interaction.[11] The overlap population of the Me $2a_1$ orbital with the dimer fragment HOMO is only slightly greater for the asymmetric than the symmetric bridge (0.381 and 0.376, respectively). However, the overlap population of the Me 1e (C–H bond) orbital with the dimer fragment LUMO is substantially greater for the asymmetric bridge (0.180) than the symmetric one (0.125). This preference for an asymmetric bridge is also evident in the molecular orbital energies, and the net stabilization of the asymmetric geometry over the symmetric one is ca. 0.5 eV. NMR experiments have shown that the μ-CH_3 protons are fluxional,[4b] and, with the assumption that the symmetric bridge is the transition state for this process, the net stabilization of 0.5 eV should roughly correspond to the barrier to fluxionality. The small value calculated is consistent with the experimental observation that all three protons and both iron atoms are equivalent down to at least −86 °C.

As has been found for the monomeric alkenyl agostic systems of Brookhart and Green, the LUMO of **5** is the antibond of the agostic interaction (Figure 1).[12] Thus the formal addition of two electrons should destroy the interaction and cause the methyl ligand to coordinate in a terminal fashion. The compound $[CpFe(CO)]_2(\mu\text{-}CO)(CH_3)^-$ is not as yet known, but the isovalent dimer $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2(CH_3)^-$, recently prepared by Bergman and Krause,[13] does contain a terminal methyl ligand. Protonation of the methylene-bridged rhodium dimer $[CpRh(CO)]_2(\mu\text{-}CH_2)$ (**6**) might be expected to lead to the dimer $[CpRh(CO)]_2(\mu\text{-}CH_3)^+$ by analogy to the chemistry of **4**. **6** exhibits markedly different reactivity toward protons than does **4**, however. Rather than adding to the methylene, the proton adds to the Rh–Rh bond of **6** to form $[CpRh(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$.[14] We believe that this difference in reactivity is dictated by the nature of the HOMO's of the methylene-bridged complexes. A detailed explanation of this effect along with a description of the electronically induced reactivity of similar hydrocarbyl-bridged dimers will be presented in a later publication.

Registry No. 5, 101519-37-3.

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(11) A molecular orbital calculation for symmetric bridging methyl groups has been reported in ref 2a.

(12) Fitzpatrick, N. J.; McGinn, M. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1637–1643.

(13) Krause, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2972–2973.

(14) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Balbach, B. *J. Am. Chem. Soc.* **1980**, *102*, 5906–5908.

Transition-Metal Chemistry of Octafluorocyclooctatetraene. Synthesis and X-ray Structure of a Novel Five-Coordinate *cis*-Dialkyl Nickel Complex

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Summary: Reaction of $Ni(COD)_2$ with 2 equiv of the phosphines PMe_3 or $PPhMe_2$ (L) in the presence of octafluorocyclooctatetraene (OFCOT) affords the first examples of Ni(0) compounds containing two coordinated fluoroolefins $[Ni(1,2,5,6\text{-}\eta\text{-}OFCOT)L_2]$ (**1**); use of exactly 2 equiv of *t*-BuNC instead of a phosphine yields the metallacyclic complex $[Ni(C_8F_8)(t\text{-}BuNC)_2]$ (C_8F_8 = perfluorobicyclo[3.3.0]octadienediyl) (**2**) which does not undergo reductive elimination in the presence of exogenous ligands to give perfluorosemibullvalene (**3**) but instead forms the first stable examples of five-coordinate *cis*-dialkyl complexes of nickel $[Ni(C_8F_8)(t\text{-}BuNC)_2L]$ (**4**) (L = *t*-BuNC, PMe_3, PPh_3), one of which, **4b** (L = PMe_3), has been characterized by a single-crystal X-ray diffraction study at −110 °C.

Reductive elimination reactions of square-planar d^8 metal complexes are of considerable importance in homogeneous catalysis and have been reviewed recently.[3] The detailed mechanism of elimination is still the focus of a great deal of theoretical and experimental work. Kinetic and theoretical studies have indicated that reductive elimination from square-planar Pd(II) and Au(III) complexes involves initial *dissociation* of a ligand to give a T-shaped intermediate.[4] In corresponding Ni(II) systems, however, theoretical studies[3] together with recent kinetic observations on catalytic hydrocyanation reactions[5] have provided powerful evidence that the key reductive elimination step is preceded by *association* with an exogenous ligand to give a five-coordinate *cis*-dialkyl nickel species. We now report the isolation and crystallographic characterization of the first stable example of such a complex.

While Ni(1,5-cyclooctadiene)$_2$ $[Ni(COD)_2]$ and $Ni(C_2H_4)L_2$ (L = PPh_3, PPh_2Me) do not react with octafluorocyclooctatetraene[6] (OFCOT), reaction of $Ni(COD)_2$ with OFCOT in the presence of 2 equiv of the more basic tertiary phosphine ligands PMe_3 or $PPhMe_2$ affords the thermally and photochemically inert 18-electron diolefin complexes **1**[7] which exhibit characteristic ^{19}F NMR spectra containing only two fluorine resonances. Cyclopentadienyl complexes of cobalt(I) and rhodium(I) adopt this mode of coordination with both OFCOT[8] and its hydrocarbon analogue cyclooctatetraene (COT),[9] but there are no ana-

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(3) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamota, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181–8188.

(4) (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868–1876. (b) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981–4991. (c) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933–4941. (d) Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140–6148. (e) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *40*, C81–C84. (f) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1973**, *51*, C39–C42. (g) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255–7265. (h) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 8440–8447. (i) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867.

(5) McKinney, R.; Roe, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 261–262.

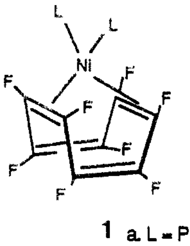
(6) (a) Lemal, D. M.; Buzby, J. M.; Barefoot, A. C. III; Grayston, M. W.; Laganis, E. D. *J. Org. Chem.* **1980**, *45*, 3118–3120. (b) Laird, B. B.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 678–680.

(7) **1a**: mp 120–122 °C dec; ^{19}F NMR (C_6D_6, shifts in ppm upfield from internal $CFCl_3$) δ 118.12 (4 F, m), 155.74 (4 F, m); ^1H NMR (C_6D_6) δ 0.65 (9 H, d, J_{P-H} = 6.2 Hz, CH_3); IR (KBr) 1708 ($\nu(C{=}C)$), 1252, 1288 cm^{-1} ($\nu(CF)$). Anal. Calcd for $C_{14}H_{18}F_8NiP_2$: C, 36.65; H, 3.95. Found: C, 36.58; H, 4.09. **1b**: mp 145–147 °C dec; ^{19}F NMR (C_6D_6) δ 117.46 (4 F, m), 151.62 (4 F, m); ^1H NMR (C_6D_6) δ 0.86 (6 H, d, J_{P-H} = 7.61 Hz, CH_3), 6.9 (5 H, m, Ph); IR (CH_2Cl_2) 1718 ($\nu(C{=}C)$, 1295, 1260 cm^{-1} ($\nu(CF)$). Anal. Calcd for $C_{24}H_{22}F_8NiP_2$: C, 49.44, H, 3.80. Found: C, 49.30, H, 3.61.

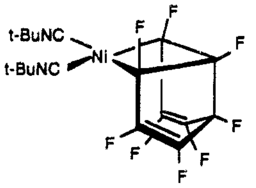
(8) Doherty, N. M.; Ewels, B. E.; Hughes, R. P.; Samkoff, D. E.; Saunders, W. D.; Davis, R. E.; Laird, B. B. *Organometallics* **1985**, *4*, 1606–1611.

0276-7333/86/2305-1053$01.50/0

logues in nickel COT chemistry.[10] Compounds 1 represent the first examples of Ni(0) compounds containing two coordinated fluoro olefins. In contrast, substitution of exactly 2 equiv of *tert*-butyl isocyanide for the phosphine ligands in the above reaction yields the *yellow* 16-electron Ni(II) dialkyl complex 2[12] containing the perfluorobicyclo[3.3.0]octadienediyl ligand. A cyclopentadienyl



1 a. L = PMe_3
b. L = $PPhMe_2$



2

cobalt complex containing this novel ligand has been previously characterized by X-ray crystallography,[13] and the mechanistic details of the transannular ring closure pathway have been the subject of a recent communication.[14] Notably only ring closure to give the perfluorobicyclo[3.3.0]octadienediyl ligand is observed for the corresponding Pd and Pt complexes, regardless of whether phosphines or *t*-BuNC are used as ancillary ligands.[13]

Realizing that reductive elimination of the *cis*-dialkyl moiety in complex 2 should lead to a hitherto elusive valence isomer of OFCOT, perfluorosemibullvalene (3), we examined its reactions with exogenous ligands. Exogenous *tert*-butyl isocyanide or tertiary phosphorus ligands reacted immediately with 2 to afford the *orange* five-coordinate adducts 4.[15] These appear to be the first examples of stable five-coordinate *cis*-dialkyl complexes of Ni(II). They are moderately air-stable and are considerably more robust thermally than the five-coordinate tris(triphenylphosphine)nickelacyclopentane (5), reported by Grubbs, which decomposes above 9 °C in solution.[16] A number of stable triagonal-bipyramidal *trans*-dialkyls of nickel have been prepared previously.[17]

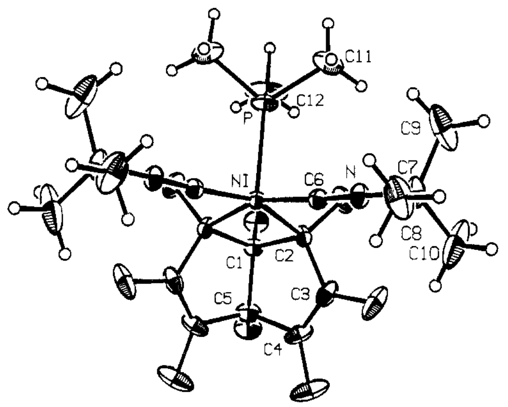
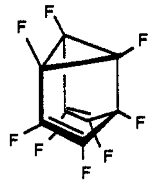


Figure 1. Ortep drawing and numbering scheme for **4b**. Selected bond distances (Å) and bond angles (deg): Ni–P, 2.3628 (14); Ni–C2, 1.955 (3); Ni–C6, 1.863 (3), C6–N6, 1.155 (4); C7–N6, 1.454 (4); C1–C2, 1.527 (4); C1–C5, 1.578 (6); C2–C3, 1.462 (5); C3–C4, 1.312 (5); C4–C5, 1.471 (4); P–Ni–C2, 97.56 (10); P–Ni–C6, 98.30 (9); C2–Ni–C6, 93.01 (12); C2–Ni–C2′, 72.98 (11); C2–C1–C2′, 99.2 (3); C6–Ni–C6′, 96.56 (13); C6–N6–C7, 176.7 (3).



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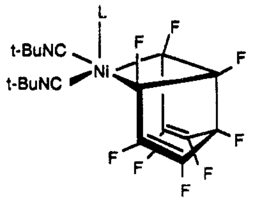
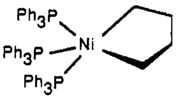


4 a. L = t-BuNC
b. L = PMe_3
c. L = PPh_3



5

In order to confirm the novel structures of these complexes, a single crystal of **4b** (grown from methylene chloride–hexane at −20 °C) was subjected to an X-ray diffraction study at −110 °C.[18] An Ortep diagram and atom numbering scheme for **4b** is shown in Figure 1, together with selected bond distances and angles. Details of the crystallographic determination are given in Table I, and fractional coordinates for the non-hydrogen atoms are compiled in Table II. The complex adopts an approximate square-pyramidal geometry about the Ni center with the added PMe_3 ligand occupying the apical position. The Ni occupies a position 0.313 (3) Å above the best plane defined by C2, C2′, C6, and C6′, and the metallacyclic ring

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(9) (a) Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: New York, 1980. (b) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University Press: Cambridge, 1978.

(10) Nickel forms a crystallographically characterized dinuclear complex $[Ni_2(COT)_2]$ with cyclooctatetraene.[11] We have found that this complex is also unreactive toward OFCOT.

(11) Brauer, D. J.; Krüger, C. *J. Organomet. Chem.* **1976**, *122*, 265–273.

(12) **2**: 107–109 °C dec; ^{19}F NMR (C_6D_6) δ 136.69 (1 F, m), 141.68 (2 F, m), 158.22 (2 F, m), 198.70 (3 F, m); ^1H NMR (C_6D_6) δ 0.85 (18 H, s); IR (KBr) 2192 (ν(C≡N)), 1691 cm^{-1} (ν(C=C)). Anal. Calcd for $C_{18}H_{18}F_8N_2Ni$: C, 45.70; H, 3.83; N, 5.92. Found: C, 45.59; H, 3.71; N, 5.84.

(13) (a) Hughes, R. P.; Samkoff, D. E.; Davis, R. E.; Laird, B. B. *Organometallics* **1983**, 2, 195–197. (b) Hughes, R. P.; Carl, R. T.; Samkoff, D. E., unpublished results.

(14) Hughes, R. P.; Carl, R. T.; Hemond, R. C.; Samkoff, D. E.; Rheingold, A. L. *J. Chem. Soc. Chem. Commun.*, in the press.

(15) **4a**: mp 94–101 °C dec; ^{19}F NMR (C_6D_6, 20 °C) δ 135.43 (1 F, m), 142.01 (2 F, m), 161.25 (2 F, m), 184.46 (2 F, m), 199.01 (1 F, m); ^{19}F NMR (CD_2Cl_2, −80 °C) δ 130.32 (1 F, m), 137.47 (2 F, m), 159.57 (2 F, m), 177.26 (2 F, m), 195.90 (1 F, m); ^1H NMR (C_6D_6, 20 °C) δ 0.90 (27 H, s, *t*-Bu); IR (KBr) 2160, 2182 (ν(C≡N)), 1695, 1688 cm^{-1} (ν(C=C)). Anal. Calcd for $C_{23}H_{27}F_8N_3Ni$: C, 49.67; H, 4.89; N, 7.55. Found: C, 49.62; H, 4.79; N, 7.42. **4b**: mp 93–97 °C dec; ^{19}F NMR (C_6D_6, 20 °C) δ 135.04 (1 F, m), 141.63 (2 F, m), 161.71 (2 F, m), 182.17 (2 F, m), 198.29 (2 F, m); ^{19}F NMR (CD_2Cl_2, −80 °C) δ 127.25 (1 F, m), 135.06 (2 F, m), 158.57 (2 F, m), 173.92 (2 F, m), 193.38 (2 F, m); ^1H NMR (C_6D_6, 20 °C) δ 0.90 (18 H, s, *t*-Bu), 1.10 (9 H, d, J_{P-H} = 6.3 Hz, CH_3); IR (KBr) 2160 (ν(C≡N)), 1707, 1690 cm^{-1} (ν(C=C)). Anal. Calcd for $C_{36}H_{33}F_8N_2NiP$: C, 45.93; H, 4.96; N, 5.10. Found: C, 45.56; H, 4.86; N, 4.91. **4c**: mp 99–103 °C dec; ^{19}F NMR (C_6D_6, 20 °C) δ 136.69 (1 F, m), 141.58 (2 F, m), 158.26 (2 F, m), 197.80 (3 F, m); ^{19}F NMR (CD_2Cl_2, −80 °C) δ 141.03 (1 F, m), 146.46 (2 F, m), 169.94 (2 F, m), 183.79 (2 F, m), 201.97 (1 F, m); ^1H NMR (C_6D_6) δ 0.83 (18 H, s, *t*-Bu), 7.21 (15 H, m, Ph); IR (CH_2Cl_2) 2188, 2197 (ν(C≡N)), 1693, 1704 cm^{-1} (ν(C=C)). Anal. Calcd for $C_{36}H_{33}F_8N_2NiP$: C, 59.15; H, 4.55; N, 3.84. Found: C, 59.08; H, 4.60; N, 3.78.

(16) Grubbs, R. H.; Miyashita, A.; Liv, M. M.; Burk, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3863–3864.

(17) (a) Jeffery, E. A. *Aust. J. Chem.* **1973**, *26*, 219–220. (b) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1973**, *106*, 1433–1452. (c) Karsch, H. H.; Klein, H. F.; Schmidbaur, H. *Chem. Ber.* **1974**, *107*, 93–101.

(18) Crystals of **4b** are orthorhombic, *Pnma*, a = 17.725 (4) Å, b = 19.030 (4) Å, c = 7.622 (1) Å, Z = 4. The structure was solved by heavy-atom methods and refined by full-matrix least-squares procedures to final agreement factors $R = \sum|(|F_o| - |F_c|)|/\sum|F_o| = 0.0497$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0511$, using 2646 reflections with $I \geq 2.0\sigma(I)$. The molecule is located on the crystallographic mirror plane and thus has rigorous C_s symmetry, with Ni, P, C1, F1, C5, F5, C12, and H12A on the mirror plane. X-ray experimental procedures, data processing, and principal computer programs were essentially as described previously.[8,19] Full details are provided as supplementary material (see paragraph at end of text).

(19) Riley, P. E.; Davis, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381–386.

Table I. Crystallographic Summary for 4b

A. Crystal Data (−110 °C)[a]	
a,Å	17.725 (4)
b,Å	19.030 (4)
c,Å	7.622 (1)
V,Å^3	2571.0 (9)
d_{calcd}, g cm^{-3} (−110 °C)	1.419
empirical formula, fw	$C_{21}H_{27}N_2F_8PNi$, 549.13
cryst system, space group, Z	orthorhombic, *Pnma*, 8
F(000), electrons	1128
B. Data Collection (−110 °C)[b]	
radiatn; λ, Å	Mo Kα; 0.71069
mode	ω scan
scan range	symmetrically over 1.0° about K$\alpha_{1,2}$ maximum
bkgd	offset 1.0 and −1.0° in omega from K$\alpha_{1,2}$ maximum
scan rate, deg min^{-1}	3–6
2θ range, deg	4.0–60.0
exposure time, h	53.3
stability analysis	
computed s, t	−0.00082 (9), 0.000014 (3)
correctn range (on l)	1.000–1.012
total reflctns measd	3855
data cryst faces	not measured due to loss of crystal
abs coeff, μ(Mo Kα), cm^{-1}	8.85
transmissn factor range	not applied
C. Structure Refinement[c]	
ignorance factor, p	0.02
reflctns used, $F_o \geq 4.0\ \sigma(F_o)$	2646
no. of variables	179
R, R_w	0.0497, 0.0511
R, R_w for all data	0.0774, 0.0528
goodness of fit, S	2.24
max shift/esd	0.39
extremes in diff map (e Å^{-3})	−0.50 to +0.54

[a] Unit-cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections with 24.4° < 2θ < 27.0°. [b] Syntex P2$_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crsytallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381. Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1511. [c] Relevant expressions are as follows. Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = (\sigma|F|)^{-2}$. $R = \sum|(|F_o| - |F_c|)|/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

Table II. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for Non-Hydrogen Atoms of 4b

atom	x	y	z	U, Å^2
Ni	0.21834 (3)	0.25	0.25354 (7)	0.02509 (13)
P	0.24610 (7)	0.25	−0.0497 (2)	0.0405 (4)
F1	0.03269 (14)	0.25	0.0768 (3)	0.0436 (9)
F2	0.12812 (11)	0.14229 (10)	0.1006 (3)	0.0507 (7)
F3	0.13854 (12)	0.09640 (11)	0.4649 (3)	0.0736 (9)
F4	0.01555 (12)	0.1652 (2)	0.6345 (3)	0.0804 (10)
F5	−0.05486 (14)	0.25	0.3556 (4)	0.0535 (10)
N6	0.32146 (14)	0.13054 (13)	0.3542 (3)	0.0354 (8)
C1	0.0745 (2)	0.25	0.2260 (5)	0.0301 (12)
C2	0.1297 (2)	0.18890 (14)	0.2442 (4)	0.0328 (8)
C3	0.1033 (2)	0.1538 (2)	0.4034 (5)	0.0453 (12)
C4	0.0456 (2)	0.1841 (2)	0.4802 (5)	0.0486 (12)
C5	0.0228 (3)	0.25	0.3946 (6)	0.040 (2)
C6	0.2820 (2)	0.17694 (15)	0.3211 (4)	0.0295 (8)
C7	0.3680 (2)	0.0694 (2)	0.3913 (5)	0.0453 (11)
C8	0.4322 (2)	0.0930 (2)	0.5050 (7)	0.079 (2)
C9	0.3975 (3)	0.0431 (3)	0.2170 (7)	0.105 (2)
C10	0.3197 (3)	0.0181 (3)	0.4815 (10)	0.122 (3)
C11	0.3019 (2)	0.1764 (2)	−0.1257 (5)	0.068 (2)
C12	0.1703 (4)	0.25	−0.2089 (8)	0.085 (4)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = {}^1/_3 \sum_i\sum_j U_{ij}a_i{}^*a_j{}^*A_{ij}$ where A is the dot product of the ith and jth direct space unit-cell vectors.

is slightly folded by 5.5° about the C2–C2′ vector. Perhaps the most notable structural feature concerns the Ni–PMe$_3$ distance [2.3628 (14) Å], which is significantly longer than the previously reported Ni–PMe$_3$ distance [2.218 (2) Å] for a formally five-coordinate complex [Ni(η^3-allyl)$_2$(PMe$_3$)],[20] in which the phosphine occupies a similar apical position. Complex **4b** provides a reasonable structural model for an intermediate in ligand-induced reductive elimination from a square-planar Ni(II) dialkyl compound, in which the exogenous ligand approaches the metal along the axis perpendicular to the original square plane of coordination.

Compounds 4 are noteworthy for two reasons. First, theoretical calculations[3] indicate that square-pyramidal *cis*-dialkyl NiR$_2$(PR$_3$)$_3$ should reductively eliminate alkane R–R, yet elimination of perfluorosemibullvalene from 4 is not observed. Reasons for this lack of reactivity may include relatively strong Ni–fluorocarbon bonds and a high energy elimination product (**3**).[21] Second, the *tert*-butyl isocyanide ligands do not undergo substitution, even in the presence of an excess of phosphine ligand, yet ^{19}F NMR studies show that the apical ligand dissociates reversibly in solution, as evidenced by significant temperature-dependent chemical shifts for the α-fluorines of the metallacyclic ring.[15] We conclude that there is no accessible pathway for interconversion of basal and apical sites in **4**. One likely pathway, a Berry pseudorotation, is probably precluded because the strained metallacyclic ring is reluctant to span apical/basal sites. A turnstile rotation of the three monodentate ligands also must be inoperative.[25]

In conclusion, the chemistry of OFCOT bound to nickel is highly dependent on the ancillary ligands, affording Ni(0) diolefin complexes with phosphine ligands and a ring-closed dialkyl complex with *t*-BuNC. The first stable examples of five-coordinate *cis*-dialkyl complexes of nickel have also resulted from this work, and further studies of the organometallic chemistry of these perfluorinated ligands are in progress.

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Registry No. **1a**, 101494-59-1; **1b**, 101518-50-7; **2**, 101494-60-4; **4a**, 101494-61-5; **4b**, 101494-62-6; **4c**, 101494-63-7; Ni(COD)$_2$, 1295-35-8.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, anisotropic thermal parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, and bond distances and angles for **4b** (Supplementary Tables 1–5) (22 pages). Ordering information is given on any current masthead page.

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(20) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 449–475.

(21) While fluorination generally results in stronger C–C bonds,[22] cyclopropanes are exceptions to this trend. Perfluorocyclopropane is less stable thermally[23] and has an estimated 40 kcal mol^{-1} higher strain energy[24] than cyclopropane.

(22) Smart, B. E. *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 14.

(23) Mitsch, R. A.; Neuvar, F. W. *J. Chem. Phys.* **1966**, *70*, 546.

(24) Bernett, W. E. *J. Org. Chem.* **1969**, *34*, 1772.

(25) Only a single proton resonance for the three *t*-BuNC ligands was observed in the ^{1}H NMR spectrum of **4a** even at −80 °C, so we cannot rule out rapid turnstile rotation or pseudorotation in this case.