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Hydroxo and Azolate Derivatives of Pentafluorophenyl–Nickel(II) Complexes. Crystal Structure of $[NBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$ and $[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-pyrazolato})]$

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Arylation of $NiBr_2 \cdot 2dme$ (dme = 1,2-dimethoxyethane) with $MgBr(C_6F_5)$ in tetrahydrofuran–dioxane and further addition of benzonitrile leads to the formation of the square-planar complex *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$. Interaction of this labile complex with aqueous QOH (Q = NBu_4) in acetone produces the hydroxo-bridged dimer $Q_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$, which has been characterized by X-ray crystallography. It is monoclinic, space group $P2_1/c$, with cell dimensions a = 12.2964 (3) Å, b = 12.9768 (3) Å, c = 19.467 (1) Å, β = 104.277 (2)°, and Z = 2. The structure consists of centrosymmetric binuclear anions $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$, where the Ni atoms have square-planar coordination, and Q^+ cations. In acetone, the bis(μ-hydroxo) complex reacts with weak acids HL [L = pyrazolate (pz), 3-methylpyrazolate (mpz), 3,5-dimethylpyrazolate (dmpz), indazolate (indz), or triazolate (tz)] to give the corresponding complexes $Q_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}L)]$ and $Q_2[\{Ni(C_6F_5)_2(\mu\text{-}L)\}_2]$ (except for L = 3,5-dimethylpyrazolate), depending on the reactant molar ratio (Ni/HL = 1 or 2, respectively). The crystals of $Q_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]$ are monoclinic, space group $P2_1/c$, with cell dimensions a = 9.9344 (3) Å, b = 13.570 (1) Å, c = 49.622 (5) Å, β = 93.17 (1)°, and Z = 4. The structure consists of binuclear $[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]^{2-}$ anions, with the Ni atoms in a square-planar disposition tetrahedrally distorted, and Q^+ cations. Conductance and spectroscopic (visible, IR, ^1H NMR, and ^{19}F NMR) data for the complexes have been collected.

Introduction

The synthesis and reactivity of late transition-metal hydroxides has been a topic of interest in the last few years owing mainly to their potential utility in organic and organometallic synthesis. It has been recognized[1] that "they represent unique opportunities as catalysts (or precursors) to carry out reactions that would be difficult to effect by other methods".

By far the most common method of preparing hydroxo–organo complexes of the nickel group elements is through metathesis reactions.[1] The same method has also been applied to the preparation of nonorganometallic hydroxo complexes.[2,3] The known hydroxo–organo–nickel complexes are binuclear species of the type $[\{NiLR(\mu\text{-}OH)\}_2]$ [L = PPh_3 (R = $CClCCl_2$)[4] or PMe_3 (R = CH_3,[5] $CH_2C_6H_4$-*o*-Me,[6] CH_2SiMe_3, CH_2CMe_2Ph, or $CH_2C_6H_5$[7])], and the trinuclear $[Ni_3(CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2]$.[6] No anionic binuclear $[\{NiR_2(\mu\text{-}OH)\}_2]^{2-}$ has been reported.

cis-$[Pd(C_6F_5)_2(PhCN)_2]$[8] has proven to be a convenient precursor in synthesis.[8,9] Here we describe the synthesis of the nickel analogue *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$, which has been used to prepare the binuclear species $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$. Moreover, the hydroxo–nickel complex reacts with weak acids (HL) to give new binuclear complexes $[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}L)]^{2-}$ and $[\{Ni(C_6F_5)_2(\mu\text{-}L)\}_2]^{2-}$ (L = azolate ligand). The bis(μ-hydroxo) and the μ-hydroxo–μ-pyrazolate complexes have been completely characterized by an X-ray analysis.

A preliminary report of this work has been given[10] and we have recently reported on the catalytic cyclotrimerization of malononitrile by the bis(μ-hydroxo)nickel complex.[11]

Results

Complexes *cis*-$[Ni(C_6F_5)_2(PhCN)_2)]$ and $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$. In tetrahydrofuran, $NiBr_2 \cdot 2dme$ (dme = 1,2-dimethoxyethane) is arylated by $MgBr(C_6F_5)$, and most of the resulting magnesium bromide is precipitated as $MgBr_2(dioxane)_2$,[12] by addition of dioxane. Addition of benzonitrile to the resulting magnesium-free solution gives the organonitrile derivative *cis*-$[Ni(C_6F_5)_2(PhCN)_2]$. The overall process may be represented as in eq 1.

$$NiBr_2 \cdot 2dme \xrightarrow{1.\ 2MgBr(C_6F_5)\ 2.\ dioxane\ 3.\ PhCN} \underset{\mathbf{1}}{cis\text{-}[Ni(C_6F_5)_2(PhCN)_2]} \quad (1)$$

Table I. Crystallographic Data for Complexes **2** and **3**

	2	**3**
$[NBu_4)_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$	$[NBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$	$[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]$
space group	$P2_1/c$	$P2_1/c$
a, Å	12.2964 (3)	9.9344 (3)
b, Å	12.9768 (3)	13.570 (1)
c, Å	19.467 (1)	49.622 (5)
β, deg	104.277 (2)	93.17 (1)
V, Å^3	3010.4 (1)	6679.3 (9)
Z	2	4
M	1272.60	1394.73
T, °C	23	23
D_c, g cm^{-3}	1.404	1.387
μ, cm^{-1}	16.393	15.455
$R(F)^a$	0.075	0.066
$R_w(F)^b$	0.068	0.060

[a] $R(F) = \sum \Delta F / \sum |F_o|$, $\Delta F = ||F_o| - |F_c||$. [b] $R_w(F) = [\sum w(\Delta F)^2 / \sum w|F_o|^2]^{1/2}$.

The infrared spectrum of complex **1** shows the bands attributed to the C_6F_5 group[13] at ca. 1630 m, 1495 vs, 1460 vs, 1050 vs, 950 vs, and 785 br, s cm^{-1}, as well as the characteristic absorptions

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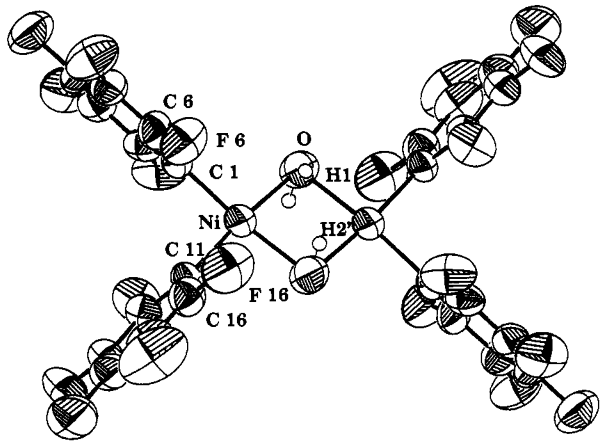

Figure 1. ORTEP drawing[37] of the $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ anion, which also defines the labeling scheme. The thermal ellipsoids enclose 50% of electron density.

of the benzonitrile ligand. A split band located at ca. 2270 cm^{-1} indicates that **1** is the cis isomer and that benzonitrile is end-on coordinated [in free PhCN the $\nu(C{\equiv}N)$ mode is found at 2230 cm^{-1}].[14] This blue shift is similar to those found in the palladium[8] and the platinum[10] analogues. The so-called "X-sensitive" mode[15] of C_6F_5, observed as a broad band at 785 cm^{-1} with a shoulder at 790 cm^{-1}, also supports the cis geometry[16,17] proposed for **1**.

Complexes *cis*-$[PdR_2(PhCN)_2]$ (R = C_6F_5[8,9] or 2,4,6-$C_6F_3H_2$[18]) have been used as starting materials in synthesis. Complex **1** reacts with QOH(aq) in acetone to give the hydroxo-bridged complex **2** in good yield (eq 2). Analytical, conductance, and spectroscopic data for **2** are consistent with the proposed formula. The presence of the OH ligand is manifested by the observation of a split band at 3650 cm^{-1} and a high-field proton resonance at −5.74 ppm, which are similar to those reported for related compounds.[4,7]

$$2\,cis\text{-}[Ni(C_6F_5)_2(PhCN)_2] + 2QOH \rightarrow \underset{\mathbf{2}}{Q_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]} + 4PhCN \quad (2)$$

The dinuclearity of complex **2** has been established by single-crystal X-ray diffraction. The crystallographic data are collected in Table I. It consists of centrosymmetric binuclear $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ anions (a view of this anion is depicted in Figure 1) and Q^+ cations, held together by electrostatic interactions. Positional parameters and bond distances and angles are collected in Tables II and III, respectively. The Ni atoms show a slight deviation from the square-planar coordination toward a tetrahedral arrangement. The two fluorophenyl rings bonded to Ni are planar and rotated 90.0 (2)° to each other. Some of the F atoms are not in the plane formed by the C atoms, the maximum deviation being 0.049 (5) Å for F(6). The Ni–O distances (1.89 (1) and 1.898 (8) Å) and the NiONi and ONiO angles (99.2 (4) and 80.8 (4)° respectively) in complex **2** are similar to those found in the noncentrosymmetric $[\{Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)\}_2]$·pyrrole,[7] but the latter contains a nonplanar Ni_2O_2 ring. However, the concordance is almost perfect when **2** is compared with the centrosymmetric $[\{Ni(bppte)(\mu\text{-}OH)\}_2]^{2+}$ cation (bppte = $PPh_2SCH_2C(Me)(CH_2PPh_2)_2$).[19] On the other hand, the Ni–C_6F_5 distances of 1.867 (8) and 1.883 (6) Å are similar to those found in the chloro-bridged complex $[\{Ni(C_6F_5)_2(\mu\text{-}Cl)\}_2]^{2-}$.[20]

Table II. Atomic Parameters for Compound **2** with Coordinates ×10^4 and Thermal Parameters as $U_{eq} = (1/3)\sum[U_{ij}{\cdot}a_i^*{\cdot}a_j{\cdot}a_i{\cdot}a_j[\cos(a_i,a_j)]] \times 10^3$ Å^2

atom	x	y	z	U_{eq}
Ni	8737 (1)	435 (1)	10037 (1)	82 (0)
O	9967 (6)	502 (6)	9460 (5)	192 (3)
C(1)	7973 (5)	258 (5)	10633 (4)	56 (2)
C(2)	6958 (6)	−260 (6)	10453 (4)	64 (2)
C(3)	6659 (4)	−713 (4)	9802 (2)	97 (2)
C(4)	6240 (6)	−387 (6)	10878 (4)	69 (2)
C(5)	5281 (4)	−930 (4)	10656 (3)	108 (2)
C(6)	6472 (7)	58 (6)	11522 (4)	69 (2)
F(2)	5768 (4)	−50 (4)	11952 (2)	105 (2)
F(3)	7471 (7)	575 (6)	11747 (4)	67 (2)
F(4)	7721 (5)	991 (4)	12407 (2)	110 (2)
F(5)	8158 (6)	665 (6)	11311 (4)	63 (2)
F(6)	9138 (4)	1176 (4)	11584 (2)	99 (1)
C(11)	7978 (5)	1440 (5)	9509 (4)	52 (2)
C(12)	7949 (5)	2438 (6)	9719 (4)	56 (2)
C(13)	8608 (4)	2730 (3)	10366 (2)	86 (1)
C(14)	7341 (7)	3208 (6)	9345 (5)	68 (2)
C(15)	7378 (5)	4193 (4)	9588 (3)	112 (2)
C(16)	6675 (7)	2998 (8)	8700 (5)	81 (3)
F(12)	6038 (4)	3757 (5)	8311 (3)	132 (2)
F(13)	6636 (7)	2028 (10)	8460 (4)	83 (3)
F(14)	5952 (5)	1808 (6)	7813 (3)	154 (3)
F(15)	7270 (7)	1281 (7)	8846 (4)	70 (2)
F(16)	7201 (5)	316 (4)	8558 (3)	123 (2)
N	7736 (4)	−2118 (4)	13456 (3)	58 (2)
C(31)	8411 (7)	−1364 (6)	13133 (5)	64 (2)
C(32)	9525 (7)	−1760 (8)	13045 (5)	74 (3)
C(33)	0018 (9)	−1046 (9)	12602 (6)	89 (3)
C(34)	1133 (10)	−1380 (11)	12506 (9)	120 (4)
C(41)	7485 (7)	−3103 (6)	13009 (4)	64 (2)
C(42)	6954 (10)	−2913 (8)	12234 (5)	89 (3)
C(43)	6798 (13)	−3896 (10)	11831 (6)	108 (4)
C(44)	6310 (8)	−3752 (8)	11039 (5)	115 (3)
C(51)	8396 (6)	−2464 (5)	14198 (4)	63 (2)
C(52)	8704 (7)	−1598 (7)	14728 (4)	86 (3)
C(53)	9185 (7)	−2027 (8)	15472 (5)	97 (3)
C(54)	9643 (15)	−1150 (14)	15984 (7)	140 (6)
C(61)	6651 (6)	−1589 (6)	13489 (4)	62 (2)
C(62)	5855 (8)	−2170 (7)	13811 (6)	77 (3)
C(63)	4923 (8)	−1488 (8)	13920 (6)	83 (3)
C(64)	4037 (10)	−2044 (11)	14196 (8)	110 (4)

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for the Anion of Compound **2**

	Bond Lengths		
Ni–O	1.89 (1)	Ni–C(11)	1.883 (6)
Ni–C(1)	1.867 (8)	Ni–O′	1.898 (8)
	Bond Angles		
O–Ni–C(1)	157.0 (3)	O′–Ni–C(1)	94.5 (3)
O–Ni–C(11)	93.8 (3)	O′–Ni–C(11)	173.8 (3)
O–Ni–O′	80.8 (14)	C(1)–Ni–C(11)	90.9 (3)
Ni–O–Ni′	99.2 (4)		

[a] Symmetry code for a primed atom: $-x + 2, -y, -z + 2$.

Azolate-Bridged Complexes. Binuclear metal azolate complexes have attracted considerable interest in recent years.[21] The high-field proton resonance (δ −5.74) of the OH bridges in complex **2** suggests that it should be prone to react with weak protic acids such as azoles (HL). Similar reactions have been successfully carried out with $[(C_5Me_5)M(\mu\text{-}OH)_3M(C_5Me_5)]^+$ (M = Rh or Ir)[22] and $[\{Pd(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$.[23] In acetone, **2** reacts with HL [pyrazole (Hpz), 3-methylpyrazole (Hmpz), 3,5-dimethylpyrazole (Hdmpz), indazole (Hindz), or triazole (Htz)] to give the cor-

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responding μ-OH-μ-L (**3**-**7**) and (μ-L)$_2$ (**8**-**11**) complexes, depending on the mole ratio of reactants (eq 3). However, dmpz

$$[(C_6F_5)_2Ni(\mu\text{-}OH)_2Ni(C_6F_5)_2]^{2-} \xrightarrow[-H_2O]{+HL} [(C_6F_5)_2Ni(\mu\text{-}OH)(\mu\text{-}L)Ni(C_6F_5)_2]^{2-}$$

L = pz (**3**), mpz (**4**), dmpz (**5**), indz (**6**), tz (**7**)

$$[(C_6F_5)_2Ni(\mu\text{-}OH)(\mu\text{-}L)Ni(C_6F_5)_2]^{2-} \xrightarrow[-H_2O]{+HL} [(C_6F_5)_2Ni(\mu\text{-}L)_2Ni(C_6F_5)_2]^{2-} \quad (3)$$

L = pz (**8**), mpz (**9**), indz (**10**), tz (**11**)

forms the μ-OH-μ-dmpz complex but not the (μ-dmpz)$_2$ one, which may be attributed to the larger steric requirement of the dmpz ligand.[22a]

The conductance data of the acetone solutions of complexes **3**-**7** are consistent[24] with the proposed formulas, and the ^{1}H NMR patterns displayed by the coordinated azolate ligands are in accordance with those found in similar complexes.[22,25] The presence of the OH group in complexes **3**-**7** is demonstrated by the ^{1}H resonance observed at ca. −4.2 ppm (compare with δ −5.75 for **2**), as well as the ν(OH) band observed at 3630-3620 cm^{-1} in the infrared spectra. Complexes **3**, **4**, **6**, and **7** contain two (**3**, **7**) or four (**4**, **6**) nonequivalent C_6F_5 groups, and accordingly their ^{19}F NMR spectra show multiplets in the *o*-fluorine region due to overlapping of the signals from every C_6F_5 group.

The ^{1}H and ^{19}F NMR data of complex **11** are consistent with the presence of two equivalent tz groups and four equivalent C_6F_5 groups, and its conductance indicates that in acetone solution this complex behaves as a 2:1 electrolyte. The ^{19}F spectra of complexes **8**-**10** show that they dissociate in acetone solution. So complex **8** gives two 1:1 signals in the *o*-fluorine region, which may be attributed to the dissociation product $[Ni(C_6F_5)_2(pz)(acetone)]^-$. The pz ligand gives only two resonance signals in the ^{1}H spectrum, which are inconsistent with the presence of monodentate pz. This result suggests the existence of fast (in the ^{1}H NMR time scale) pz exchange, but the ^{1}H and ^{19}F spectra of **8** remained unchanged between −70 and +25 °C. The existence of azolate exchange processes in palladium complexes containing the asymmetric ligand mpz has recently been reported.[23] Similarly, dissociation of complexes **9** and **10** cannot be inferred from their ^{1}H NMR spectra, but the ^{19}F spectra indicate that dissociation takes place. Thus the ^{19}F spectra from a recently prepared acetone solution of complex **10** consist (*o*-fluorine region only) of one set of resonance signals at δ −109.0 (s, br), −110.6 (s, br), and −115.2 (m) (within the set the relative intensities are 1:1:2, respectively), which may be assigned to the equimolecular mixture $[(C_6F_5)_2(acetone)Ni(N^1\text{-}N^2)]^-$ + $[(C_6F_5)_2(acetone)Ni(N^2\text{-}N^1)]^-$ (N^1-N^2 stands for the asymmetric indz ligand) resulting from the dissociation of **10**, and a multiplet at δ −113.6, probably due to **10**, for which two structures are also possible, the asymmetric $[(C_6F_5)_2Ni(N^1\text{-}N^2)_2Ni(C_6F_5)_2]^{2-}$ and the symmetric $[(C_6F_5)_2Ni(N^1\text{-}N^2)(N^2\text{-}N^1)Ni(C_6F_5)_2]^{2-}$, but the binuclear single-bridged complex $[(C_6F_5)_2(acetone)Ni(N^1\text{-}N^2)Ni(acetone)(C_6F_5)_2]^-$ cannot be ruled out. Although the 1:1 mixture is initially found, after ca. 1 h from the preparation of the acetone solution, the dissociation is complete and the spectrum exhibits only the former group of signals attributed to $[Ni(C_6F_5)_2(indz)(acetone)]^-$. The behavior of complex **9** is similar and signals at δ −108.8 (s, br), −109.7 (s, br), and −115.2 (m) with relative intensities 1:1:2 are assigned to the final dissociation product (ca. 1 h) $[Ni(C_6F_5)_2(mpz)(acetone)]^-$, but additional resonances (partly overlapping the δ −115.2 multiplet) observed in the spectra of very recently prepared solutions indicate that there is again slow dissociation.

Complexes **1**-**7** and **11** give an absorption maximum located at 21 800-24 400 cm^{-1} in the visible spectra, which is attributed to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition of nickel(II) in a square-planar field.[26]

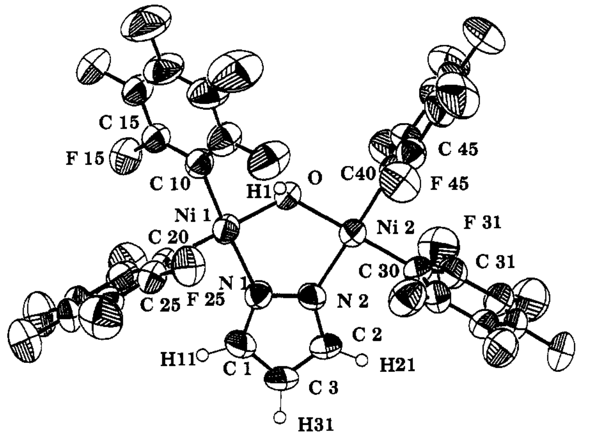

Figure 2. ORTEP diagram[37] and atom-labeling scheme for the $[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]^{2-}$ anion.

Binuclear species involving bis(μ-pyrazolate) bridges usually exhibit a boat conformation for the M(NN)$_2$M six-membered central ring. However, for complexes of the type M(μ-X)(μ-pz)M a similar puckered central ring should not be anticipated. For example, the central five-membered ring in $[\{PtCl(C_2H_4)\}_2(\mu\text{-}Cl)(\mu\text{-}pz)]$ is planar (within 0.09 (1) Å).[27] For this reason, the molecular structure of **3** was determined by X-ray analysis. Atomic coordinates and thermal parameters for compound **3** are given in Table IV and bond lengths and angles in Table V. The structure consists of binuclear $[\{Ni(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}pz)]^{2-}$ anions (Figure 2) joining Q$^+$ cations by electrostatic interactions and benzene molecules of crystallization. The two Ni atoms are bridged by one hydroxo group, Ni(1)-O = 1.892 (4) Å and Ni(2)-O = 1.890 (4) Å (angle Ni(1)-O-Ni(2) = 119.3(2)°), and one pyrazolate group, Ni(1)-N(1) = 1.916(5) Å and Ni(2)-N(2) = 1.896(5) Å. The five-membered ring containing the Ni atoms has an approximate envelope conformation with the O atom at the flap (0.539 (4) Å out of the plane defined by Ni and N atoms). The atomic distribution around Ni is square planar slightly distorted towards a tetrahedral arrangement, the deviations from plane being 0.007 (1), 0.091 (4), −0.092 (6), 0.087 (6), and −0.093 (5) Å for Ni(2), O, C(10), C(20), and N(1), respectively, and 0.008 (1), 0.014 (4), 0.013 (6), −0.018 (5), and −0.018 (7) Å for Ni(2), O, C(30), N(2), and C(40), respectively.

Discussion

Although anhydrous NiBr$_2$ was previously used as the starting material in an arylation reaction similar to that of eq 1,[28] the dme adduct has been the preferred reactant in this work because of its higher reactivity,[29] and the arylation occurs smoothly at ambient temperature. In principle the formation of **1** could proceed by the two reaction pathways a and b. In pathway a, the benzonitrile

pathway a

$$NiBr_2{\cdot}2dme + 2MgBr(C_6F_5) + 6diox \rightarrow [Ni(C_6F_5)_2(diox)_2] + 2MgBr_2(diox)_2\downarrow + 2dme$$

$$[Ni(C_6F_5)_2(diox)_2] + 2PhCN \rightarrow [Ni(C_6F_5)_2(PhCN)_2] + 2diox$$

pathway b

$$2NiBr_2{\cdot}2dme + 4MgBr(C_6F_5) + 6diox \rightarrow 3MgBr_2(diox)_2\downarrow + Mg^{2+} + [\{Ni(C_6F_5)_2(\mu\text{-}Br)\}_2]^{2-} + 4dme$$

$$[\{Ni(C_6F_5)_2(\mu\text{-}Br)\}_2]^{2-} + Mg^{2+} + 4PhCN + 2diox \rightarrow 2[Ni(C_6F_5)_2(PhCN)_2] + MgBr_2(diox)_2\downarrow$$

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Table IV. Atomic Parameters for Compound **3** with Coordinates $\times 10^4$ and Thermal Parameters as $U_{eq} = (1/3)\sum[U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j[\cos(a_i,a_j)]] \times 10^3$ Å^2

atom	x	y	z	U_{eq}	atom	x	y	z	U_{eq}
Ni(1)	930 (1)	884 (1)	6019 (0)	57 (0)	C(42)	−1925 (10)	−155 (6)	7081 (2)	86 (3)
Ni(2)	505 (1)	−881 (1)	6453 (0)	57 (0)	C(43)	−3079 (9)	−665 (8)	7026 (2)	96 (3)
O	−238 (4)	68 (3)	6209 (1)	61 (1)	F(43)	−4095 (5)	−591 (4)	7201 (1)	140 (2)
N(1)	2179 (5)	−192 (4)	6047 (1)	55 (1)	C(44)	−3238 (8)	−1216 (6)	6800 (2)	85 (3)
C(1)	3351 (7)	−367 (6)	5937 (2)	69 (2)	F(44)	−4385 (4)	−1718 (4)	6747 (1)	124 (2)
C(2)	3045 (7)	−1546 (5)	6219 (1)	71 (2)	C(45)	−2199 (7)	−1266 (5)	6632 (2)	71 (2)
C(3)	3928 (8)	−1210 (6)	6037 (2)	78 (2)	F(45)	−2412 (4)	−1808 (3)	6404 (1)	95 (1)
N(2)	1982 (5)	−935 (4)	6227 (1)	57 (1)	N(3)	6846 (5)	−2463 (4)	7951 (1)	75 (2)
C(10)	−267 (6)	1975 (5)	6032 (1)	60 (2)	C(50)	6653 (8)	−3152 (7)	8183 (2)	79 (2)
C(11)	−984 (7)	2412 (6)	5818 (2)	74 (2)	C(51)	5212 (9)	−3332 (7)	8247 (2)	97 (3)
F(11)	−872 (4)	2069 (3)	5564 (1)	95 (1)	C(52)	5131 (10)	−4077 (8)	8469 (2)	100 (3)
C(12)	−1820 (8)	3223 (7)	5844 (2)	88 (3)	C(53)	3790 (13)	−3999 (12)	8603 (3)	128 (4)
F(12)	−2468 (5)	3610 (4)	5621 (1)	134 (2)	C(60)	6057 (10)	−1512 (7)	7986 (2)	87 (3)
C(13)	−1950 (8)	3632 (6)	6084 (2)	97 (3)	C(61)	6350 (11)	−934 (8)	8246 (2)	99 (3)
F(13)	−2754 (5)	4435 (4)	6109 (1)	148 (2)	C(62)	5275 (15)	−143 (9)	8272 (3)	133 (5)
C(14)	−1294 (8)	3245 (6)	6306 (2)	96 (2)	C(63)	5489 (17)	479 (10)	8515 (3)	165 (5)
F(14)	−1430 (6)	3638 (4)	6551 (1)	158 (2)	C(70)	6338 (10)	−2907 (8)	7681 (2)	89 (3)
C(15)	−494 (7)	2436 (5)	6269 (1)	75 (2)	C(71)	6962 (13)	−3874 (8)	7612 (2)	109 (3)
F(15)	160 (5)	2091 (4)	6502 (1)	111 (2)	C(72)	6661 (13)	−4158 (12)	7322 (2)	132 (4)
C(20)	2045 (6)	1635 (5)	5801 (1)	57 (2)	C(73)	7499 (24)	−3585 (16)	7135 (4)	182 (7)
C(21)	2941 (7)	2331 (5)	5900 (1)	64 (2)	C(80)	8351 (8)	−2239 (8)	7952 (2)	89 (3)
F(21)	3004 (4)	2536 (3)	6171 (1)	86 (1)	C(81)	8791 (9)	−1619 (7)	7723 (2)	103 (3)
C(22)	3803 (8)	2858 (6)	5752 (2)	81 (2)	C(82)	10304 (12)	−1423 (10)	7754 (3)	161 (5)
F(22)	4672 (5)	3521 (4)	5868 (1)	122 (2)	C(83)	11144 (17)	−2041 (17)	7717 (5)	372 (12)
C(23)	3790 (8)	2719 (7)	5482 (2)	85 (3)	N(4)	949 (5)	2409 (4)	4383 (1)	70 (2)
F(23)	4628 (5)	3228 (4)	5326 (1)	131 (2)	C(90)	1418 (10)	1423 (6)	4268 (2)	79 (2)
C(24)	2933 (9)	2036 (7)	5369 (2)	82 (3)	C(91)	2257 (11)	772 (7)	4464 (2)	90 (3)
F(24)	2931 (5)	1871 (4)	5100 (1)	124 (2)	C(92)	2837 (9)	−52 (7)	4309 (2)	96 (3)
C(25)	2100 (7)	1529 (5)	5525 (2)	68 (2)	C(93)	3705 (12)	−738 (10)	4481 (3)	119 (4)
F(25)	1275 (4)	845 (3)	5398 (1)	99 (1)	C(100)	223 (7)	2926 (5)	4147 (1)	80 (2)
C(30)	1244 (6)	−1837 (5)	6696 (1)	61 (2)	C(101)	−379 (13)	3923 (7)	4210 (2)	105 (3)
C(31)	2253 (7)	−1657 (6)	6884 (2)	74 (2)	C(102)	−1019 (16)	4404 (9)	3963 (3)	131 (4)
F(31)	2802 (4)	−736 (4)	6895 (1)	97 (1)	C(103)	−1611 (13)	5375 (8)	4020 (3)	134 (4)
C(32)	2805 (8)	−2330 (8)	7065 (2)	92 (3)	C(110)	2144 (8)	3004 (6)	4490 (2)	78 (2)
F(32)	3798 (5)	−2096 (5)	7247 (1)	137 (2)	C(111)	3201 (10)	3236 (9)	4296 (2)	102 (3)
C(33)	2291 (8)	−3264 (7)	7057 (2)	98 (3)	C(112)	4244 (14)	3867 (14)	4468 (4)	184 (7)
F(33)	2849 (5)	−3953 (4)	7230 (1)	155 (2)	C(113)	5309 (22)	4005 (13)	4333 (5)	258 (9)
C(34)	1301 (8)	−3508 (6)	6878 (2)	97 (3)	C(120)	59 (8)	2279 (7)	4617 (2)	87 (2)
F(34)	804 (6)	−4443 (4)	6868 (1)	148 (2)	C(121)	−1267 (10)	1679 (10)	4550 (2)	107 (3)
C(35)	794 (7)	−2799 (6)	6705 (2)	78 (2)	C(122)	−2062 (12)	1695 (13)	4806 (2)	148 (6)
F(35)	−257 (5)	−3096 (3)	6531 (1)	102 (1)	C(123)	−3461 (13)	1264 (12)	4760 (3)	199 (6)
C(40)	−971 (6)	−772 (5)	6677 (1)	59 (2)	C(200)	9913 (44)	756 (12)	173 (3)	172 (10)
C(41)	−909 (7)	−235 (5)	6909 (1)	68 (2)	C(201)	8763 (23)	328 (29)	45 (7)	178 (9)
F(41)	230 (5)	287 (3)	6977 (1)	101 (1)	C(202)	11161 (35)	430 (18)	122 (4)	183 (12)

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound **3**

	Bond Lengths		
Ni(1)–O	1.892 (4)	Ni(2)–O	1.890 (4)
Ni(1)–N(1)	1.916 (5)	Ni(2)–N(2)	1.900 (5)
Ni(1)–C(10)	1.901 (6)	Ni(2)–C(30)	1.891 (6)
Ni(1)–C(20)	1.887 (6)	Ni(2)–C(40)	1.896 (6)
	Bond Angles		
O–Ni(1)–N(1)	86.0 (2)	O–Ni(2)–N(2)	86.3 (2)
O–Ni(1)–C(10)	92.1 (2)	O–Ni(2)–C(40)	92.1 (2)
N(1)–Ni(1)–C(20)	93.1 (2)	N(2)–Ni(2)–C(30)	93.6 (3)
C(10)–Ni(1)–C(20)	89.3 (3)	C(30)–Ni(2)–C(40)	87.9 (3)
Ni(1)–O–Ni(2)	119.3 (2)		

replaces the dioxane in the intermediate dioxane–nickel complex, and in pathway b, the $Ni(C_6F_5)_2$ fragment is trapped by benzonitrile with the concomitant release of $MgBr_2$. Analogue bromo-bridged compounds have been detected or isolated in similar reactions with the pentafluorophenyl–palladium[16] and 2,4,6-trifluorophenyl–palladium[18] systems, but the dioxane complexes of nickel[28] and palladium[30] have also been reported. However pathway b must be ruled out in the formation of complex **1** because complete precipitation of magnesium takes place in the arylation reaction and magnesium is absent in the solution to which benzonitrile is added.

It is noteworthy that the replacement of PhCN by OH^- is readily achieved with the nickel and palladium[10] complexes, but *cis*-$[Pt(C_6F_5)_2(PhCN)_2]$ cannot be used for preparing the hydroxo–platinum complex because in acetone–water nucleophilic attack by OH^- of bonded PhCN is favorably competitive.[10]

In the appropriate conditions, the reaction represented by eq 2 may be reversed and the benzonitrile complex is the reaction product when **2** is treated with benzonitrile in the presence of tetrafluoroboric acid (eq 4). Consequently, the reactions represented by eqs 2 and 4 may be related to the general equilibrium given by eq 5. Moreover, the reactions leading to the formation

$$Q_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2] + 4PhCN + 2HBF_4 \rightarrow 2\,cis\text{-}[Ni(C_6F_5)_2(PhCN)_2] + 2QBF_4 + 2H_2O \quad (4)$$

$$[(C_6F_5)_2Ni(\mu\text{-}OH)_2Ni(C_6F_5)_2]^{2-} + 2H^+ + 4L' \rightleftharpoons 2\,cis\text{-}[Ni(C_6F_5)_2L'_2] + 2H_2O \quad (5)$$

of complexes **3**–**11** could also be related to a similar equilibrium because $2H^+ + 4L'$ is equivalent to 2HL (HL = pyrazoles or triazole, and the deprotonated L^- acts as a bidentate ligand joining two metal centers).

The protonation of $[\{Pt(L\text{-}L)(\mu\text{-}OH)\}_2]^{2+}$ [L-L = 1,1′-bis(diphenylphosphino)ferrocene] with HBF_4 to give the corresponding aqua complex has been reported.[3] Attempts made to prepare $[Ni(C_6F_5)_2(H_2O)_2]$ from **2** and HBF_4 were unsuccessful.

Experimental Section

Carbon, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 1430 spectrophotometer and NMR spectra of acetone-d_6 solutions on a Bruker Model AC 200E (^1H, standard $SiMe_4$) or a Varian

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[30] García, G.; López, G. *Inorg. Chim. Acta* **1981**, *52*, 87.

Model FT 80A (^{19}F, standard $CFCl_3$) instrument. A Varian Unity 300 spectrometer was used for the variable-temperature spectra of complex **8**. Decomposition temperatures were determined on a Reichert microscope. Conductivities (solvent acetone, $c \simeq 5 \times 10^{-4}$ M) were measured with a Philips PW 9501/01 conductimeter. Visible spectra (in acetone) were recorded on a Hitachi U-2300 spectrophotometer. Tetrahydrofuran solutions of $MgBr(C_6F_5)$ were prepared by treating C_6F_5Br with Mg, as described elsewhere.[30]

***cis*-[Ni(C_6F_5)$_2$(PhCN)$_2$] (1).** A freshly prepared solution of MgBr(C_6F_5) (from 6.275 mmol of Mg and 6.275 mmol of bromopentafluorobenzene) in tetrahydrofuran (thf) (20 mL) was added to a yellow-orange thf (20 mL) solution of $NiBr_2 \cdot 2dme$[29] (2.51 mmol), which turned red. The mixture was stirred under nitrogen atmosphere for 1 h. Dioxane (25 mL) was added dropwise with constant stirring for 30 min to precipitate the magnesium bromide as its dioxane adduct, and the mixture was then set aside in a refrigerator for 3 h. The magnesium bromide was removed by filtration (under nitrogen atmosphere), and benzonitrile (5.02 mmol) was added to the magnesium-free solution. After being stirred for 15 min, the solution was concentrated under reduced pressure until half the original volume. Addition of hexane precipitated complex **1** as a yellow solid, which was filtered off, washed with hexane, and air-dried. The product was recrystallized from dichloromethane–hexane in 62% yield.

Anal. Calcd for $C_{26}F_{10}H_{10}N_2Ni$: C, 52.1; H, 1.7; N, 4.7. Found: C, 52.4; H, 1.6; N, 4.6. Mp: 145 °C dec. $\Lambda_M = 12\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$): 2270, 2265 (C≡N str), 755, 685. Visible [cm^{-1} (ϵ_{max})]: 22 000 (420). ^{1}H (δ): 8.04 (m, Ph). ^{19}F (δ): −116.3 (d, 4 F_o, J_{om} = 25.4 Hz), −161.5 (t, 2 F_p, J_{mp} = 19.2 Hz), −164.7 (m, 4 F_m).

[NBu_4]$_2$[{Ni(C_6F_5)$_2$(μ-OH)}$_2$] (2). A 20% aqueous solution (0.433 mL) of [NBu_4]OH (0.332 mmol) was added to an acetone (10 mL) solution of **1** (0.166 mmol). After being stirred at room temperature for 30 min, the solution was concentrated under vacuum. On addition of water, orange crystals of **2** precipitated, which were filtered off, washed with water and air-dried; 82% yield.

Anal. Calcd for $C_{56}F_{20}H_{74}O_2N_2Ni_2$: C, 51.6; H, 5.7; N, 2.1. Found: C, 51.7; H, 6.0; N, 2.3. Mp: 217 °C dec. $\Lambda_M = 186\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$): 3660, 3640 (OH str), 520 (Ni–O str). Visible [cm^{-1} (ϵ_{max})]: 21 800 (720). ^{1}H (δ): −5.74 (s, 2 H, OH). ^{19}F (δ): −114.5 (d, 8 F_o, J_{om} = 28.5 Hz), −167.2 (t, 4 F_p, J_{mp} = 19.4 Hz), −168.6 (m, 8 F_m).

[NBu_4]$_2$[{Ni(C_6F_5)$_2$}$_2$(μ-OH)(μ-L)] [L = pz (3), mpz (4), dmpz (5), indz (6), tz (7)] and [NBu_4]$_2$[{Ni(C_6F_5)$_2$(μ-L)}$_2$] [L = pz (8), mpz (9), indz (10), tz (11)]. An acetone (10 mL) solution containing HL [0.077 mmol (**3–7**) or 0.154 mmol (**8–11**)] and **2** (0.077 mmol) was stirred at room temperature for 30 min. The solution was then concentrated under reduced pressure to almost dryness, and the residue was extracted with a minimum amount of dichloromethane. Addition of diethyl ether–hexane (1:1) resulted in the precipitation of the yellow complexes **3–11**, which were separated by filtration, washed with diethyl ether and air-dried. The reaction of 3,5-dimethylpyrazole with **2** in the 2:1 mol ratio led to a mixture of complex **9** and unreacted 3,5-dimethylpyrazole.

3 was obtained in 72% yield. Anal. Calcd for $C_{59}F_{20}H_{76}N_4ONi_2$: C, 52.3; H, 5.7; N, 4.1. Found: C, 52.4; H, 5.6; N, 4.4. Mp: 178 °C. $\Lambda_M = 203\ \Omega^{-1}\ cm\ mol^{-1}$. IR ($cm^{-1}$): 3630 (OH str), 740, 620 (pz). Visible [cm^{-1} (ϵ_{max})]: 22 900 (748). ^{1}H (δ): 6.21 (d, 2 H, 3- and 5-H, J = 2.0 Hz), 5.70 (t, 1 H, 4-H, J = 2.0 Hz), −4.24 (s, 1 H, OH). ^{19}F (δ): −113.4 (m, 8 F_o), −166.8 (m, 4 F_p + 8 F_m).

4 was obtained in 86% yield. Anal. Calcd for $C_{60}F_{20}H_{78}N_4ONi_2$: C, 52.6; H, 5.7; N, 4.1. Found: C, 52.6; H, 5.7; N, 4.0. Mp: 154 °C. $\Lambda_M = 196\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$): 3630 (OH str), 755 (mpz). Visible [cm^{-1} (ϵ_{max})]: 22 900 (797). ^{1}H (δ): 6.29 (d, 1 H, 5-H, J = 1.35 Hz), 5.52 (d, 1 H, 4-H, J = 1.35 Hz), 1.52 (s, 3 H, Me), −4.16 (s, 1 H, OH). ^{19}F (δ): −113.1 (m, 8 F_o), −167.2 (m, 4 F_p + 8 F_m).

5 was obtained in 64% yield. Anal. Calcd for $C_{61}F_{20}H_{80}N_4ONi_2$: C, 53.0; H, 5.8; N, 4.1. Found: C, 52.9; H, 6.0; N, 4.0. Mp: 265 °C. $\Lambda_M = 175\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$): 3620 (OH str), 1520, 1035, 735 (dmpz). Visible [cm^{-1} (ϵ_{max})]: 23 000 (751). ^{1}H (δ): 5.20 (s, 1 H, 4-H), 1.48 (s, 6 H, Me), −4.24 (s, 1 H, OH). ^{19}F (δ): −112.2 (d, 4 F_o, J_{om} = 26.4 Hz), −113.0 (d, 4 F_o, J_{om} = 34.1 Hz), −166.2 (t, 2 F_p, J_{mp} = 17.4 Hz), −168.1 (m, 2 F_p + 8 F_m).

6 was obtained in 87% yield. Anal. Calcd for $C_{63}F_{20}H_{78}N_4ONi_2$: C, 53.9; H, 5.6; N, 4.0. Found: C, 53.9; H, 5.5; N, 4.0. Mp: 169 °C. $\Lambda_M = 171\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$): 3630 (OH str), 1200, 910, 800, 760 (indz). Visible [cm^{-1}, (ϵ_{max})]: 23 300 (768). ^{1}H (δ): 7.25 (m, 1 H), 6.84 (s, 1 H, 3-H), 6.56 (m, 2 H), 6.12 (m, 1 H), −4.06 (s, 1 H, OH). ^{19}F (δ): −113.4 (m, 8 F_o), −166.8 (m, 4 F_p + 8 F_m).

7 was obtained in 78% yield. Anal. Calcd for $C_{58}F_{20}H_{75}N_5ONi_2$: C, 51.4; H, 5.6; N, 5.2. Found: C, 51.3; H, 5.6; N, 5.7. Mp: 135 °C. $\Lambda_M = 189\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$): 3630 (OH str), 1210, 1080, 740, 675 (tz). Visible [cm^{-1} (ϵ_{max})]: 23 400 (808). ^{1}H (δ): 6.50 (s, 2 H, tz), −4.25 (s, 1 H, OH). ^{19}F (δ): −113.9 (m, 8 F_o), −165.6 (t, 2 F_p, J_{mp} = 18.7 Hz), −165.8 (t, 2 F_p, J_{mp} = 22.2 Hz), −167.0 (m, 8 F_m).

8 was obtained in 71% yield. Anal. Calcd for $C_{62}F_{20}H_{78}N_6Ni_2$: C, 53.0; H, 5.6; N, 6.0. Found: C, 52.9; H, 5.5; N, 6.0. Mp: 222 °C. IR (cm^{-1}): 750, 730 (pz). ^{1}H (δ): 6.95 (d, 2 H, 3- and 5-H, J = 1.9 Hz), 5.48 (t, 4-H, J = 1.9 Hz). ^{19}F (δ): −110.5 (s, br, 2 F_o), −116.0 (s, br, 2 F_o), −167.5 (m, 2 F_p + 4 F_m).

9 was obtained in 72% yield. Anal. Calcd for $C_{64}F_{20}H_{82}N_6Ni_2$: C, 53.6; H, 5.8; N, 5.9. Found: C, 53.6; H, 5.8; N, 5.9. Mp: 193 °C. IR (cm^{-1}): 750 (mpz). ^{1}H (δ): 7.36 (d, 2 H, 5-H, J = 1.5 Hz), 5.22 (d, 2 H, 4-H, J = 1.5 Hz), 1.55 (s, 6 H, Me).

10 was obtained in 81% yield. Anal. Calcd for $C_{70}F_{20}H_{82}N_6Ni_2$: C, 55.9; H, 5.5; N, 5.6. Found: C, 55.5; H, 5.7; N, 5.4. Mp: 252 °C. IR (cm^{-1}): 1210, 910, 810, 760 (indz). ^{1}H (δ) 8.22 (s, 2 H, 3-H), 7.72 (d, 2 H, 7-H, J = 8.3 Hz), 7.21 (d, 2 H, 4-H, J = 8.9 Hz), 6.69 (m, 2 H, 6-H), 6.49 (m, 2 H, 5-H).

11 was obtained in 73% yield. Anal. Calcd for $C_{60}F_{20}H_{76}N_8Ni_2$: C, 51.2; H, 5.4; N, 8.0. Found: C, 50.9; H, 5.4; N, 7.8. Mp: 243 °C. $\Lambda_M = 213\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR ($cm^{-1}$): 1210, 1080, 740, 675 (tz). Visible [cm^{-1} (ϵ_{max})]: 24 400 (861). ^{1}H (δ): 7.34 s, 4 H, tz). ^{19}F (δ): −114.5 (d, 8 F_o, J_{om} = 23.4 Hz), −167.2 (t, 4 F_p, J_{mp} = 18.8 Hz), −168.6 (m, 8 F_m).

Reaction of 2 with Benzonitrile. Benzonitrile (0.31 mmol) was added to a dichloromethane (10 mL) solution of **2** (0.1 g, 0.076 mmol), and the mixture was treated with a solution of tetrafluoroboric acid and diethyl ether (7 μL of 54% solution; 0.048 mmol of HBF_4). The solution was then concentrated under reduced pressure to almost dryness, and the addition of Et_2O/hexane (1:1) resulted in the precipitation of [NBu_4][BF_4], which was removed by filtration. The resulting yellow solution was concentrated to half the original volume, and the yellow solid that precipitated on addition of hexane was filtered off, washed with hexane, and identified as complex **1** (yield 21 mg).

It is important to note that the actual amount of HBF_4 used in the above experiment is smaller than the theoretical one required by eq 3 (0.152 mmol HBF_4). If, however, a larger amount of HBF_4 is used, the cleavage of the Ni–C_6F_5 bonds occurs.

Crystal Structure Analysis. Single-crystal X-ray diffraction analyses for **2** and **3** [crystals suitable for X-ray diffraction were obtained by solvent diffusion (benzene–hexane) at room temperature] were performed by application of general procedures that were previously described.[31] The pertinent crystallographic data for both compounds are summarized in Table I.

A total of 5121 unique reflections up to $\theta = 65°$ for compound **2** were collected using a 0.30 × 0.17 × 0.10 mm crystal on a Philips PW1100 diffractometer equiped with graphite-monochromated Cu Kα radiation, $\lambda = 1.5418$ Å, and using a $\omega/2\theta$ scan mode. The data were collected for Lorentz and polarization effects. The structure was solved by heavy-atom method followed by normal Fourier synthesis. An empirical absorption correction[32] was applied (minimum and maximum absorption correction being 0.654 and 1.134). A total of 2788 reflections were considered as observed with the criterion $I > 3\ \sigma(I)$. Most of the H atoms were obtained by difference Fourier synthesis, the remaining ones (attached to the cationic channels) being located at their expected positions. Two positions were found for the H atom attached to the bridging O atom, consistent with a disorder model. The least-squares refinement was done using an anisotropic model (isotropic for H atoms some of them as fixed contributors), with 479 variables, the ratio of freedom being 1.61. The final difference Fourier map contained a peak of 0.46 e/Å^3.

Intensity data (up to $\theta = 60°$) for compound **3** were collected on a Philips PW1100 diffractometer equipped with graphite-monochromated Cu Kα radiation using $\omega/2\theta$ scan mode on a 0.27 × 0.16 × 0.08 mm crystal. The data were corrected for Lorentz and polarization effects and the structure was solved using the same methods as described above. The H atoms were obtained as in compound **2**. The minimum and maximum factors of the empirical absorption correction[32] were 0.825 and 1.271, respectively. The anisotropic refinements (isotropic for H atoms and some of them as fixed contributors) were carried out by least-square methods using 1047 variables and 5814 reflections considered as observed with the $I > 3\ \sigma(I)$ criterion. The ratio of freedom was 1.55. The maximum peak in the final difference map is 0.93 e/Å^3.

In both cases an appropriate weighting scheme was used in the least-squares refinement as to give no trends in $\langle w\Delta^2F \rangle$ vs $\langle F_o \rangle$ and $\langle (\sin\theta)/\lambda \rangle$ with $w = k/(\sigma_1^2\sigma_2^2)$ where $k = 1$, $\sigma_1 = f(F_o)$, and $\sigma_2 = g[(\sin\theta)/\lambda]$.[33]

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All the calculations were performed with the XRAY76 system[34] and the programs DIRDIF (structure expansion)[35] and PARST (geometrical calculations)[36] running on a Vax 6410 computer. The scattering factors for neutral atoms were taken from ref 37.

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Supplementary Material Available: Tables of complete bond lengths and angles (Tables S1 and S5), thermal parameters (Tables S2 and S6), coordinates for H atoms (Tables S3 and S7), and bond lengths and angles involving H atoms (Tables S4 and S8) (24 pages); tables of observed and calculated structure factors (Tables S9 and S10) (61 pages). Ordering information is given on any current masthead page.

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Chemoselective Oxidation of 3,5-Di-*tert*-butylcatechol by Molecular Oxygen. Catalysis by an Iridium(III) Catecholate through Its Dioxygen Adduct

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The selective oxidation of 3,5-di-*tert*-butylcatechol ($DTBCH_2$) to 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) by molecular oxygen is catalyzed by the Ir(III) catecholate complex $[(\text{triphos})\text{Ir}(\text{DTBC})]^+$ through its dioxygen adduct $[(\text{triphos})\text{Ir}(\text{OO})(\text{DTBSQ})]^+$ [triphos = $MeC(CH_2PPh_2)_3$; DTBC = 3,5-di-*tert*-butylcatecholate; DTBSQ = 3,5-di-*tert*-butylsemiquinonate]. The following overall stoichiometric equation is suggested by analysis of the oxidation products and H_2O_2: $DTBCH_2 + O_2 \rightarrow DTBQ + H_2O_2$. The rates of reaction of the substrate as well as the formation of products are shown to be first order with respect to catalyst and substrate concentrations and zero order with respect to the partial pressure of O_2 in the range 15–725 psi. The kinetic parameters for the oxidation reaction are estimated in the temperature range 38–60 °C. Kinetic and thermodynamic data are consistent with a rate-determining step involving the attack of free catechol to the O_2 adduct. For partial pressures of O_2 higher than 725 psi, the oxygenation of $DTBCH_2$ to 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione competes with DTBQ formation.

Introduction

As part of our studies on the transport and activation of dioxygen by metal species,[1-4] we have recently communicated the preparation and characterization, including an X-ray analysis, of iridium catecholate dioxygen adducts of the formula $[(\text{triphos})\text{Ir}(\text{OO})(\text{SQ})]\text{BPh}_4$ (triphos = $MeC(CH_2PPh_2)_3$; SQ = DTBSQ = 3,5-di-*tert*-butylsemiquinonate (**2a**) or PhenSQ = 9,10-phenanthrenesemiquinonate (**4a**)) (Scheme I).[5]

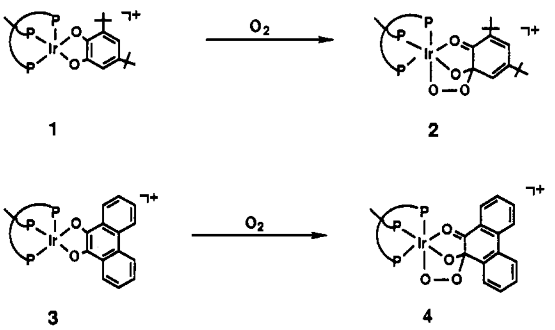
In a preceding article,[4] we reported that the related rhodium complex $[(\text{triphos})\text{Rh}(\text{DTBC})]\text{BPh}_4$ (**5**) (DTBC = 3,5-di-*tert*-butylcatecholate) reacts in CH_2Cl_2 solution with O_2 at low temperature to give a dioxygen adduct, $[(\text{triphos})\text{Rh}(\text{OO})(\text{DTBSQ})]\text{BPh}_4$ (**6**), which was assigned the "open" structure (a) shown in Scheme II.

In light of the iridium results, the rhodium complex, which, by the way, has never been isolated in the solid state, has carefully been re-examined by concluding that it shares the primary geometry with the iridium compounds, i.e. the "closed" one (b).[6]

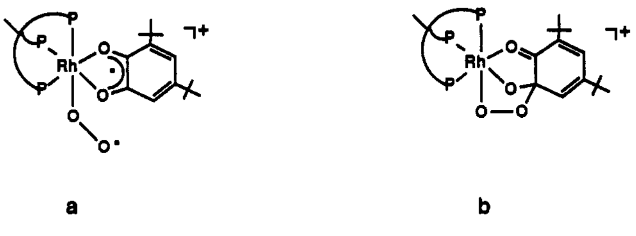
Both the rhodium and iridium dioxygen adducts catalyze the oxidation of 3,5-di-*tert*-butylcatechol ($DTBCH_2$) under a steady stream of O_2 to give 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) and H_2O_2.[4,5] However, while the iridium-assisted reaction is rigorously chemoselective, the rhodium complex is able also to oxygenate the catechol, producing appreciable amounts of 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (DTBA) (*intra*diol C–C cleavage) and of 3,5-di-*tert*-butyl-2-pyrone (DTBPyr) (*extra*diol C–C cleavage)[4] (Scheme III).

Since very few kinetic and thermodynamic data for metal-catalyzed oxidation reactions of catechols to *o*-quinones are reported in the literature,[7] we decided to study the kinetics of the chemoselective oxidation of $DTBCH_2$ to DTBQ at different dioxygen pressures and concentrations of the iridium catalyst and

Scheme I



Scheme II



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