

Nickel Complexes with Heterobutadiene Ligands

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The reactions of 4,4-bis(trifluoromethyl)-substituted hetero-1,3-dienes with Ni(cod)₂ and Ni(PMe₃)₂(cod) afford stable coordination compounds containing a trigonal planar Ni(0) center. The substitution of co-ligands by *tert*-butylisonitrile leads to five-membered nickelacycles by an unprecedented oxidative [4+1] cycloaddition of the hetero-1,3-diene to Ni(0) under formation of new Ni–C and Ni–O or Ni–N bonds. The nature of the resulting nickelacycloheteropentene derivatives decisively depends on the electronic and steric nature of the hetero-1,3-dienes. All compounds have been characterized by NMR, IR, or mass spectroscopy. X-ray crystal structure determinations are reported for four typical examples.

Introduction

The introduction of the trifluoromethyl group or the substitution of selected hydrogen atoms by fluorine in organic compounds gained growing interest during the past decade.¹ In particular, selectively fluorinated heterocyclic compounds have attracted much attention in terms of their biological and physiological activities, which are often dramatically raised or changed by the introduction of fluorine in the molecules.²

The large dipole moment of the CF₃ group and its chemical stability as well as the enhanced lipophilic behavior render it attractive as a functional group. Considerable efforts have been made to develop effective routes to trifluoromethyl-substituted organic compounds. Trifluoromethylation,^{1a,3} fluorination,⁴ and halogen-exchange reactions⁵ are possible means, but most of these methods suffer from low selectivity and/or drastic reaction conditions and are generally only suitable for the synthesis of trifluoromethylated aromatic compounds.

An attractive alternative approach makes use of the fluorinated heterobutadienes **1a–1d**, which are readily available from hexafluoroacetone.⁶

These unsaturated fluoroorganics rank among the most reactive conjugated heterodienes. A rich organic chemistry evolved from their outstanding properties, resulting in many types of new compounds containing trifluoromethyl substituents.⁷ They are known to add to a variety of substrates, in particular to carbenes and carbene homologues. Reactions of 1,3-diaza-1,3-butadienes **1d** with in situ generated SiCl₂,^{8,9} with GeCl₂,¹⁰ or with SnCl₂¹¹ were shown to give metallacyclopentene derivatives via [4+1] cycloaddition.

In this report, we present the first transition metal complexes of the heterobutadienes **1a–1d**. Due to the specific reactions occurring at a transition metal center and particularly at a metal–carbon bond (e.g., insertion) and, furthermore, due to the “Umpolung”¹⁰ of the heterobutadiene backbone by coordination to a metal center, the scope of reactions with these heterobutadienes

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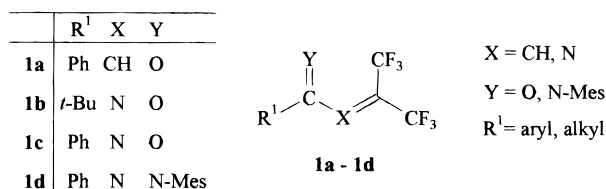
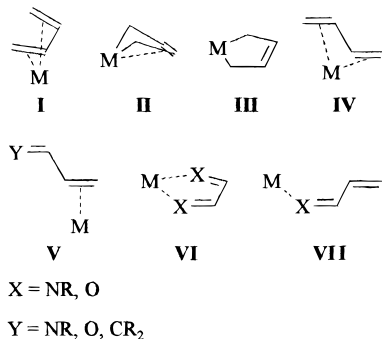
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**Figure 1.** Structural formula of heterobutadienes **1a–1d**.**Figure 2.** Coordination modes of butadienes to transition metal centers.**Table 1. Selected Transition Metal Butadiene Complexes**

complex	type	metal center and reference
L _n M(butadiene)	I	Cr, Mo, W; ^{22a-c} Ni, ^{22d} Ru ^{15b}
L _n M(heterobutadiene)	I	Fe ²⁶
L ₂ M(butadiene)	II	Ru; ²² Ti, Hf, Zr; ¹⁶ Nb, Ta, Ln, U, Th ¹⁷
L _n M(C ₄ F ₆)	III	Pt; ^{22d} Fe, Rh ^{22e-g}
L _n M(butadiene)	IV	Zr ^{16a-c}
M(PR ₃) ₂ (butadiene)	V	Pd, Pt ^{22d}
L _n M(heterobutadiene)	III, VI	Ti, Zr; ¹⁹ Si; ⁷ Pt; ²⁴ Mo ^{18b,25}
L _n M(heterobutadiene)	VII	Pd; ^{27a} Cr ^{27b}

should increase considerably, thus resulting in new perspectives for organic synthesis. Particularly useful in this respect would be the formation of metallaheterocycles via a [4+1] cycloaddition reaction, due to the generation of a metal–carbon σ -bond (M⁺–C⁻).

The coordination chemistry of butadienes and heterobutadienes toward transition metal centers is of broad general interest, since numerous organic synthesis and catalytic processes are based on those complexes.^{12,13} As a consequence, conjugated diene complexes of metals from all transition metal groups have been reported, and a variety of coordination modes have been described.¹⁴ Figure 2 represents the coordination modes of mono-nuclear butadiene and heterobutadiene complexes, and typical examples are presented in Table 1.

The vast majority of the middle and late transition metal diene complexes adopt the η^4 -*s-cis*-1,3-diene structure **I**, like (butadiene)Fe(CO)₃,^{15a} while the early transition metals of groups 3–5 prefer the σ^2 , η^2 -metal-

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lacyclopentene structure **II** or the η^4 -*s-trans*-1,3-diene structure **IV**, as for example Cp₂Zr(butadiene).¹⁶ Borderline cases are also known (e.g., between **I** and **II**, which differ only slightly in their geometrical parameters), and interconversions and/or dynamic behavior in solution is also often encountered.^{17b} Regarding heterobutadienes, extended work on the coordination of 1,4-diaza-1,3-butadienes (DAD) to several transition metal fragments was reported by tom Dieck¹⁸ and others,^{19–20} including also coordination of DAD to Ni(0) and Ni(II) centers.¹⁹ The structural types **V**, **VI**, and **VII** are dominant in the coordination chemistry of heterobutadienes, e.g., 1-aza-1,3-butadienes, 1-oxa-1,3-butadienes, or DAD,²⁰ but structural types **I** and **III** have also been observed (see Table 1).^{20,21}

Several transition metal centers have been envisaged during the course of this work to achieve coordination with the heterobutadienes **1a–1d**. However, it turned out that there are only a few successful cases, due to the high reactivity of the heterobutadienes, which is responsible for low selectivity or unwanted side reaction. Thus, reactions with the co-ligands at the metal center (preferably phosphines) and/or fluorination of the metal center with concomitant formation of imidazole derivatives are often observed.

The metal center of choice turned out to be nickel(0). It should be noted here that L₂Ni(0) fragments are isolobal to carbene homologues. The coordination chemistry of nickel(0) is of interest for synthetical and catalytical reasons, and a number of reviews have appeared,^{12,13} as well as reports on oxidative addition and coupling reactions at Ni(0) centers, forming metal–carbon σ -bonded Ni(II) complexes.^{28,29} In particular, stoichiometric reactions of carbon dioxide with unsatur-

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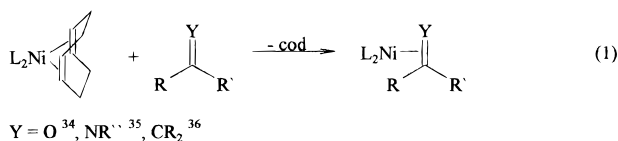
ated cosubstrates at Ni(0) centers have been investigated intensively by different groups.³⁰ These reactions lead to five-membered cyclic nickel(II) complexes. Moreover, there are many other examples of insertion reactions leading to nickelaheterocycles.³¹

Reactions of 1,3-butadienes and hetero-1,3-butadienes with Ni(0) fragments have been described in the literature, but there is a complete lack of reports on formal oxidative cycloadditions of the [4+1] type.^{32,33} Heterobutadienes **1a–1d** seemed promising candidates to fill this gap.

We now report on respective reactions and the isolation and characterization of the first [4+1] cycloaddition products of heterobutadienes with nickel(0) complexes.

Results and Discussion

A. [2+1] Cycloaddition of Hetero-1,3-butadienes 1a–1d to Nickel(0) Centers. Reactions of unsaturated compounds with nickel(0) complexes according to eq 1 are well-known (cod = 1,5-cyclooctadiene, L₂ = 2 PR₃, cod, bipy, tmeda).



The stability of the resulting coordination compounds is strongly dependent on the co-ligands L₂ and the substitution pattern of the unsaturated substrate. Some of the complexes have been characterized by X-ray crystallography,^{34c} while others could only be identified by subsequent reaction with CO₂.^{30c,d,36a}

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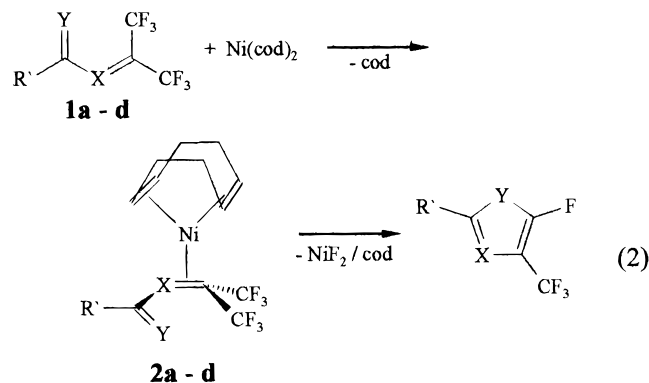
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The reactions of hetero-1,3-butadienes **1a–d** with Ni(cod)₂ led to red crystals of the coordination compounds **2a** and **2b** in quantitative yields (eq 2), while **2c** and **2d** could not be isolated: removal of the solvent from the resulting red solutions afforded brown oils, spectroscopically identified as the fluoride elimination products, the 5-fluoro-4-trifluoromethyloxazoles³⁷ and -imidazoles,³⁸ respectively, analogous with the tin(II) chloride reaction.³⁹



¹⁹F NMR spectroscopic data of **2a** and **2b** provide strong evidence for a π-coordination of the hetero-1,3-butadiene via the vinyl double bond in **2a** and the imine double bond in **2b**, indicated by a decreased shielding of the ¹⁹F nuclei. In comparison to the uncoordinated hetero-1,3-butadienes, the coordination to the Ni(cod) fragment causes a downfield shift of the ¹⁹F resonance of about 9 ppm, while the IR spectrum displays the ν(C=O) band at 1643.3 cm⁻¹, consistent with a noncoordinated C=O group in **2a** and **2b**. The proton NMR of **2a** shows an upfield chemical shift for the olefinic proton in the coordinated heterobutadiene **1a** of Δδ = -2.71 ppm, the signal being observed at δ 4.27. The olefinic protons of the coordinated 1,5-cod ligand cause two separate signals for both complexes **2a** and **2b**, indicating a rigid conformation in solution at room temperature. Furthermore **2a** and **2b** were detected by mass spectroscopy (**2a**, m/z = 434, 21.2; **2b**, m/z = 416, 100). The solid-state structure of **2a** confirms the expected coordination of the hetero-1,3-butadiene (Figure 3). Crystallographic data are given in Table 6, and selected bond distances and angles are given in Table 2.

The structure of **2a** reveals an almost trigonal planar coordination geometry with an elongated olefinic double

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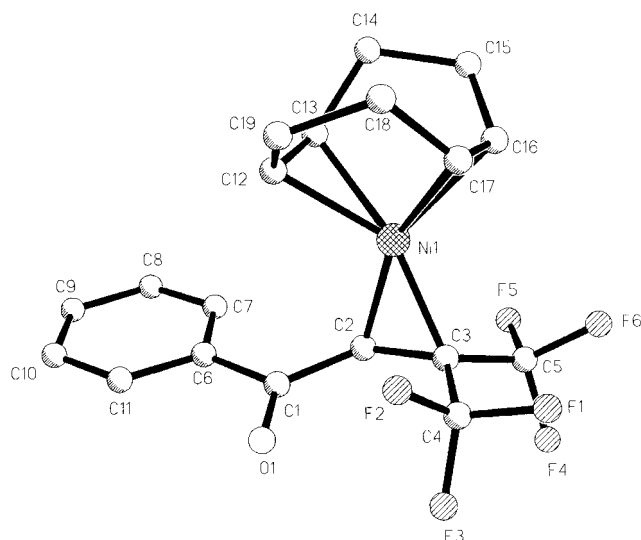


Figure 3. Crystal structure of Ni(cod)(η^2 -Ph-CO-CH=C(CF₃)₂) (**2a**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 2a

C(1)–O(1)	1.216(3)	C(1)–C(2)	1.471(3)
C(1)–C(6)	1.510(3)	C(2)–C(3)	1.442(3)
C(3)–C(4)	1.507(3)	C(3)–C(5)	1.504(3)
Ni(1)–C(2)	1.955(2)	Ni(1)–C(3)	1.962(2)
C(12)–C(13)	1.360(3)	C(16)–C(17)	1.360(4)
Ni(1)–C(12)	2.087(2)	Ni(1)–C(13)	2.118(2)
Ni(1)–C(16)	2.119(2)	Ni(1)–C(17)	2.131(2)
O(1)–C(1)–C(6)	118.4(2)	C(6)–C(1)–C(2)	118.2(2)
C(2)–C(1)–O(1)	123.4(2)	C(1)–C(2)–C(3)	127.6(2)
C(2)–C(3)–C(4)	122.5(2)	C(2)–C(3)–C(5)	116.7(2)
Ni(1)–C(2)–C(3)	68.7(1)	C(2)–C(3)–Ni(1)	68.1(1)
C(3)–Ni(1)–C(2)	43.2(1)	C(1)–C(2)–Ni(1)	113.7(2)
Ni(1)–C(3)–C(4)	113.2(2)	Ni(1)–C(3)–C(5)	115.7(2)
C(4)–C(3)–C(5)	112.9(2)	C(16)–C(17)–C(18)	124.6(2)
C(14)–C(13)–C(12)	125.4(2)	C(13)–C(12)–C(19)	125.9(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 3d

C(1)–N(1)	1.285(3)	C(1)–C(51)	1.501(3)
C(1)–N(2)	1.380(3)	C(2)–N(2)	1.395(3)
Ni(1)–C(2)	1.939(2)	Ni(1)–N(2)	1.859(2)
Ni(1)–P(1)	2.174(1)	Ni(1)–P(2)	2.194(1)
P(1)–C(11/12/13)	1.822	P(2)–C(21/22/23)	1.822
N(1)–C(1)–C(51)	124.7(2)	C(51)–C(1)–N(2)	115.3(2)
N(2)–C(1)–N(1)	119.9(2)	C(1)–N(2)–C(2)	126.4(2)
N(2)–C(2)–C(3)	120.8(2)	N(2)–C(2)–C(4)	115.2(2)
C(1)–N(1)–C(61)	122.8(2)	C(3)–C(2)–C(4)	113.6(2)
Ni(1)–N(2)–C(2)	71.6(1)	N(2)–C(2)–Ni(1)	65.4(1)
C(2)–Ni(1)–N(2)	43.0(1)	C(1)–N(2)–Ni(1)	129.9(2)
Ni(1)–C(2)–C(3)	119.3(2)	Ni(1)–C(2)–C(4)	114.3(2)
C(2)–Ni(1)–P(1)	110.4(1)	P(1)–Ni(1)–P(2)	101.6(1)
P(2)–Ni(1)–N(2)	105.0(1)	C(3)–C(2)–C(4)	113.6(2)

bond in the coordinated heterobutadiene **1a** (1.442(3) Å). The bonded carbon atoms of the coordinated heterobutadiene bond define one coordination plane together with the nickel atom, while both olefinic bonds of the 1,5-cod ligand are oriented perpendicular to this plane. The bond length of the carbonyl function (1.216(3) Å), the sum of the bond angles around carbon (360.0°), and the overall geometry exclude an interaction of the oxygen atom with the nickel atom. The coordination geometry around the nickel center, as well as the nickel carbon bond lengths, both to the cod ligand and to the coordinated heterobutadiene **1a**, and also the olefinic bond length in the heterobutadiene are in excellent

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 4d

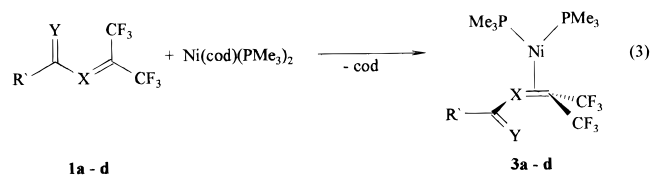
C(1)–N(1)	1.362(2)	C(1)–N(2)	1.294(2)
C(2)–N(2)	1.457(2)	Ni(1)–C(2)	1.978(2)
Ni(1)–N(1)	1.864(2)	C(1)–C(14)	1.499(3)
Ni(1)–C(20)	1.879(2)	Ni(1)–C(25)	1.818(2)
C(20)–N(3)	1.148(3)	C(25)–N(4)	1.150(3)
C(2)–C(3)	1.512(3)	C(2)–C(4)	1.520(3)
C(2)–Ni(1)–N(1)	82.7(1)	N(1)–Ni(1)–C(20)	94.5(1)
C(20)–Ni(1)–C(25)	89.1(1)	C(25)–Ni(1)–C(2)	93.9(1)
Ni(1)–N(1)–C(1)	113.5(1)	N(1)–C(1)–N(2)	121.4(2)
C(1)–N(2)–C(2)	111.2(2)	N(2)–C(2)–Ni(1)	111.0(1)
Ni(1)–N(1)–C(5)	124.4(1)	C(5)–N(1)–C(1)	121.6(2)
N(1)–C(1)–C(14)	122.6(2)	C(14)–C(1)–N(2)	116.0(2)
N(2)–C(2)–C(3)	106.2(2)	N(2)–C(2)–C(4)	105.5(2)
Ni(1)–C(2)–C(3)	113.1(1)	Ni(1)–C(2)–C(4)	109.5(1)
C(3)–C(2)–C(4)	111.2(2)	Ni(1)–C(25)–N(4)	175.0(2)
C(25)–Ni(1)–N(1)	175.3(1)	Ni(1)–C(29)–N(3)	176.1(2)
C(20)–N(3)–C(21)	177.9(2)	C(25)–N(4)–C(26)	178.1(2)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound 6a

C(1)–O(1)	1.366(3)	C(1)–C(2)	1.331(4)
C(2)–C(3)	1.521(5)	C(3)–Ni(1)	1.950(3)
Ni(1)–O(1)	1.856(2)	Ni(1)–Ni(2)	2.672(1)
Ni(1)–C(12)	1.818(3)	Ni(1)–O(2)	1.920(2)
C(12)–N(1)	1.142(4)	Ni(2)–O(1)	1.930(2)
Ni(2)–C(28)	1.817(3)	C(28)–N(2)	1.150(4)
N(2)–C(29)	1.460(4)	N(1)–C(13)	1.456(5)
Ni(2)–O(2)	1.859(2)	C(3)–C(4)	1.525(5)
C(3)–C(5)	1.504(5)	C(19)–C(20)	1.503(5)
O(1)–C(1)–C(2)	116.5(3)	C(1)–C(2)–C(3)	117.3(3)
C(2)–C(3)–Ni(1)	104.5(2)	C(3)–Ni(1)–O(1)	87.8(1)
Ni(1)–O(1)–C(1)	113.8(2)	C(3)–Ni(1)–C(12)	95.7(2)
C(12)–Ni(1)–O(2)	99.6(1)	O(2)–Ni(1)–O(1)	76.9(1)
Ni(1)–C(3)–C(4)	111.2(2)	Ni(1)–C(3)–C(5)	111.3(3)
C(2)–C(3)–C(4)	108.1(3)	C(2)–C(3)–C(5)	109.2(3)
C(4)–C(3)–C(5)	112.2(3)	Ni(1)–O(1)–Ni(2)	89.7(1)
C(2)–C(1)–C(6)	127.3(3)	C(6)–C(1)–O(1)	115.7(2)
Ni(1)–C(12)–N(1)	178.8(3)	Ni(2)–C(28)–N(2)	177.9(3)
C(12)–N(1)–C(13)	177.7(5)	C(28)–N(2)–C(29)	176.5(3)
C(12)–Ni(1)–O(1)	176.5(1)	C(28)–Ni(2)–O(2)	175.4(1)
C(3)–Ni(1)–O(2)	164.0(1)	C(19)–Ni(2)–O(1)	162.9(1)

accordance with the only known trigonal (cod)(olefin)-Ni(0) complex that was structurally characterized.⁴⁰

The substitution of the cod ligand by **1a**, **1c**, and **1d** in Ni(PMe₃)₂(cod) (eq 3) resulted in the coordination compounds **3a**, **3c**, and **3d** in quantitative yields, while the reaction with heterobutadiene **1b** did not result in the formation of a stable Ni(0) complex.



In **3a**, the ¹⁹F nuclei of the trifluoromethyl groups are even more deshielded than in **2a** ($\Delta\delta = 12$ ppm), which is consistent with a stronger interaction between the hetero-1,3-butadiene **1a** and the Ni(PMe₃)₂ moiety. The ³¹P{¹H} NMR spectrum displays two separate signals: a doublet at $\delta -13.01$, with a coupling constant of ²J_{P-P} = 17.2 Hz, and a multiplet (dq) at $\delta -15.80$ (²J_{P-P} = 17.2 Hz, ⁴J_{P-F} = 8.6 Hz, ⁴J_{P-F} = 8.6 Hz). Small amounts of impurities (i.e., excess **1a**) catalyze a fast ligand

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Table 6. Crystallographic Data for Ni(η^2 -[Ph-CO-CH=C(CF₃)₂])[η^4 -(1,5-cod)] (2a**), Ni(η^2 -[Ph-C(N-Mes)-N=C(CF₃)₂])(PMe₃)₂ (**3d**), (*t*-Bu-NC)₂Ni-N(Mes)-C(Ph)=N-C(CF₃)₂ (**4d**), and [(*t*-Bu-NC)Ni-O-C(Ph)=CH-C(CF₃)₂]₂ (**6a**)**

	2a	3d	4d	6a
formula	C ₁₉ H ₁₈ F ₆ NiO	C ₂₅ H ₃₄ F ₆ N ₂ NiP ₂	C ₂₉ H ₃₄ F ₆ N ₄ Ni	C ₃₂ H ₃₀ F ₁₂ N ₂ Ni ₂ O ₂
fw (g mol ⁻¹)	435.041	597.191	611.311	820.001
temp (K)	199(2)	199(2)	194(2)	203(2)
cryst size (mm)	0.1 × 0.15 × 0.5	0.6 × 0.45 × 0.45	0.21 × 0.3 × 0.6	0.3 × 0.45 × 0.45
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	<i>P2₁/c</i>	<i>Pca2₁</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> (Å)	12.115(1)	19.754(2)	11.479(1)	18.994(2)
<i>b</i> (Å)	9.311(1)	12.066(1)	18.482(1)	11.377(1)
<i>c</i> (Å)	15.057(1)	12.019(1)	15.128(1)	18.074(2)
α (deg)	90	90	90	90
β (deg)	91.44(1)	90	108.71(1)	108.09(1)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	1697.9(3)	2864.7(4)	3039.9(4)	3712.6(7)
<i>Z</i>	4	4	4	4
cryst color, habit	red block	red block	orange block	red block
<i>d</i> calc (g cm ⁻³)	1.702	1.385	1.336	1.467
μ Mo K α (mm ⁻¹)	1.211	0.844	0.699	1.104
<i>F</i> (000)	888	1240	1272	1664
θ range (deg)	3.0 to 27.0	3.16 to 26.91	3.0 to 26.0	3.26 to 25.95
limiting indices	-15 ≤ <i>h</i> ≤ 15 0 ≤ <i>k</i> ≤ 11 0 ≤ <i>l</i> ≤ 19	0 ≤ <i>h</i> ≤ 25 0 ≤ <i>k</i> ≤ 15 -15 ≤ <i>l</i> ≤ 15	0 ≤ <i>h</i> ≤ 14 -22 ≤ <i>k</i> ≤ 0 -18 ≤ <i>l</i> ≤ 17	-23 ≤ <i>h</i> ≤ 22 0 ≤ <i>k</i> ≤ 14 0 ≤ <i>l</i> ≤ 22
no. of reflns coll	3826	6192	5934	7475
no. of indep reflns	3682	6192	5934	7229
ρ_{\max} , ρ_{\min} (e Å ⁻³)	0.679, -0.419	0.271, -0.188	0.663, -0.334	0.729, -0.691
goodness of fit on <i>F</i> ²	1.069	1.143	1.044	1.046

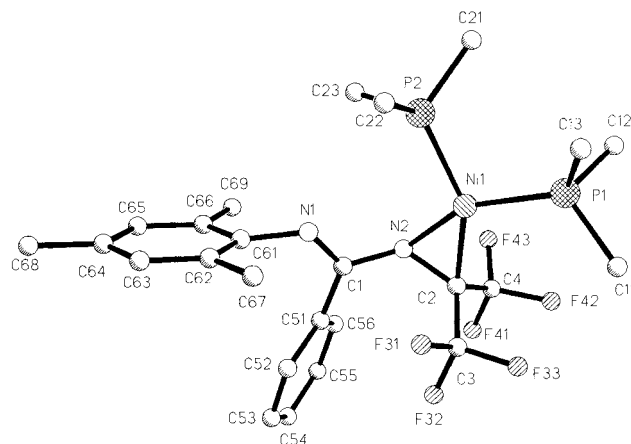


Figure 4. Crystal structure of Ni(PMe₃)₂(η^2 -Ph-C(N-Mes)-N=C(CF₃)₂) (**3d**).

exchange in **3a**, giving rise to a single ³¹P resonance at δ -14.72. In **3d**, the 1,3-diaza-1,3-butadiene **1d** is bonded to the (Me₃P)₂Ni(0) fragment in the same manner. The imine moiety exhibits a strong interaction with the Ni(0) center, as the two phosphine ligands again show different ³¹P resonances: a doublet at δ -12.32, with a coupling constant of ²*J*_{P-P} = 10.0 Hz, and an unresolved multiplet at δ -14.16, arising from an ABX₆ spin system. Furthermore, **3a** and **3d** were detected by mass spectroscopy (**3a**, *m/z* = 479, 18.9; **3d**, *m/z* = 521, [**3d** - PMe₃]⁺, 4.3). Crystals suitable for X-ray analysis of **3d** (Figure 4) were obtained by slowly removing the solvent of the filtered solution. Crystallographic data are given in Table 6, and selected bond distances and angles for **3d** are given in Table 3.

The coordination geometry around the nickel center in **3d** can be described as trigonal planar (sum of angles around Ni: 359.3°). The *N*-mesityl-substituted imine double bond does not participate in any interactions

with the Ni atom. The C(1)-N(1) bond length (1.285(3) Å) and the coordination geometry around the sp² imine carbon atom are in good accordance with this finding. The coordinated imine bond C(2)-N(2) in **3d** is significantly elongated; in fact it is in the range for C-N single bonds (1.395(3) Å). Accordingly, the Ni-N bond in **3d** (1.859(2) Å) is the shortest of structurally investigated η^2 -imine complexes (cf.: Ni-N = 1.915(3) Å in (PR₃)₂-Ni(η^2 -*t*-Bu-N=CHPh);⁴¹ but Ni-N = 1.82(1) Å in (PMe₃)-NiCl(σ -C, σ -N-C[CH(SiMe₃)₂]=N-*t*-Bu)⁴²), whereas the nickel-carbon bond (1.939(2) Å) is similar to the foregoing example (Ni-C, 1.959(4);⁴¹ but Ni-C, 1.84(1) Å⁴²). Ni-P bond distances (2.1742(8) and 2.1944(8) Å) range within the upper region of documented Ni-P distances^{41,42} and indicate a low degree of back-donation from the Ni center. Nevertheless there is no fast exchange of the trimethylphosphine ligands in solution at room temperature (see above). The sum of the involved angles around N(2) in **3d** amounts to the tetrahedral value of 327.9°, which is significantly more than usually found in three-membered azacycles (sum of angles around 280°).⁴³ The overall geometry of **3d** suggests that the complex is a borderline case between nickel(0) and nickel(II).

B. [4+1] Cycloaddition of the Hetero-1,3-butadienes 1a-1d to Nickel(0) Centers. To accomplish oxidative [4+1] cycloadditions at Ni(0) moieties, several ligand properties must be tuned carefully. Soft electron-donating ligands obviously are less suitable, and sterical hindrance in a square planar coordination sphere reduces the variety of suitable ligands drastically. Trimethylphosphine, a good but soft electron-donating ligand of modest sterical demand, obviously does not

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(42) Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Sernau, V.; Carmona, E.; Gutierrez, E.; Monge, A. *Polyhedron* **1995**, *14*, 323.

(43) Drück, U.; Littke, W. *Acta Crystallogr.* **1979**, *B35*, 1905.

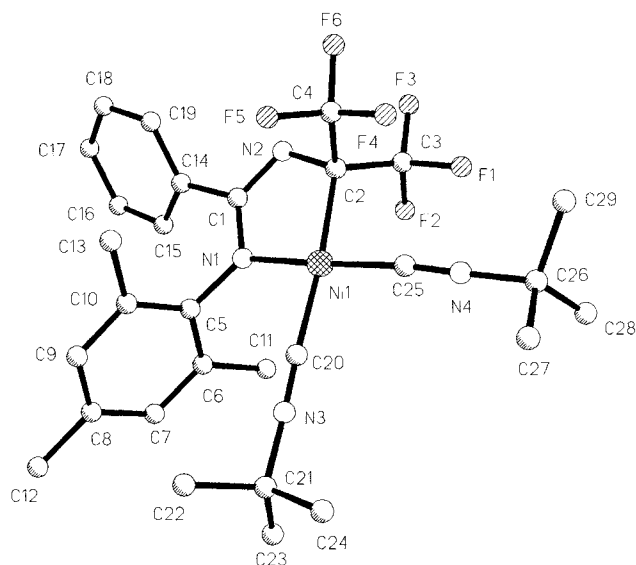
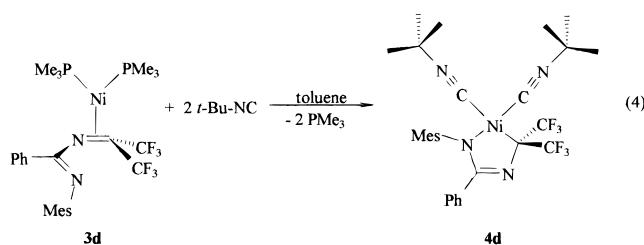


Figure 5. Crystal structure of $\text{Ni}(-\text{N}(\text{Mes})-\text{C}(\text{Ph})=\text{N}-\text{C}(\text{CF}_3)_2)(t\text{-Bu-NC})_2$ (**4d**).

allow for an oxidative [4+1] cycloaddition of the hetero-1,3-butadienes to the Ni(0) moiety.

Substitution of both trimethylphosphine ligands in **3d** by 2 equiv of *tert*-butylisocyanide (eq 4) did not result in just another Ni(0) coordination compound, but [4+1] cycloaddition of the heterobutadiene did occur.

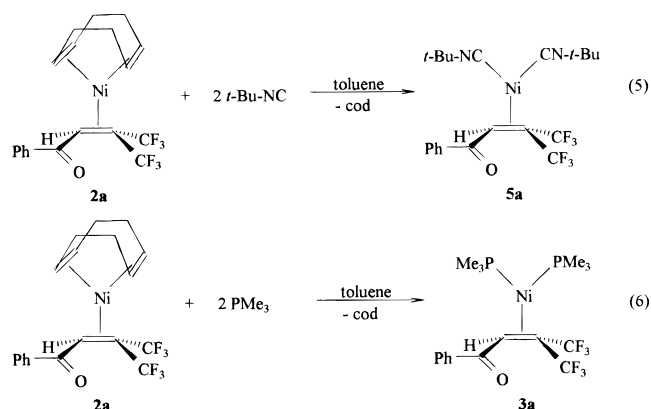


Orange crystals of **4d** could be isolated from the toluene solution in quantitative yield. The compound shows typical features for Ni(II) complexes. The IR spectrum of **4d** displays two absorption bands at $\nu(\text{C}\equiv\text{N}) = 2205.3 \text{ cm}^{-1}$ and $\nu(\text{C}\equiv\text{N}) = 2188.1 \text{ cm}^{-1}$, characteristic for *tert*-butylisocyanide coordinated to nickel(II) centers.^{34a} The ^1H NMR spectrum in solution at room temperature of **4d** reveals two different resonances ($\delta = 0.58$, s, 9 H; $\delta = 0.94$, s, 9 H) for the *tert*-butyl protons, thus indicating two nonequivalent isocyanide ligands, due to a rigid square planar arrangement around the nickel center. This is in agreement with the results of an X-ray study (Figure 5), indicating a slightly distorted square planar coordination geometry around the nickel center. The mean deviation from the best plane is 0.0498 Å. Crystallographic data are given in Table 6, and selected bond distances and angles for **4d** are given in Table 4.

The bond distances and angles correspond well to localized bonds within a metallaheterocyclopentene moiety. The five-membered metallacycle is almost planar, with the Ni atom deviating by 0.0133 Å from the plane. The endocyclic bond lengths for the organic part in **4d**, C(1)–N(1) (1.362(2) Å), C(1)–N(2) (1.294(2) Å), and C(2)–N(2) (1.457(2) Å), mirror the change in the electronic structure of the coordinated heterobutadiene

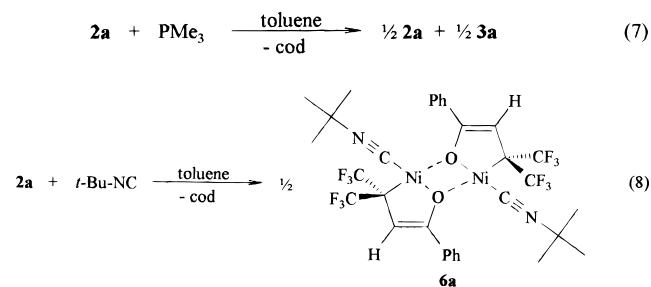
1d in **4d**, compared to that in **3d** (C(1)–N(1), 1.285(3) Å; C(1)–N(2), 1.380(3) Å; and C(2)–N(2), 1.395(3) Å). The nickel bonds Ni(1)–C(2), 1.978(2), and Ni(1)–N(1), 1.864(2) Å, like all other distances and angles match well the expectations for a nickel(II) cycloaddition product.

Quite remarkably, the reaction of **2a** with 2 equiv of *tert*-butylisocyanide (eq 5) led again to a [2+1] cycloaddition product **5a** in quantitative yield, analogous with the reaction of **2a** with 2 equiv of trimethylphosphine, which gave **3a** (eq 6).



5a was isolated as an orange solid from toluene. Recrystallization from benzene afforded orange crystals in quantitative yield. According to NMR spectroscopy, **5a** is subject to stereochemical nonrigidity in solution at room temperature. The isocyanide ligands exhibit one broad singlet in the proton NMR, while the trifluoromethyl groups in the ^{19}F NMR appear as two quartets. The coordination via the olefinic double bond is indicated by a downfield ^{19}F chemical shift, compared to the free ligand **1a** ($\Delta\delta = 10$ ppm).

Whereas the reaction of **2a** with only 1 equiv of trimethylphosphine led to **3a** (eq 7), the analogous reaction of **2a** with only 1 equiv of *tert*-butylisocyanide gave a dimeric compound **6a** (eq 8).



The ^{19}F NMR spectrum of the isolated red crystals of compound **6a** exhibits one singlet at $\delta 19.50$. This clearly is at variance with the findings for **5a** and rules out a π -bonded coordination via the olefinic double bond. The equivalence of both trifluoromethyl groups indicates a [4+1] cycloaddition product with formation of a pentacycle, instead. The IR spectrum of **6a** displays only one absorption band at 2213.9 cm^{-1} . This is consistent with the $\text{C}\equiv\text{N}$ stretching frequency of isocyanide ligands coordinated to Ni(II) centers.^{34a} From signal intensities in the ^1H NMR spectrum, a ratio **1a**:*t*-Bu-NC of 1:1 can be inferred. A tricoordinate Ni(II) center, stabilized by only one neutral donor ligand, should be unstable, and

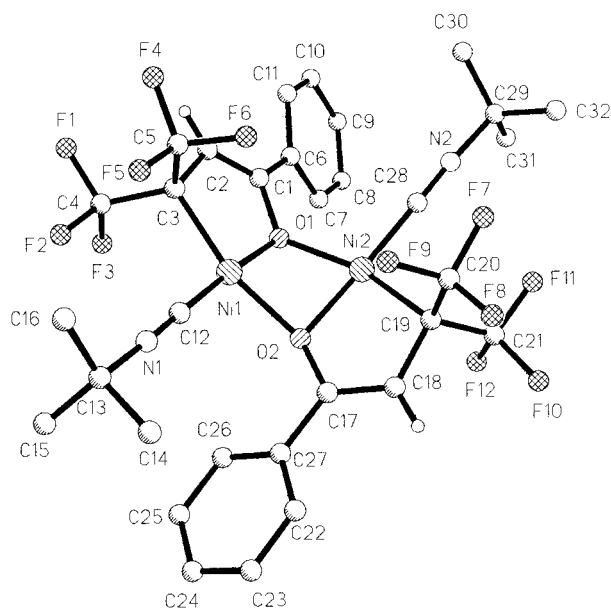


Figure 6. Crystal structure of $[\text{Ni}(-\text{O}-\text{C}(\text{Ph})=\text{CH}-\text{C}(\text{CF}_3)_2)(t\text{-Bu}-\text{NC})_2]$ (**6a**).

therefore dimerization had to be envisaged. In fact, the postulated dimeric structure was confirmed by an X-ray crystallographic study (Figure 6). Crystallographic data are given in Table 6, and selected bond distances and angles for **6a** are given in Table 5. The *tert*-butyl groups in **6a** are disordered and could not be resolved computationally. This has no influence on the structural findings concerning the environment of the central metal atoms.

The oxygen of one 1-nickela-2-oxa-cyclopentene moiety is acting as a bridge to the second metallaheterocycle and thus establishes the dimeric structure. Although the distance between both nickel atoms (2.6718(6) Å) is in the range for Ni–Ni single bonds, a bonding interaction seems not to be operating. Both nickel atoms are surrounded almost equally, although there is no center of symmetry in the molecule. They possess a distorted square planar environment constituted by two oxygen atoms, one isonitrile carbon atom, and the bistrifluoromethyl-substituted carbon atom of the former heterobutadiene. The bridging oxygen atoms deviate slightly from this plane (mean deviation from planarity 0.0584 Å). The nickelaheterocycles are nearly planar (mean deviation from planarity 0.0026 Å). Similar to the ring in **4d**, the bonds in the heterocycle are not delocalized, as discrete single and double bonds are found around the ring (Ni(1)–O(1) 1.856(2) Å, O(1)–C(1) 1.366(3) Å, C(1)–C(2) 1.331(4) Å, C(2)–C(3) 1.521(5) Å, and C(3)–Ni(1) 1.950(3) Å). A comparison with compound **2a** underlines the difference in the electronic structure of both compounds (**2a**: O(1)–C(1) 1.216(3) Å, C(1)–C(2) 1.471(3) Å, C(2)–C(3) 1.442(3) Å). The Ni and O atoms form a folded four-membered ring; the planes defined by the atoms Ni(1), O(1), O(2) and Ni(2), O(2), O(1) include an angle of 128.4°. The bridging Ni–O bonds are only slightly longer (Ni(1)–O(2) 1.920(2) Å, Ni(2)–O(1) 1.930(2) Å) than the Ni–O bonds within the metallacyclopentenes. Although there is no direct precedent of **6a**, dimeric organonickel alkoxides and Ni(II) complexes with Schiff base type ligands have been

described, and bond lengths and angles are in good accordance.^{44,45}

Conclusion

The nickel(0) complexes **2a** and **3d** undergo intramolecular coupling reactions of the nickel moiety and the hetero-1,3-butadiene ligand with formation of compounds **6a** and **4d**, containing localized, unsaturated, five-membered nickelaheterocycles. The generation of the nickelaheterocycles can be viewed as formal [4+1] cycloaddition of heterobutadienes **1a–1d** to a Ni(0) moiety with formation of metal–carbon σ -bonds. This type of reaction, analogous with the Diels–Alder addition, is unprecedented for nickel(0) centers. In addition, these complexes provide the first examples of a coordination of fluoromethyl-substituted heterobutadienes to a transition metal center. The concomitant “Umpolung” of the heterobutadiene backbone should decisively extend the scope of reactions for organic synthesis.

Experimental Section

General Considerations. All operations were performed under an atmosphere of dry nitrogen and with thoroughly dried glassware by use of standard high-vacuum-line techniques. Pentane, diethyl ether, toluene, and THF were distilled under nitrogen from sodium/potassium alloy. All organic reagents were purified by conventional methods. Elemental analyses were determined by Microanalytisches Labor der TU München. In all cases where satisfying elemental analyses could not be obtained (compounds **2** and **3**), mass spectra give the correct composition by identification of the molecular peak and a reasonable fragmentation pattern. High-resolution electron impact (EI) and chemical ionization (CI) mass spectral data were obtained employing a Varian Mat 311A spectrometer; peaks are reported as m/z (assignment, relative intensity). ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F , and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a JEOL JNM-LA400 spectrometer operating at 399.8, 100.5, 376.1, and 161.8 MHz, respectively. ^1H and ^{13}C NMR chemical shifts (δ) are referenced to the internal residual proton or natural abundance ^{13}C resonances of the deuterated solvent relative to TMS ($\delta = 0$). ^{19}F and ^{31}P NMR spectra are referenced to external CF_3COOH ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$), respectively. All measurements were carried out at 25 °C in C_6D_6 . Exceptions are given separately. Chemical shifts are reported according to the δ convention in parts per million (ppm) and coupling constants J are in Hz. IR data were collected on a Nicolet 5DX FT-IR spectrophotometer. $\text{Ni}(\text{cod})_2$ was a donation of Dr. K. Pörschke, MPI für Kohleforschung, Mülheim a. d. Ruhr, and was not further purified prior to use. PMe_3 ⁴⁶ and $\text{Ni}(\text{cod})(\text{PMe}_3)_2$ ⁴⁷ were prepared by literature methods. The heterobutadienes **1a**,⁴⁸ **1b**,⁴⁹ **1c**,⁴⁹ and **1d**⁵⁰ were either prepared by literature methods or provided by Prof. K.

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Burger (University of Leipzig). All other reagents were purchased from Aldrich.

Preparations. Ni(cod)(η^2 -Ph-CO-CH=C(CF₃)₂) (2a). Ni(cod)₂ (1.62 g, 5.89 mmol) was suspended in 50 mL of pentane, and the suspension was cooled to -78 °C. Heterobutadiene **1a** (1.2 mL, 6.5 mmol) was added while stirring the suspension. The color changed from yellow to orange. After the reaction was stirred for 3 h and allowed to warm to room temperature, the solvent was removed under reduced pressure. The product was dissolved in 50 mL of toluene. The resulting deep red solution was filtered, and slowly removing the solvent under reduced pressure gave red crystals of **2a**. Yield: 2.39 g (93.4%). Mass spectrum (CI): 434 (21.2), [M]⁺; 268 (42.3), [1a]⁺; 166 (43.8), [M⁺ - 1a]. ¹H NMR (C₆D₆): δ 1.31–2.03 (m, 8H, CH₂), 4.27 (s, 1H, CH), 4.58 (m, 2H, CH), 5.38 (m, 2H, CH), 7.06–7.20 (m, 3H, Ph), 7.82–7.85 (m, 2H, Ph). ¹⁹F NMR (C₆D₆): δ 21.50 (q, ⁴J_{(F-F)}} = 9.2 Hz, 3F, CF₃), 26.63 (q, ⁴J_{(F-F)}} = 9.2 Hz, 3F, CF₃). IR (Nujol): 1643.3 (m), ν (C=O); 1572.9 (w), ν (C=C). Anal. Calcd for C₁₉H₁₈F₆NiO: C, 52.46; H, 4.17. Found: C, 51.23; H, 4.20.

Ni(cod)(η^2 -*t*-Bu-CO-N=C(CF₃)₂) (2b). Ni(cod)₂ (1.51 g, 5.50 mmol) was suspended in 50 mL of pentane, and the suspension was cooled to -78 °C. Heterobutadiene **1b** (1.1 mL, 5.7 mmol) was added while stirring the suspension. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for 24 h. The color changed from yellow to orange-red. The reaction mixture was filtered, and slowly removing the solvent under reduced pressure gave an orange microcrystalline solid of compound **2b** (0.69 g). The residue was dissolved in 30 mL of toluene and filtered, and after slowly removing the solvent under reduced pressure red crystals of **2b** (1.48 g) were isolated. Yield: 2.17 g (94.8%). Mass spectrum (CI): 416 (100), [M]⁺; 166 (43.7), [M⁺ - 1b]. ¹H NMR (C₆D₆): δ 1.37 (s, 9H, *t*-Bu), 1.46–1.54 (m, 4H, 2 CH₂), 1.87–1.91 (m, 4H, 2 CH₂), 5.00 (br, 2H, 2 CH), 6.02 (m, 2H, 2 CH). ¹⁹F NMR (C₆D₆): δ 17.97 (s, 6F, 2 CF₃). Anal. Calcd for C₁₆H₂₁F₆NNiO: C, 46.1; H, 5.1; N, 3.4. Found: C, 43.3; H, 4.9; N, 3.2.

Ni(PMe₃)₂(η^2 -Ph-CO-CH=C(CF₃)₂) (3a). A pentane solution of Ni(PMe₃)₂(cod) was prepared by addition of 2 equiv of PMe₃ (0.67 mL, 6.46 mmol) to a stirred suspension of Ni(cod)₂ (0.89 g, 3.23 mmol) in 50 mL of pentane at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. After cooling the resulting green solution again to -78 °C, heterobutadiene **1a** was added. The mixture was allowed to warm to room temperature and stirred for 20 h. The green solution turned to an orange suspension. The solvent and volatile components were removed in vacuo, and the residue was dissolved in 30 mL of toluene. The resulting red solution was filtered, and by slowly removing the solvent 1.39 g of a wine red solid (89.8%) was obtained. IR (Nujol): 1632.0 (m), ν (C=O); 1573.7 (w), ν (C=C). Mass spectrum (CI): 479 (18.9), [M]⁺; 403 (1.5), [M⁺ - PMe₃]; 326 (3.3), [M⁺ - 2 PMe₃]; 210 (63.3%), [M⁺ - 1a]. ¹H NMR (C₆D₆): δ 0.82 (d, ²J_{(H-P)}} = 7.0 Hz, 18H, 2 PMe₃), 3.93 (s, 1H, CH), 7.09–7.17 (m, 3H, Ph), 8.17–8.21 (m, 2H, Ph). ¹⁹F NMR (C₆D₆): δ 23.19 (q, ⁴J_{(F-F)}} = 9.2 Hz, 3F, CF₃), 29.35 (q, ⁴J_{(F-F)}} = 9.2 Hz, 3F, CF₃). ³¹P{¹H} NMR (C₆D₆): δ -14.72 (s, PMe₃). Anal. Calcd for C₁₇H₂₄F₆NiOP₂: C, 42.63; H, 5.05. Found: C, 40.66; H, 4.22.

Ni(PMe₃)₂(η^2 -Ph-CO-N=C(CF₃)₂) (3c). A pentane solution of Ni(PMe₃)₂(cod) was prepared, analogous with the procedure for **3a**, by using 0.93 g of Ni(cod)₂ (3.38 mmol) and 0.70 mL of PMe₃ (6.8 mmol). At -78 °C 0.65 mL (3.38 mmol) of heterobutadiene **1c** was added. The mixture was allowed to warm to room temperature and stirred for 20 h. After filtration, the solvent was removed slowly under reduced pressure and 1.51 g of a red microcrystalline solid (93.1%) was obtained. ¹H NMR (C₆D₆): δ 0.92 (br, 18H, 2 PMe₃), 7.06–7.11 (m, 3H, Ph), 8.13–8.14 (m, 2H, Ph). ¹⁹F NMR (C₆D₆): δ 19.88 (s, 6F, 2 CF₃). ³¹P{¹H} NMR (C₆D₆): δ -13.00 (br, PMe₃). Anal.

Calcd for C₁₆H₂₃F₆NNiOP₂: C, 40.04; H, 4.83; N, 2.92. Found: C, 37.71; H, 5.2; N, 2.67.

Ni(PMe₃)₂(η^2 -Ph-C(N-Mes)-N=C(CF₃)₂) (3d). A pentane solution of Ni(PMe₃)₂(cod) was prepared, analogous with the procedure for **3a**, by using 0.74 g of Ni(cod)₂ (2.69 mmol) and 0.56 mL of PMe₃ (5.38 mmol). At -78 °C 0.75 mL (2.52 mmol) of heterobutadiene **1d** was added and the mixture allowed to warm to room temperature with continuing stirring for 20 h. The reaction mixture was filtered, and slowly removing the solvent under reduced pressure yielded 1.40 g of orange crystals of **3d** (93.0%). Mass spectrum (CI): 520 (7.0), [M⁺ - PMe₃]. ¹H NMR (C₆D₆): δ 0.88 (d, ²J_{(H-P)}} = 7.6 Hz, 9H, PMe₃), 1.13 (d, ²J_{(H-P)}} = 8.2 Hz, 9H, PMe₃), 2.16 (s, 3H, *p*-CH₃, mes), 2.32 (s, 6H, 2 *o*-CH₃, mes), 6.80 (s, 2H, *m*-H, mes), 6.93–7.07 (m, 3H, Ph), 7.62–7.65 (m, 2H, Ph). ¹⁹F NMR (C₆D₆): δ 19.90 (s, 6F, 2 CF₃). ³¹P{¹H} NMR (C₆D₆): δ -12.32 (d, ²J_{(P-P)}} = 10.0 Hz, PMe₃), -14.16 (m, PMe₃). Anal. Calcd for C₂₅H₃₄F₆N₂-NiP₂: C, 51.85; H, 5.92; N, 4.84. Found: C, 48.35; H, 5.67; N, 4.33.

Ni(-N(Mes)-C(Ph)=N-C(CF₃)₂)(*t*-Bu-NC)₂ (4d). To a solution of 0.17 g of **3d** (0.28 mmol) in 40 mL of toluene was added with stirring 0.1 mL (0.96 mmol) of *tert*-butylisocyanide at -78 °C. The reaction mixture was stirred for 15 h at -78 °C and then allowed to warm to room temperature, filtered, and concentrated to dryness in vacuo. The resulting yellow solid was recrystallized from benzene at room temperature to afford 0.17 g (99.3%) of orange crystals of **4d**. IR (Nujol): 2205.3 (m), ν (C=N); 2188.1 (m), ν (C=N); 1557.0 (w), ν (C=N). ¹H NMR (C₆D₆, rt): δ 0.58 (s, 9H, *t*-Bu), 0.94 (s, 9H, *t*-Bu), 1.92 (s, 3H, *p*-CH₃, mes), 2.47 (s, 6H, 2 *o*-CH₃, mes), 6.51 (s, 2H, *m*-H, mes), 6.89 (br, 3H, Ph), 7.58 (br, 2H, Ph). ¹⁹F NMR (C₆D₆): δ 17.21 (s, 6F, 2 CF₃). Anal. Calcd for C₂₉H₃₄F₆N₄Ni: C, 56.97; H, 5.61; N, 9.17. Found: C, 56.06; H, 5.59; N, 8.56.

Ni(*t*-Bu-NC)₂(η^2 -Ph-CO-CH=C(CF₃)₂) (5a). To a solution of 0.53 g of **2a** (1.20 mmol) in 40 mL of toluene was added with stirring 0.25 mL (2.41 mmol) of *tert*-butylisocyanide at -78 °C. The reaction mixture was stirred for 1 h at -78 °C and then allowed to warm to room temperature, filtered, and concentrated to dryness in vacuo. The resulting orange solid was recrystallized at room temperature from benzene to afford 0.59 g (99.7%) of orange crystals of compound **5a**. IR (Nujol): 2181.5 (m), ν (C=N); 2156.6 (m), ν (C=N); 1649.3 (w), ν (C=O). ¹H NMR (C₆D₆): δ 0.68 (s, 18H, 2 *t*-Bu), 4.75 (s, 1H, CH), 7.01–7.10 (m, 3H, Ph), 8.08–8.10 (m, 2H, Ph). ¹⁹F NMR (C₆D₆): δ 22.06 (q, ⁴J_{(F-F)}} = 9.3 Hz, 3F, CF₃), 26.95 (q, ⁴J_{(F-F)}} = 9.3 Hz, 3F, CF₃). Anal. Calcd for C₂₁H₂₄F₆N₂NiO: C, 51.15; H, 4.91; N, 5.68; Ni, 11.90. Found: C, 50.83; H, 4.91; N, 5.68; Ni, 12.30.

[Ni(-O-C(Ph)=CH-C(CF₃)₂)(*t*-Bu-NC)]₂ (6a). To a solution of 1.05 g of **2a** (2.41 mmol) in 20 mL of toluene was added with stirring 0.25 mL (2.41 mmol) of *tert*-butylisocyanide at -40 °C. The reaction mixture changes its color spontaneously from dark red to light green but returns to red within a few seconds. The solution was then allowed to warm to room temperature and was stirred for 15 h. Slowly removing the solvent gave red crystals of compound **6a**. Yield: 0.98 g (99.2%). IR (Nujol): 2213.9 (m), ν (C=N); 1645.6 (w), ν (C=C). ¹H NMR (C₆D₆): δ 0.45 (s, 18H, 2 *t*-Bu), 4.77 (s, 2H, CH), 6.85 (br, 6H, Ph), 7.51 (br, 4H, Ph). ¹⁹F NMR (C₆D₆): δ 19.50 (s, 12F, 4 CF₃). Anal. Calcd for C₃₂H₃₀F₁₂N₂Ni₂O₂: C, 46.87; H, 3.69; N, 3.42. Found: C, 46.93; H, 3.61; N, 3.24.

X-ray Structural Solution and Refinement. The same general procedures were employed to collect the X-ray diffraction data for complexes **2a**, **3d**, **4d**, and **6a**. Crystal data collection and refinement parameters are given in Table 6, while selected bond lengths and angles are presented in Tables 2, 3, 4, and 5. Diagrams showing the solid-state conformation of **2a**, **3d**, **4d**, and **6a** can be found in Figures 3, 4, 5, and 6, respectively.

Compounds 2a, 3d, 4d, and 6a. Suitable single crystals of **2a**, **3d**, **4d**, and **6a** were sealed into glass capillaries and

used for measurement of precise cell constants and for intensity data collection. X-ray intensity data were recorded at -74 °C for **2a** and **3d**, at -79 °C for **4d**, and at -70 °C for **6a** on a Enraf-Nonius CAD4 diffractometer utilizing monochromated Mo K α radiation ($\lambda = 0.71073$ Å). During data collections, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. The structures were solved by direct methods (SHELXS-86)⁵¹ and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).⁵² Diffraction intensities were corrected for Lp and absorption effects. The thermal motions of all non-hydrogen atoms were treated anisotropically. All hydrogen atoms were calculated in idealized positions, and their isotropic thermal parameters were tied to that of the adjacent carbon by a factor of 1.5. The only exceptions are the olefinic protons in the bonded heterobutadiene in structure **6a**. They were refined directly. The

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structure of **2a** converged for 244 refined parameters to R1 (wR2) = 0.0314 (0.0794) for 3826 reflections with $F > 4\sigma(F)$. The structure of **3d** converged for 335 refined parameters to R1 (wR2) = 0.0292 (0.0894) for 6192 reflections with $F > 4\sigma(F)$. The structure of **4d** converged for 361 refined parameters to R1 (wR2) = 0.0353 (0.0880) for 5934 reflections with $F > 4\sigma(F)$. The structure of **6a** converged for 451 refined parameters to R1 (wR2) = 0.0402 (0.0942) for 7475 reflections with $F > 4\sigma(F)$. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-408605, 408604, 408603, 408606, the names of the authors, and the full journal citation.

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Supporting Information Available: Tables of crystal data, bond lengths, atomic coordinates, and thermal parameters for **2a**, **3d**, **4d**, and **6a** (21 pages). See any current masthead page for ordering and Internet access instructions.

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