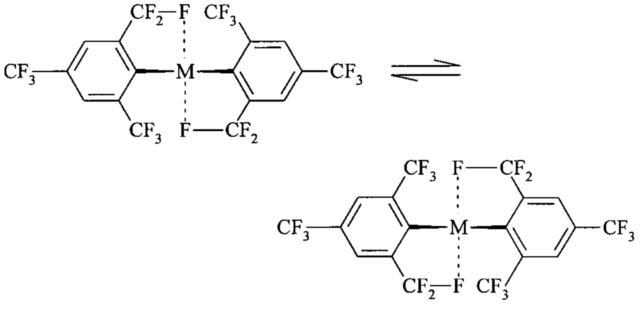
o-CF_3 groups. The energy of activation ($\Delta G^{\ddagger}$) for this process was determined to be 12.5 kcal/mol by line-shape analysis.[13] Related processes involving intramolecular exchange of fluorinated aryl ligands in early transition metals exhibit similar activation energies.[14] Interestingly, the analagous fluxional process could not be frozen out in the related palladium complex bis(2,4,6-tris(trifluoromethyl)phenyl)(2,2′-bipyridine)palladium, even at 183 K.[15]



M = Ni(1,2-dimethoxyethane)

Below 195 K, the −55.2 ppm resonance, due to the *o*-CF_3 substituent interacting with Ni in **1,** experiences significant broadening independent of the other two resonances. Unfortunately, this exchange process could not be explored further, due to temperature limitations of the solvent used (d_8-toluene). However, it is likely that this broadening is due to slowing of the C(phenyl)−C(trifluoromethyl) bond rotation of the *o*-CF_3 groups interacting with the metal. This interpretation of the observed broadening allows us to make the following assignments of the downfield resonances: the peak at −55.2 ppm is due to the *o*-CF_3 group interacting with the metal, and the peak at −59.0 ppm is due to the "free" *o*-CF_3 substituent. A downfield chemical shift in the ^{19}F NMR spectrum due to interaction of a fluorocarbon residue with a metal is common and has become a diagnostic test for such complexes.[16]

Acknowledgment. This research was supported by the Advanced Technology Program of the NIST (ATP Project 95-05-0038) and the BFGoodrich Pacing Research Fund. We thank Dr. R. Lattimer for recording the FD-MS of **1** and Prof. Juan Forniés for insightful comments.

Supporting Information Available: Listings of atomic coordinates, anisotropic thermal parameters, and all bond lengths and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0100784

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(15) See ref 8.

(16) A more complete listing of examples in which ^{19}F NMR has been used for determining or confirming the presence of significant fluorocarbon−metal interaction can be found in the reviews in refs 4 and 5.