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Synthesis, Structure, and Properties of $\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ and $(^tBu_2PC_2H_4P^tBu_2)Ni(\eta^2\text{-}C_6F_6)$[1]

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Thermolysis of $(^tBu_2PC_2H_4P^tBu_2)NiMe_2$ in benzene or reduction of $(^tBu_2PC_2H_4P^tBu_2)NiCl_2$ with Mg* in THF/benzene affords a solution of mononuclear $(^tBu_2PC_2H_4P^tBu_2)Ni(\eta^2\text{-}C_6H_6)$ (**1**) and dinuclear $\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ (**2**) in equilibrium. Complex **2** has been isolated; the X-ray structure analysis reveals an antifacial coordination of the $[(^tBu_2PC_2H_4P^tBu_2)Ni^0]$ moieties to adjacent C═C bonds of a formal cyclohexatriene ligand. According to solid-state and solution NMR the structure of **2** is static in the solid and fluxional in solution. Displacement of the benzene ligand in **1** or **2** by C_6F_6 affords mononuclear $(^tBu_2PC_2H_4P^tBu_2)Ni(\eta^2\text{-}C_6F_6)$ (**5**) for which the molecular structure is also reported.

Introduction

Nickel(0) complexes with benzene or other arene ligands are relatively rare. Following first reports of Stone and co-workers on complexes $L_2Ni\{C_6(CF_3)_6\}$ and $(L_2Ni)_2\{\mu\text{-}C_6(CF_3)_6\}$ ($L_2 = C_8H_{12}$; L = $P(OR)_3$, PR_3),[2] Jonas prepared a series of compounds of the type $\{R_2P(CH_2)_nPR_2\}Ni(\text{arene})$ (R = *c*-C_6H_{11}; n = 2, 3; arene = benzene, naphthalene, anthracene).[3] The derivatives $(R_3P)_2Ni(\eta^2\text{-}C_{14}H_{10})$ (R = Et,[4] Bu,[4] *c*-C_6H_{11}[5]), $(Et_2PC_2H_4PEt_2)Ni(\eta^{3,4}\text{-}C_{14}H_{10})$,[6] and $(^iPr_2PC_2H_4P^iPr_2)Ni(\eta^2\text{-}C_{10}H_8)$[7] have been structurally characterized. The alkene complex type coordination mode of the *anellated* aromatic ring ligands may be explained on the basis that the arene $4n + 2$ electrons are partially localized in a diene and a $4n - 2$ electron section. While the nickel atom is complexed to the diene part, aromaticity is preserved in the remaining part of the ligand. In addition, it has been shown by solution[8,9] and solid-state[8] NMR that the coordination of the arene ligands to the nickel center is dynamic with respect to an exchange of coordinated and noncoordinated C═C bonds in the same and in different rings.

In the case of *benzene*, the mononuclear and dinuclear complexes $(R_2PC_3H_6PR_2)Ni(C_6H_6)$ and $\{(R_2PC_2H_4PR_2)Ni\}_2(\mu\text{-}C_6H_6)$ (R = *c*-C_6H_{11}) have been isolated.[3] An alkene-type *two-electron* coordination of the benzene ligand to nickel appears to be likely, but so far no structural or spectroscopic data have been available to support this assumption. Unlike for anellated arenes, an alkene-type coordination of benzene induces a more or less complete localization of C═C and C−C bonds and requires that the resonance energy is largely overcome. Our interest in complexes of this type arose from two facts. We had recently synthesized $(\eta^1\text{-}^tBu_2PCH_2P^tBu_2)Ni(\eta^6\text{-}C_6H_6)$ in which the benzene ligand as a *six-electron* donor displays a decisively different binding mode[10] and realized the paucity of Ni(0)−benzene complex reference data. Second, our recent studies on complexes with the related $(^tBu_2PC_2H_4P^tBu_2)Ni^0$ moiety revealed interesting features of this complex fragment due to the combination of an exceedingly bulky ligand and the relatively small Ni atom.[11−13] It thus appeared worthwhile to synthesize and determine the properties of $(^tBu_2PC_2H_4P^tBu_2)Ni^0$−benzene complexes.[14]

Results and Discussion

$(^tBu_2PC_2H_4P^tBu_2)Ni(\eta^2\text{-}C_6H_6)$ (1) and $\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ (2). When a yellow solution of $(^tBu_2PC_2H_4P^tBu_2)NiMe_2$[12] in benzene is heated to 50−60 °C for several hours, the color of the solution changes to red. As is shown below, the mononuclear Ni(0)−benzene complex **1** is formed as the primary product under these conditions. However, after exchange of the solvent by diethyl ether or pentane and cooling to −30/−78 °C, red cubes of the dinuclear Ni(0)−benzene complex **2** can be isolated in about 60% yield. Thermolysis of $(^tBu_2PC_2H_4P^tBu_2)NiMe_2$ in C_6D_6 affords the ring deuterated derivative $\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6D_6)$ (**2**-*d*$_6$). Complex **2** can also be prepared by reduction of $(^tBu_2PC_2H_4P^tBu_2)NiCl_2$[12] with activated magnesium (Mg*)[15] in the presence of benzene (46%)

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[1] Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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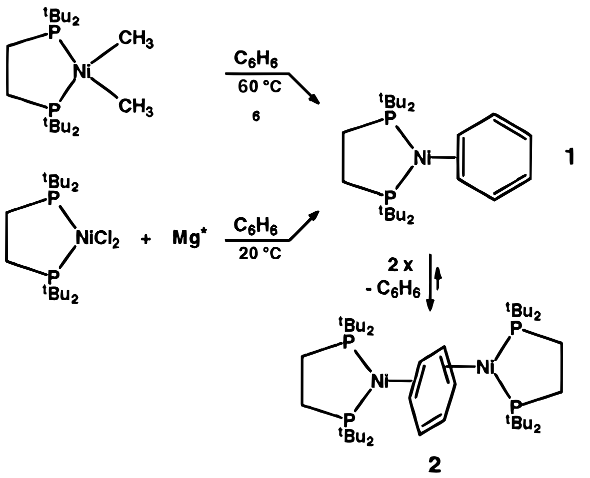
Scheme 1



(Scheme 1). Details of the mechanism of these reactions are discussed elsewhere.[12]

Solid **2** is stable at 20 °C and decomposes at 132 °C. It readily dissolves in various solvents at 20 °C and displays different stabilities. In benzene and toluene solution the complex dissociates and exchange of the benzene ligand occurs (see below). The resulting solutions, in which the [(d^{t}bpe)Ni^0] fragment is still stabilized by arene coordination, are stable. No oxidative addition of an arene C−H bond proceeds to yield complexes of type [(d^{t}bpe)Ni^{II}(H)(Ar)]. In contrast, the red solutions of **2** in pentane, diethyl ether, or THF at 20 °C are not stable for long and change color to dark red in the course of several hours. The color can be attributed to the presence of {(d^{t}bpe)Ni}$_2$(μ-H)$_2$[12] which, for a solution of **2** in THF-d_8, has also been identified by ^{1}H and ^{31}P NMR. Presumably, the destabilized [(d^{t}bpe)Ni^0] fragment resulting from partial dissociation of **2** in these solvents captures protons from traces of moisture to give {(d^{t}bpe)Ni}$_2$(μ-H)$_2$.

In the FAB mass spectrum of **2**, the molecular ion m/z = 830 (10%) is observed which fragments by cleavage of the bridging benzene ligand to produce [(d^{t}bpe)Ni]$^+$ (376) as the basis ion. In the IR spectrum a =C−H stretching band is observed at 3024 cm^{-1} (shoulder) while further bands are apparently obscured by bands of the phosphane ligand (3000−2850 cm^{-1}). Absorption bands at 1446, 1115, 996, and 717 cm^{-1} are assigned to ring and C−H bending vibrations of the benzene ligand [uncoordinated C$_6$H$_6$:[16] 3064, 1482, 1037, 673 cm^{-1}]. For **2**-d_6, containing a deuterated benzene ligand, *three* =C−D stretching bands are observed at 2270, 2255, and 2221 cm^{-1} in addition to the ring and C−D bending vibrations [1394, 825, 611, 530 cm^{-1}; uncoordinated C$_6$D$_6$,[16] 2288, 1333, 814, 496 cm^{-1}].

Molecular Structure of 2. The molecular structure of **2** has been determined by single-crystal X-ray structure analysis (−173 °C) and is depicted in Figure 1. The complex displays an exact C_2 axis of symmetry which lies in the plane of the benzene ligand and passes through the midpoints of the bonds C3−C3* and C5−C5*.

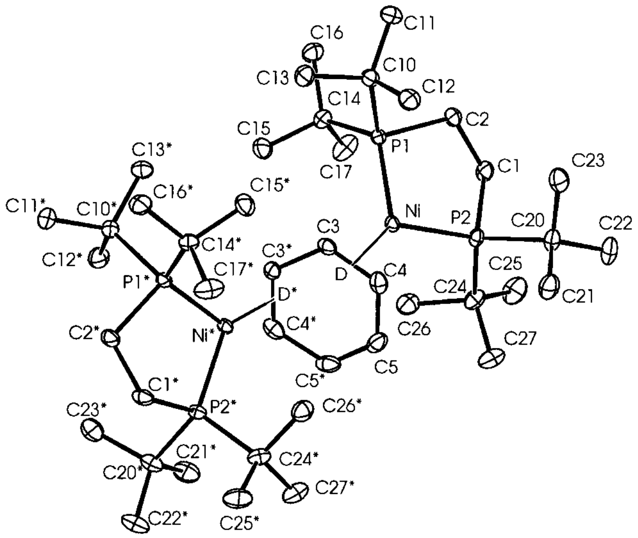


Figure 1. Molecular structure of **2** in the crystal. Selected distances (Å): Ni···Ni* 4.759(1), Ni−P1 2.160(1), Ni−P2 2.166(1), Ni−C3 2.021(1), Ni−C4 2.005(1), C3−C4 1.421(1), C4−C5 1.451(2), C3−C3* 1.474(2), C5−C5* 1.340(2). Selected bond and plane angles (deg): P1−Ni−P2 93.88(1), C3−Ni−C4 41.3(4), C3*−C3−C4 119.0(1), C3−C4−C5 119.6(1), C4−C5−C5* 121.4(1), P1,P2,Ni/C3,C4,Ni 17, C3,C4,C5/C3,C4,Ni 105, P1,P2,Ni,D/C3,C4,C5 109.

In **2** two *TP*-3 [(d^{t}bpe)Ni^0] moieties are antifacially coordinated to adjacent C=C bonds of a bridging benzene ligand. The C−C bond lengths within the benzene ligand alternate significantly (±0.07 Å) so that the ligand can best be regarded as a 2-fold-coordinated cyclohexatriene ligand. The coordinated C=C bonds [C3−C4 1.421(1) Å] are longer and the uncoordinated C=C bond [C5−C5* 1.340(2) Å] is significantly shorter than the C−C distances in uncoordinated benzene [C−C 1.380 Å,[17] 1.389 Å [16b]]. Furthermore, the bond C3−C3* 1.474(2) Å, connecting the coordinated C=C bonds, and the bond C4−C5 1.451(2) Å, connecting a coordinated C=C bond and the uncoordinated C=C bond, are longer than the C−C bond of uncoordinated benzene. As a result, the averaged C−C bond length in **2** [1.42(6) Å] is longer than the length in uncoordinated benzene. The bonds Ni−C3/4 2.01(1) Å (mean) are as expected for a Ni(0)−η^2-alkene complex (2.00 Å). They are significantly shorter than in (η^1-^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)Ni(η^6-C$_6$H$_6$) (2.14 Å),[10] for which the benzene ligand (C−C 1.41 Å) is less perturbed.

The Ni−P bond length of 2.163(4) Å (mean) and the angle P1−Ni−P2 93.88(1)° may be compared to the corresponding values of the cyclododecatriene complex (d^{t}bpe)Ni(η^2-C$_{12}$H$_{18}$) (2.18 Å; 93.1°)[11] and the COT derivative (d^{t}bpe)Ni(η^2-C$_8$H$_8$) (2.21 Å; 92.5°).[13] The carbon skeleton of the central benzene ligand is planar, and the carbon atoms C3−C5 diverge from the best plane by only 0.01 Å (mean). The coordinated C=C bond C3−C4 deviates from the Ni coordination plane (P1,P2,Ni) by 17°, resulting in an increase in the P1···P1* distance, presumably due to steric repulsion of the corresponding ^{t}Bu groups. The plane of the benzene ligand and the Ni coordination plane form an angle of 108°, so that the benzene ligand is tilted away from the metal. Similarly, the H atoms attached to the coordi-

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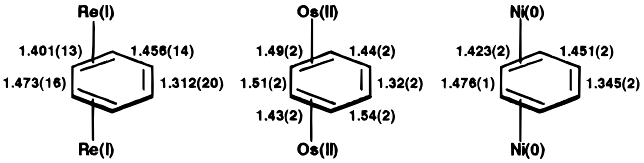
nated C═C bonds are bent out of the C3−C5 plane away from the Ni atom by 20° (mean), indicating partial sp^3 hybridization of the coordinated carbon atoms.

The geometry of the cyclohexatriene coordination in **2** is the same as in $\{Cp^*Re(CO)_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$[18] and $[\{(NH_3)_5Os\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)](CF_3SO_3)_4$.[19] While there is a large standard deviation of the data for the Os(II) complex, the C_6H_6 ligand structural data for **2** agree well with those of the Re(I) complex.



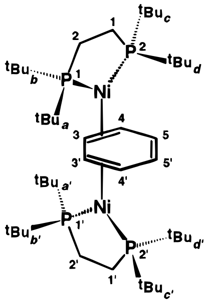
Clearly, the $\mu\text{-}\eta^2(1,2)\text{:}\eta^2(3,4)$ coordination mode and the cyclohexatriene character of the benzene ligand in these complexes result from a strong back-bonding capabilty of the d^6 Re(I), Os(II), and d^{10} Ni(0) metal centers. Upon coordination of the first metal center to the benzene molecule the delocalization of the benzene π electrons[20] becomes largely disturbed, leading to a ligand with significant cyclohexatriene character, in which one C═C bond is fixed by coordination and the other two C═C bonds form a conjugated diene type structural element. Thus, it is to be expected that coordination of the second metal center proceeds at a conjugated double bond [C(3)−C(4)], rather than at the transannular single bond C(4)−C(5), and will be more facile than the coordination of the first metal center. In contrast, the poorly back-bonding metal centers Cu(I) and Ag(I) form the dinuclear or oligomeric benzene complexes $\{(CF_3SO_3)Cu\}_2(\mu\text{-}\eta^2(1,2)\text{:}\eta^2(4,5)\text{-}C_6H_6)$[21] and $\{(\mu\text{-}\eta^2(1,2)\text{:}\eta^2(4,5)\text{-}C_6H_6)AgClO_4\}_n$.[22] In these complexes the aromatic character of the benzene ligand is preserved and the C_6 ring acts predominantly as a donor to the metal centers, which are antifacially coordinated to the transannular C−C bonds.[23]

Solid-State CP/MAS NMR of 2. In addition to X-ray analysis the molecular structure of **2** has been studied by solid-state ^{13}C and ^{31}P CP/MAS NMR spectroscopy. In the ^{13}C NMR spectrum the three kinds of chemically different C atoms of the cyclohexatriene type ligand give rise to six signals, i.e., two for the C atoms of the uncoordinated C═C bond [δ_C 121.2, 120.6] and four for those of the coordinated C═C bonds [δ_C 59.8, 59.2, 58.5, 57.9]. The splitting of the signals is thought to be caused by subtle differences in the environment of the nuclei which are concealed in the X-ray analysis (idealized C_2 symmetry) but become discernible by solid-state NMR (C_1 symmetry).[24] The arithmetic mean of the chemical shifts of δ_C = 79.5 corresponds to the solution NMR chemical shift (Table 1). Furthermore, the chemical shifts compare well with those of $\{Cp^*Re(CO)_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$[18] and $[\{(NH_3)_5Os\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)](CF_3SO_3)_4$[19] (solution NMR; Table 1). For the two d^{t}bpe ligands, four signals for PCH_2 and eight signals each for the four chemically different groups P*C*Me$_3$ and PC*Me*$_3$ are expected on the basis of C_1 symmetry, but these are not fully resolved (PCH_2, δ_C 25.0, 24.0; P*C*Me$_3$, δ_C 36.2, 35.1; PC*Me*$_3$, δ_C 31.9, 30.9, 30.5). In addition, a NQS ^{13}C CP/MAS NMR experiment has shown that the solid-state structure of **2** is static; i.e., neither a rotation of the (d^{t}bpe)Ni fragments occurs about the Ni−(C═C) bond axes nor a rotation of the cyclohexatriene type ring which would cause an exchange of coordinated and uncoordinated C═C bonds (cf. solution NMR).

Table 1. Solution ^{1}H and ^{13}C NMR Data for the C_6H_6 Ligand in 1 and 2 and Various Reference Compounds[a]

	δ_H		δ_C		^1J(CH) (Hz)
C_6H_6	7.26		128.5		159
(d^{t}bpe)Ni(η^2-C_6H_6) (**1**)[d]		5.68		103.3	155
$\{$(d^{t}bpe)Ni$\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ (**2**)[e]		4.63		80.1	153
(d^{t}bpe)Ni(C_2H_4)[11]	1.82[b]		33.4[b]		152[b]
$(\eta^1\text{-}{}^tBu_2PCH_2P^tBu_2)Ni(\eta^6\text{-}C_6H_6)$[10]	5.95		92.0		168
$Cp^*Re(CO)_2(\eta^2\text{-}C_6H_6)$[f,18]		5.87			
$\{Cp^*Re(CO)_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$[18]	6.41[f] 4.14 2.85	(4.47)[c]	127.3[g] 50.6 40.9	(72.9)[c]	
$[(NH_3)_5Os(\eta^2\text{-}C_6H_6)]^{2+}$ [h,19]	7.25[i] 6.55 5.22	6.45			
$[\{(NH_3)_5Os\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)]^{4+}$ [h,19]	6.53 4.63 4.33	(5.16)[c]	127.6 53.1 49.6	(76.8)[c]	

[a] The first column of δ_H and δ_C gives the resonance(s) for the static C_6H_6 ligand and the second column the coalescence signal for the dynamic ligand. Temperature 20/27 °C, unless otherwise indicated. [b] Data for ethene ligand. [c] Calculated value for coalesced signals. Solvents: [d] 90% THF-d_8 + 10% C_6D_6; [e] THF-d_8; [f] C_6D_6 or C_6H_6/C_6D_6; [g] $CDCl_3$; [h] acetone-d_6. [i] −87 °C.



In the ^{31}P NMR spectrum the signals of two AB spin systems are found [$\delta_{P1/2}$ 75.4, 74.5; $\delta_{P1'/2'}$ 72.7, 71.6] in agreement with an apparent C_1 symmetry. The coupling constants $^2J(P1,P2)_{cis}$ and $^2J(P1',P2')_{cis}$ have been determined to be 105 ± 5 Hz on the basis of *J*-resolved 2D ^{31}P NMR spectra. This value is substantially larger than for other (d^{t}bpe)Ni(0)−η^2-alkene complexes in solution (70−78 Hz)[11] and in the solid state (cf. data in ref 24) and reflects that $^2J(PP)_{cis}$ increases with an increasing electron density at the Ni center. It has, however, also been noted that couplings $^2J(PP)_{cis}$ can be larger for the solid state than for solution.[25]

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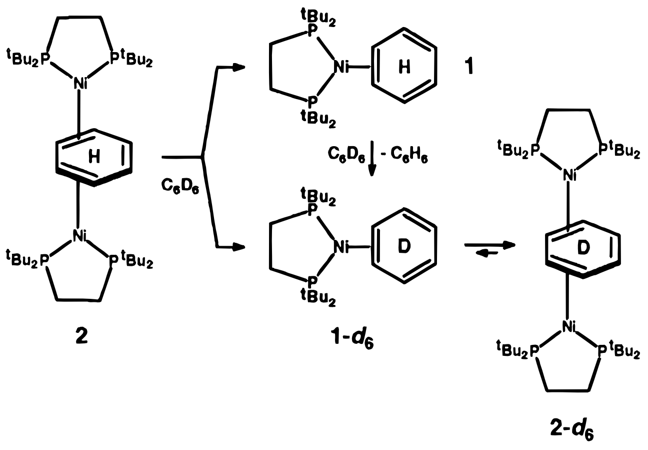
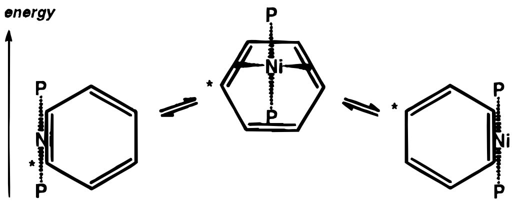
(24) We have observed this phenomenon quite frequently. For example, in the solid state ^{31}P CP/MAS NMR spectrum the phosphorus nuclei of (d^{t}bpe)Ni(C_2H_2)[11] and (d^{t}bpe)Ni(η^2-C_8H_{12})[11] give rise to AB spin systems. The coupling constants ^2J(PP) were determined by *J*-resolved 2D spectroscopy to be 53 and 75 Hz, respectively.

Scheme 2



Scheme 3



Equilibrium between 1 and 2. When **2** is dissolved in C_6D_6 and the ^{31}P NMR spectrum (27 °C) is recorded immediately afterward, two closely adjoining signals of the dinuclear complexes **2** and **2**-d_6 (δ_P 77.74, 77.80) and an intense high-field signal at δ_P 74.4 are observed. The latter is assigned to the mononuclear derivatives **1** and $(^tBu_2PC_2H_4P^tBu_2)Ni(\eta^2\text{-}C_6D_6)$ (**1**-d_6). Correspondingly, in the ^1H NMR spectrum signals of the benzene ligand of **1** (δ_H 6.20) and of uncoordinated C_6H_6 (δ_H 7.20) are observed in addition to those of the benzene ligand in **2** (δ_H 5.10).[26] After 30 min at 40 °C **2** has almost completely disappeared. The spectra indicate that **2** dissolved in C_6D_6 dissociates slowly to afford a mixture of **1** and **1**-d_6; exchange of the C_6H_6 ligand in **1** by C_6D_6 yields further **1**-d_6. Partial condensation of two molecules of **1**-d_6 (or **1**-d_6 and **1**) produces dinuclear **2**-d_6 (Scheme 2). It follows from these exchange reactions that dinuclear **2** is in equilibrium with mononuclear **1** in the presence of additional benzene. However, the ligand exchange is slow on the NMR time scale as can be concluded from the sharp ^1H and ^{31}P NMR signals even at 60 °C.

Dinuclear **2** is thermodynamically somewhat more stable than mononuclear **1**. The equilibrium between **2** and **1** is shifted markedly to mononuclear **1** in the presence of a large excess of benzene. Thus, when **2** is dissolved in undiluted benzene (27 °C), a mixture of about 75% **1** and 25% **2** is formed. The equilibrium is shifted further in favor of **1** (83%) when the temperature of the benzene solution is raised to 60 °C (^{31}P NMR). The fact that dinuclear **2** crystallizes preferentially from a benzene solution (20 °C) is explained by its lower solubility and the equilibrium between **1** and **2**, which ensures that **2** is continuously available.[27]

Solution NMR Spectra and Structural Dynamics of 1 and 2. The solution ^1H and ^{13}C NMR data (27 °C) of the benzene ligand in **1** and **2**, together with various reference data, are compiled in Table 1. The ^1H and ^{13}C NMR spectra of a THF-d_8 solution (27 °C) of dinuclear **2** display resonances for the bridging benzene ligand at δ_H 4.63 and δ_C 80.1 with $^1J(CH) = 153$ Hz. If 10% of benzene (C_6H_6) is added to the solvent, additional resonances corresponding to the benzene ligand of mononuclear **1** are observed at δ_H 5.68 and δ_C 103.3 with $J(CH) = 155$ Hz.[26] The corresponding ^{31}P NMR spectra display singlets for **2** at δ_P 78.1 and for **1** at δ_P 75.2.

The d^{t}bpe ligand in **2** gives rise to two ^1H NMR multiplets [PCH_2, P^tBu_2] and three ^{13}C NMR signals [$PCMe_3$, $PCMe_3$, PCH_2] with the expected intensities. The d^{t}bpe ^1H and ^{13}C signals of **1** are very similar to those of **2** and can be hardly distinguished. In the ^1H NMR spectrum of **2** recorded at −80 °C all signals are *slightly* broadened so that the couplings to phosphorus can no longer be resolved. Since we observed only minor changes in the ^1H NMR spectrum of **2**, the low-temperature ^{13}C NMR spectrum was not measured. No low-temperature NMR data of **1** are available.[28]

As compared to uncoordinated C_6H_6 (Table 1), the ^1H and ^{13}C resonances are gradually shifted to high field upon coordination of one or two [(d^{t}bpe)Ni^0] moieties to C_6H_6 (chemical shift differences between **1** and **2**: $\Delta\delta_H = 1$ ppm, $\Delta\delta_C = 23$ ppm) and the coupling constant $^1J(CH)$ is lowered; for **2** the latter is close to that of the ethene ligand in (d^{t}bpe)Ni(C_2H_4). These changes indicate a significantly increased charge transfer to the benzene ligand on going from mononuclear **1** to dinuclear **2**. The concomitant *deshielding* of the phosphorus nuclei ($\Delta\delta_P = 3$ ppm) indicates that the electron withdrawal from the [(d^{t}bpe)Ni^0] moieties and thus the *acceptor strength of the benzene ligand increase* when benzene is coordinated to two Ni atoms instead of one Ni atom.[29]

On the basis of the molecular structure of **2** we assume that **1** in the ground-state structure similarly displays a cyclohexatriene ligand which is $\eta^2(1,2)$-coordinated by one of its C=C bonds to a single *TP*-3 [(d^{t}bpe)Ni^0] moiety. The NMR spectra of **1** and **2** show, however, that the structures of both 16e complexes in solution are dynamic and that an internal exchange of coordinated and uncoordinated C=C bonds occurs, which is rapid on the NMR time scale, even at −80 °C. This exchange leads to an equilibration of the C=C bonds, the ^{31}P nuclei, and the substituents at phosphorus (CH_2, ^tBu). The mechanism of this exchange process is best explained for **1** by an intermediary $\eta^4(1-4)$-coordination of the cyclohexatriene ligand to an 18e *T*-4 Ni(0) center (Scheme 3) and for **2** by an intermediary $\eta^4(1\text{-}4){:}\eta^2(5,6)$-coordination to *T*-4 and *TP*-3 Ni(0) centers. The structural dynamics of the cyclohexatriene ligands in **1** and **2** correspond mechanistically to the

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[25] Wu, G.; Wasylishen, R. E. *Inorg. Chem.* **1992**, *31*, 145.

[26] The NMR chemical shifts of the complexes depend on the solvent (THF-d_8, THF-d_8/C_6D_6, or C_6D_6).

[27] Attempts to isolate a mixture of about 80% **1** and 20% **2** by quenching a heated benzene solution to a solid and subsequent freeze drying under high vacuum (−10 °C, 2 d) resulted, however, in only a partial fortification of **1**.

[28] The recording of low-temperature solution NMR spectra of **1** is impeded by the necessity of having a significant amount of benzene (C_6D_6, mp 6.8 °C) present in the solution.

[29] In contrast, an increased *shielding* of the COT ^1H and ^{13}C nuclei *and* of the ^{31}P nuclei ($\Delta\delta_P = 14$ ppm) is observed when going from the mononuclear (d^{t}bpe)Ni(η^2-C_8H_8) to the dinuclear $\{(d^tbpe)Ni\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_8H_8)$; i.e., the individual charge transfer of each [(d^{t}bpe)Ni^0] moiety to the COT ligand decreases when the latter is coordinated to two Ni atoms instead of one.[13]

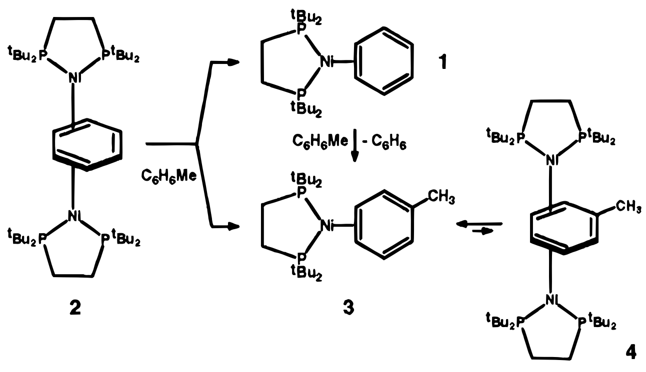
C=C bond exchange process proposed for the COT ligands in (d^{t}bpe)Ni(η^2-C_8H_8) and {(d^{t}bpe)Ni}$_2$(μ-η^2:η^2-C_8H_8).[13] For both types of complexes the exceedingly low energy barrier of the exchange processes is presumably due to the presence of 16e ground-state complexes and their energetically easy conversion into 18e activated complexes.[30]

The character of the cyclohexatriene type ligand in the 16e complexes **1** and **2** differs fundamentally from that of the 6e benzene ligand in the 18e complex (η^1-$^tBu_2PCH_2P^tBu_2$)Ni(η^6-C_6H_6), where only one phosphorus atom donates its electrons to Ni(0). The benzene ^{13}C NMR resonance of the latter is at a higher field (δ_C 92.0; Table 1) as compared to mononuclear **1** (δ_C 103.3), although in the latter two phosphorus atoms are coordinated to the Ni atom. Even more striking is the difference in the benzene ligand coupling constant ^1J(CH). While the (average) values for **1** and **2** (155, 153 Hz) are smaller than for uncoordinated benzene (159 Hz) and correspond to ^1J(CH) of an alkene ligand, the value for the η^6-C_6H_6 ligand (168 Hz) is larger and appears to be typical for η^6-C_6H_6 complexes [(CO)$_3$Cr(η^6-C_6H_6), $^1J(CH) = 175$ Hz].[31,32]

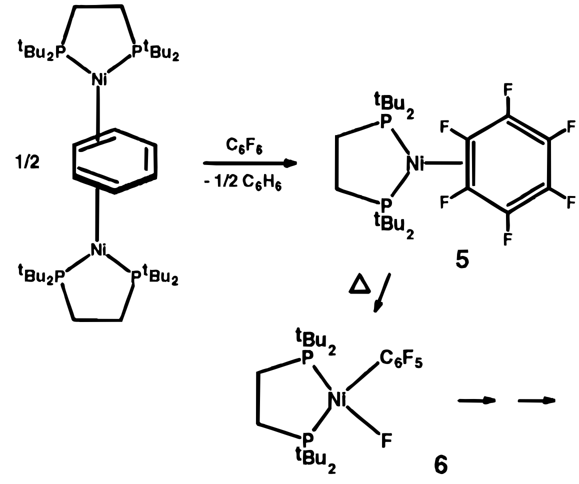
The mono- and dinuclear d^{10} Ni(0) complexes **1** and **2** appear more closely related to the *18e* d^6 Re(I) complexes Cp*Re(CO)$_2$(η^2-C_6H_6) and {Cp*Re(CO)$_2$}$_2$(μ-η^2:η^2-C_6H_6)[18] and Os(II) complexes [(NH$_3$)$_5$Os(η^2-C_6H_6)](CF$_3$SO$_3$)$_2$ and [{(NH$_3$)$_5$Os}$_2$(μ-η^2:η^2-C_6H_6)](CF$_3$SO$_3$)$_4$[19] (Table 1). For the dinuclear complexes the coordination of the cyclohexatriene ligand is static in solution at ambient temperature with respect to the NMR time scale. For the mononuclear complexes an exchange of coordinated and uncoordinated C=C bonds proceeds which, however, is sufficiently slowed down at low temperature to observe the static structure by solution NMR [Os(II)]. While no ^{13}C NMR data are given for the mononuclear derivatives, a comparison of the C_6H_6 ligand ^{13}C chemical shifts for the dinuclear complexes [Re(I), δ_C 72.9, mean; Os(II), δ_C 76.8, mean] and the observed time average of **2** (δ_C 80.1) suggests a decreasing metal back-bonding to the bridging benzene ligand in the series Re(I) > Os(II) > Ni(0).

Arene Exchange Reactions of 1 and 2: Synthesis of (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(η^2-C$_6$F$_6$) (5). As described above, the dinuclear **2** dissolved in benzene is in slow equilibrium with mononuclear **1**. We were therefore interested to determine whether the benzene ligand in **2** exchanges with other simple arenes. Complex **2** remains unchanged when dissolved in a mixture of 90% mesitylene and 10% THF-d_8 at 27 °C (^1H, ^{31}P NMR) and has been recovered from this mixture. However, the benzene ligand is partially replaced when **2** is dissolved in toluene. The ^{31}P NMR spectrum of a solution of **2** in toluene-d_8 displays, besides the signals for a residual amount of **2** (δ_P 77.7) and a trace of **1** (δ_P 74.4), the signals of mononuclear (d^{t}bpe)Ni(η^2-$C_6D_5CD_3$) (**3**-d_8) (δ_P 74.2) as the major component and of dinuclear {(d^{t}bpe)Ni}$_2$(μ-η^2:η^2-$C_6D_5CD_3$) (**4**-d_8) (δ_P 77.2) as the minor component (Scheme 4). The higher field ^{31}P chemical shifts of the toluene complexes as compared with the corresponding benzene derivatives are in accord with the weaker acceptor strength of the toluene ligand. In spite of this trend, the shifts of the corresponding benzene and toluene complexes are rather similar and indicative of the same binding modes, which also includes similar structural dynamics. It is most likely that the exchange reactions of **2** (and **1**) with toluene to yield **3** and **4** are equilibrium reactions. The toluene derivatives are probably thermodynamically less stable than the benzene complexes, and the equilibrium is shifted to their side only by a large excess of toluene. So far we have not succeeded in isolating **3** and **4** in the pure state.

Scheme 4



Scheme 5



Whereas substitution of the benzene ligand in **2** by electron richer arenes is unfavorable, it is facilitated in the case of electron poorer arenes such as hexafluorobenzene.[33] When the red suspension of **2** in diethyl ether is stirred with an excess of C_6F_6 at 20 °C, the solution turns yellow. Upon cooling the solution to −30 °C orange crystals of the mononuclear C_6F_6 complex **5** precipitate in 58% yield (Scheme 5). Complex **5** is analogous to the mononuclear complexes **1** and **3**, which

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[30] Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A.; Eds.; Academic Press: New York, 1975; p 377.

[31] Aydin, R.; Günther, H.; Runsink, J.; Schmickler, H.; Seel, H. *Org. Magn. Reson.* **1980**, *13*, 210.

[32] The peculiarity of ^1J(CH) of metal−η^6-C_6H_6 complexes has recently also been noted by: Yao, Z.; Klabunde, K. J.; Asirvatham, A. S. *Inorg. Chem.* **1995**, *34*, 5289.

[33] C_6F_6 is of ambiguous electronic character because the six F substituents exert strong −I and +M effects (18 electron pairs!) simultaneously. This accounts for both a high electron affinity (0.52−0.86 eV; cf. benzene, −1.15 eV) and an ionization energy (10.2 eV) larger than that of benzene (9.3 eV) but smaller than that of ethene (10.5 eV).[38]

have not yet been isolated. There is no indication of the formation of a dinuclear C_6F_6 complex analogous to **2** or **4**.

Solid **5** decomposes at 115 °C. No EI mass spectrum (160 °C) has been obtained due to the decomposition of the complex. In the IR spectrum **5** displays prominent bands of the C_6F_6 ligand at 1679, 1591, 1530, 1293, 1231, 1076, 935, and 911 cm^{-1}, quite different from the spectrum of uncoordinated C_6F_6.[16a] Because of strong coupling of ring and C−F stretching vibrations accompanied by intensified overtone and combination bands, no meaningful assignment of C═C frequencies can be given. Complex **5** dissolves sparingly in pentane and modestly in diethyl ether and THF. However, the orange solutions decompose completely at 20 °C in the course of several days (see below).

^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR Spectra of 5. In the ^{1}H and ^{13}C NMR spectra (−80 °C) **5** exhibits two proton (PCH_2, CH_3) and three carbon resonances ($PCMe_3$, CH_3, PCH_2) for the d^{t}bpe ligand. The C_6F_6 ligand displays a doublet (δ_C 120.7) due to coupling to fluorine [$^1J(CF) = -260$ Hz]. The ^{19}F NMR spectrum (−80 °C) of **5** shows a triplet (δ_F −166.9) due to coupling to equivalent phosphorus atoms [$J(PF) =$ ca. 10 Hz] and the ^{31}P NMR spectrum (−80 °C) a septet at δ_P 79.0 because of coupling with six equivalent fluorine atoms [$J(PF) = 9.4$ Hz]. The ^{13}C complexation shift of the C_6F_6 ligand in **5** ($\Delta\delta_C = -19.4$) is on the order of that of the C_6H_6 ligand in **1** ($\Delta\delta_C = -25.2$), but the ^{19}F NMR data do not differ appreciably from those of uncoordinated C_6F_6 [δ_C 140.1, δ_F −167.0, $^1J(CF) = -253$ Hz (−260 Hz);[34] THF-d_8]. The ^{31}P resonance of **5**, although lying at a lower field than that of the mononuclear benzene derivative **1** (δ_P 74.4), coincides with the resonance of the dinuclear benzene complex **2** (δ_P 78.1). Apparently, the acceptor strength that C_6F_6 displays[33] toward the [(d^{t}bpe)Ni(0)] fragment in **5** is not much larger than that of benzene in **1**.

The NMR spectra indicate a C_{2v} symmetrical structure of **5** in solution. Excluding a 20e (d^{t}bpe)Ni(η^6-C_6F_6) complex and on the basis of the structure in the crystal (see below), we assume that the ground-state structure of **5** in solution displays an η^2-C_6F_6 ligand and C_S symmetry. According to NMR data the structure of **5** in solution is dynamic even at −80 °C and the spectra represent the time average of different conformations. The structural dynamics of **5** are easily explained by an internal exchange of coordinated and uncoordinated formal C═C bonds of the C_6F_6 ligand as depicted in Scheme 3. On the basis of the sharp ^{13}C NMR signals (75.5 MHz) the exchange process is fast at −80 °C, and solution NMR provides little further information about the ground-state structure. For this reason an X-ray single-crystal structure analysis was undertaken.

Molecular Structure of 5. The molecular structure of **5**, as determined by X-ray structure analysis, is depicted in Figure 2. As can be seen from the figure, a C_6F_6 ligand is η^2-coordinated via a formal C═C bond to a *TP*-3 [(d^{t}bpe)Ni^0] moiety. Defining the coordination plane of the nickel atom by P1, P2, Ni, and the midpoint of the C1−C6 bond, the coordinated atoms C1 and C6 diverge only slightly from this plane (P1,P2,Ni/C1,C6, Ni 5°). The Ni−P bond lengths of 2.232(5) Å (mean) are longer and the Ni−C bond lengths of 1.94(1) Å (mean) are shorter than in the *Ni(0)*−benzene complex **2** [Ni−P 2.163(4) Å, Ni−C 2.01(1) Å; P1−Ni−P2 93.88(1)°] and are similar to those in the *Ni(II)*−dialkyl complex (d^{t}bpe)$NiMe_2$ [Ni−P 2.215(5) Å, Ni−C 2.00(1) Å; P1−Ni−P2 90.5(1)°];[12] the angle P1−Ni−P2 92.22(4)° is of intermediate size.

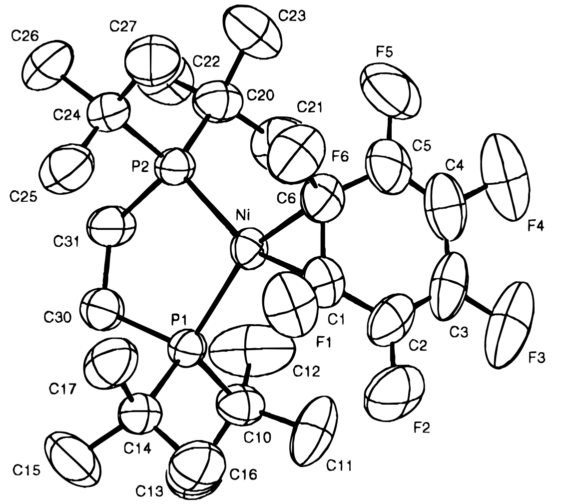

Figure 2. Molecular structure of **5** in the crystal. Selected bond distances (Å): Ni−P1 2.229(1), Ni−P2 2.236(1), Ni−C1 1.954(4), Ni−C6 1.934(4), C1−C6 1.486(6), C1−C2 1.423(6), C2−C3 1.352(8), C3−C4 1.416(9), C4−C5 1.288(8), C5−C6 1.435(7), C1−F1 1.386(5), C2−F2 1.353(6), C3−F3 1.332(5), C4−F4 1.371(6), C5−F5 1.346(6), C6−F6 1.373(5). Selected bond and plane angles (deg): C6−C1−C2 116.8(4), C1−C2−C3 123.1(5), C2−C3−C4 118.0(5), C3−C4−C5 122.7(6), C4−C5−C6 123.3(6), C5−C6−C1 115.6(4), P1−Ni−P2 92.22(4), P1,P2,Ni/C1,C6,Ni 5, C1,C6,Ni/(C1−C6) 114, (C1−C6)/C1,C6,F1,F6 136.

The six-membered ring of the C_6F_6 ligand is planar; the carbon atoms deviate from the best plane by less than 0.04 Å. The fluorine substituents at the coordinated C atoms, F1 and F6, are strongly bent (44°) out of this plane away from the Ni atom. In contrast, the fluorine substituents F2 and F5 on the adjacent C atoms are only slightly bent (3°) away from the metal while the fluorine substituents F3 and F4 do not deviate from the plane at all. The plane of the C_6F_6 ligand makes an angle of 114° to the plane through C1,C6,Ni. The C−C bonds of the C_6F_6 ligand display a strong alternation of bond lengths consistent with marked charge localization. The coordinated C═C bond C1−C6 at 1.486(6) Å is the longest in the ring, and the adjacent C═C bonds C2−C3 and C4−C5 at 1.32(5) Å (mean) are the shortest. The remaining C−C single bonds C1−C2, C3−C4, and C5−C6 of 1.42(1) Å are of intermediate length (gas-phase C_6F_6: C−C 1.39 Å, C−F 1.33 Å by electron diffraction).[35] Correspondingly, the bonds C1−F1 and C6−F6 [mean 1.38(1) Å] are slightly longer than the C−F bonds at the uncoordinated C atoms [mean 1.35(2) Å]. The structural features of **5** indicate that the geometry of C1 and C6 can be considered as distorted tetrahedral and the Ni(0)−η^2-C_6F_6 coordination mode displays a significant participation of the nickelacyclopropane canonical form. Consequently, one of the C═C bonds of the fluorine-substituted, formal

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[34] (a) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Thieme: Stuttgart, Germany, 1984; p 520 ff. (b) Initially a value of $|^1J(CF)| = 362$ Hz for C_6F_6 was reported[34c] and also cited by others,[52a] which, however, is incorrect. (c) van der Kelen, G. P. *Bull. Soc. Chim. Belg.* **1963,** *72,* 644; *Chem. Abstr.* **1964**, *60*, 2464f.

[35] Almenningen, A.; Bastiansen, O.; Seip, R.; Seip, H. M. *Acta Chem. Scand.* **1964**, *18*, 2115.

Table 2. Representative Examples of C_6F_6 Complexes

compd	remarks	ref
$(F_3P)_3Cr(\eta^6\text{-}C_6F_6)$	cocondensation, <2% yield; dec >100 °C	51
$(\eta^6\text{-}C_6H_6)Cr(\eta^6\text{-}C_6F_6)$	cocond, 8%; MS; IR/RA; NMR (C_6F_6) δ_C 121.7, ^1J(CF) = −303 Hz; δ_F −193.3	51, 52
$Mo(\eta^6\text{-}C_6F_6)_2$	cocond, <2%; dec 135 °C; MS; δ_F −177.7	53
$W(\eta^6\text{-}C_6F_6)_2$	cocond, 2%; dec 180 °C; MS; δ_F −176.9; X-ray	53
$[Cp^*Ru(\eta^6\text{-}C_6F_6)]CF_3SO_3$	80%; δ_F −174.4	54
$CpIr(\eta^4\text{-}C_6F_6)$	X-ray, C_6F_6 nonplanar, "open book" conformation; rigid struct (NMR)	37
$Cp^*Ir(\eta^4\text{-}C_6F_6)$	rigid struct (NMR)	37
$(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)Ru(\eta^4\text{-}C_6F_6)$	cocond, 4%; X-ray, C_6F_6 "open book" conformation; rigid struct (NMR)	55
$CpRh(PMe_3)(\eta^2\text{-}C_6F_6)$	X-ray; C_6F_6 coordination static at 130 °C	36, 38
$Cp^*Rh(PMe_3)(\eta^2\text{-}C_6F_6)$	rigid struct (NMR)	46, 38
$CpIr(PMe_3)(\eta^2\text{-}C_6F_6)$	rigid struct (NMR)	38
$CpIr(C_2H_4)(\eta^2\text{-}C_6F_6)$	X-ray; rigid struct, 2 isomers	37
$Cp^*Ir(C_2H_4)(\eta^2\text{-}C_6F_6)$	rigid struct, 2 isomers	37

cyclohexatriene ligand becomes localized, resulting in localization of the diene system (C2−C5) in the uncoordinated part of the six-membered ring.

Well-characterized complexes with η^6-, η^4-, or η^2-C_6F_6 ligands are so far mainly known for d^6 and d^8 metal centers (Table 2). The η^2-C_6F_6 binding mode has been encountered for 18e d^8 complexes such as $CpRh(PMe_3)(\eta^2\text{-}C_6F_6)$[36,38] and $CpIr(C_2H_4)(\eta^2\text{-}C_6F_6)$.[37,38] In these complexes a C_6F_4 section of the C_6F_6 ligand is planar and the F substitutents of the coordinated C−C bond [C−C bond length: 1.397(12) Å (Rh), 1.47(2) Å (Ir)] are strongly bent out of the plane [43.8° (Rh), 47.9° (Ir)], as in **5**. In contrast, the η^2-C_6F_6 coordination is rigid (NMR) in these complexes, whereas it is highly dynamic for the 16e d^{10} Ni(0) complex **5**. Furthermore, **5** is closely related to the 16e d^{10} Ni(0) complexes $L_2Ni\{\eta^2\text{-}C_6(CF_3)_6\}$,[2] which have already been mentioned, and the structurally characterized Pt(0) complexes $(Et_3P)_2Pt\{\eta^2\text{-}C_6(CF_3)_6\}$[2b,39] and $(Ph_3P)_2Pt\{\eta^2\text{-}C_6(1,2\text{-}3,4\text{-}5,6\text{-}C_2F_4)_3\}$.[40] Available NMR data indicate that these complexes are also fluxional at low temperature. The exact nature of $[Ni(C_6F_6)]$, prepared by cocondensation of Ni and C_6F_6,[41] is still an open question.[42]

Thermolysis of 5 To Afford (d^tbpe)NiF(C_6F_5) (6). Complex **5** decomposes in solution at 20 °C in the course of several days. The ^{19}F and ^{31}P NMR signals of such a solution (THF-d_8) indicate the formation of **6** as the main product (see experimental part). Further signals are attributed to small amounts of uncoordinated d^tbpe (8%; δ_P = 35.8), C_6F_6 (14%; δ_F = −164.8), and C_6F_5−C_6F_5[43] [6%; δ_F = −140.5 (ortho), −164.5 (meta), −156.7 (para)], while the turbidity of the solution is explained by the formation of insoluble NiF_2. Presumably, complex **5** undergoes an oxidative addition reaction of a C−F bond of the C_6F_6 ligand to the $[(d^tbpe)Ni^0]$ fragment with the formation of **6** which then reacts further to afford the observed byproducts (Scheme 5). No attempt to isolate **6** has been made since $(R_3P)_2NiX(C_6F_5)$ (R = Et, Ph; X = Cl, Br, I)[44] and *trans*-$(Et_3P)_2NiF(C_6F_5)$[45] are already known. The latter complex was obtained from a slow reaction of $(Et_3P)_2Ni(1,5\text{-}C_8H_{12})$ with C_6F_6 (30 °C; several days) in which an intermediate C_6F_6 complex has not been detected. The cleavage of C_6F_5−F bonds by transition metals is well documented.[38,46,47]

Experimental Section

All reactions and manipulations were performed using Schlenk-type techniques under an inert atmosphere of argon. Solvents were dried by distillation from $NaAl(C_2H_5)_4$. $(^tBu_2PC_2H_4P^tBu_2)NiCl_2$ and $(^tBu_2PC_2H_4P^tBu_2)NiMe_2$[12] were prepared as reported. Activated magnesium (Mg*)[15] was kindly provided by the group of Bogdanovic. Microanalyses were performed by the Mikroanalytisches Labor Dornis und Kolbe, Mülheim, Germany. ^1H NMR spectra (δ relative to internal TMS) were measured at 200, 300, and 400 MHz, ^{13}C NMR spectra (δ relative to internal TMS) at 50.3, 75.5, and 100.6 MHz, ^{19}F NMR spectra (δ relative to external $CFCl_3$) at 282.4 MHz, and ^{31}P NMR spectra (δ relative to external 85% aqueous H_3PO_4) at 81 and 162 MHz on Bruker AM-200, WM-300, and AMX-400 instruments. Solvent for solution NMR was THF-d_8 unless indicated otherwise. EI mass spectra at 70 eV under fractional evaporation were recorded on a Varian 311A, FAB mass spectra (matrix: 3,5-dimethoyxbenzyl alcohol) on a Finnigan MAT 95, and IR spectra (KBr) on a Nicolet 7199 FT-IR instrument.

Solid-state ^{13}C and ^{31}P CP/MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer, equipped with a double bearing probe. The ZrO_2 rotor (7 mm internal diameter) was charged with the complex under argon and sealed by a Kel-F inset. Optimal contact time for ^{13}C CP was 2−3 ms, and that for ^{31}P CP, ca. 2 ms. The spinning rate was between 2 and 5 kHz. The external standard for ^{13}C NMR was adamantane [$\delta(CH_2)$ 38.40, relative to TMS], and that for ^{31}P NMR, solid NaH_2PO_4 [δ(P) 0.314, relative to 85% H_3PO_4(aq)]. For *J*-resolved 2D ^{31}P CP/MAS spectra the pulse sequence $CP(\phi_1)-t_1/2-\pi(^{31}P,\phi_2)-t_1/2-ACQ(\phi_3,t_2)$ was used.[25] The t_1 increment was synchronized with the sample rotation period. The ^{31}P π pulse width was ca. 7 μs. The spectral width along the f_1

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dimension and the number of points were chosen to allow for the best resolution.

{(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni}$_2$(μ-η^2:η^2-C$_6$H$_6$) (2). Method a. A suspension of (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(CH$_3$)$_2$ (407 mg, 1 mmol) in benzene (2 mL) was heated to 60 °C for 6 h. Benzene was evaporated under vacuum (20 °C), and the residue was dissolved in diethyl ether (50 mL). At −30/−78 °C red cubes crystallized which were freed from the mother liquor, washed twice with cold pentane, and dried under vacuum at 0 °C; yield 246 mg (59%).

Method b. A suspension of (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)NiCl$_2$ (448 mg, 1 mmol) and Mg* (50 mg, excess) in a THF/benzene mixture (3:1; 30 mL) was stirred (20 °C) until the Ni complex was completely dissolved. The solvent was evaporated under vacuum and the residue treated with pentane (70 mL). Excess magnesium and MgCl$_2$ were removed by filtration. At −30/−78 °C red crystals were obtained which were isolated as described above; yield 190 mg (46%), mp 132 °C (dec). IR (20 °C): 3024 cm^{-1} (=C−H), 1446 (C=C), 1115, 996, 717 (=C−H). FAB-MS: *m/z* (%) 830 M$^+$ (10), 376 [(d^{t}bpe)Ni]$^+$ (100). ^{1}H NMR (400 MHz, 27 °C) (C$_6$H$_6$; see Table 1): δ 1.60 (m, 8H, PCH$_2$), 1.24 (m, 72H, CCH$_3$). A similar spectrum was observed at −80 °C, but the multiplets were not resolved. ^{13}C NMR (100.6 MHz, 27 °C) (C$_6$H$_6$ see Table 1): δ 35.3 ('t', 8C, *C*CH$_3$), 31.2 (s, 24C, CH$_3$), 24.0 [4C, ^1J(PC) = 17.2 Hz, PCH$_2$]. ^{31}P NMR (162 MHz, 27 °C): δ 78.1; (−80 °C) δ 74.1. Anal. Calcd for C$_{42}$H$_{86}$Ni$_2$P$_4$ (832.4): C, 60.60; H, 10.41; Ni, 14.10; P, 14.88. Found: C, 60.48; H, 10.51; Ni, 14.20; P, 15.08.

{(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni}$_2$(μ-η^2:η^2-C$_6$D$_6$) (2-*d*$_6$). The synthesis was carried out analogously to that of **2** by employing C$_6$D$_6$. IR (20 °C): 2270, 2255, 2221 cm^{-1} (C−D), 1394 (C=C$_{\text{ring}}$), 825, 611, 530 cm^{-1} (C−D).

(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(η^2-C$_6$F$_6$) (5). Complex **2** (832 mg, 1 mmol) was dissolved (20 °C) in a mixture of diethyl ether (40 mL) and C$_6$F$_6$ (20 mL). Orange crystals precipitated, which were washed twice with cold pentane and dried under vacuum at 20 °C; yield 595 mg (58%), mp 115 °C (dec). IR (20 °C): 1679, 1591, 1530, ca. 1465, 1347, 1331, 1293, 1231, 1076, 935, 911 (C$_6$F$_{6\,\text{coord}}$) cm^{-1}. ^{1}H NMR (200 MHz, −80 °C): δ 1.84 (m, 4H, PCH$_2$), 1.27 (m, 36H, CH$_3$), d^{t}bpe. ^{13}C NMR (75.5 MHz, −80 °C): δ 120.7 ('d', 6C, ^1J(CF) = −259.4 Hz, CF), C$_6$F$_6$; 35.6 (m, 4C, *C*CH$_3$), 30.4 (s, 12C, C*C*H$_3$), 23.6 (m, 2C, PCH$_2$), d^{t}bpe. ^{19}F NMR (282.4 MHz, −80 °C): δ −166.9, *J*(PF) = 7.6 Hz. ^{31}P NMR (121.5 MHz, −80 °C): δ 79.0, *J*(PF) = 9.3 Hz; (81 MHz, 27 °C): δ 80.1, *J*(PF) = 10.2 Hz. Anal. Calcd for C$_{24}$H$_{40}$F$_6$NiP$_2$ (523.2): C, 51.18; H, 7.16; Ni, 10.42; F, 20.24; P, 11.00. Found: C, 51.16; H, 7.28; Ni, 10.46; P, 11.12.

(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(F)(C$_6$F$_5$) (6): Spectroscopic Data. ^{19}F NMR (282 MHz, 27 °C): δ −114.9 [dd, 2F, ^3J(FF) = 27 Hz, ^4J(FF) or ^4J(PF) = 11.4 Hz, F$_{\text{ortho}}$], −165.5 Hz [t, 1F, ^3J(FF) = 19 Hz), F$_{\text{para}}$], −166.7 (m, 2F, F$_{\text{meta}}$), C$_6$F$_5$; −388.5 [dd, 1F, ^2J(PF)$_{trans}$ = 95.4 Hz, ^2J(PF)$_{cis}$ = 34.3], NiF. ^{31}P NMR (121 MHz, 27 °C): δ 85.9 [m, 1P, ^2J(PF)$_{trans}$ = 95 Hz, ^2J(PP) = 33 Hz, P *trans* ^{19}F], 78.5 [m, 1P, couplings not determined, P *cis* ^{19}F].

Crystal Structure Determination of 2. A crystal (red plate) of dimensions 0.25 × 0.31 × 0.45 mm was used for X-ray crystallography. Preliminary examination and data collection were performed at −173 °C with Mo Kα radiation (λ = 0.710 69 Å) on an Enraf-Nonius CAD4 computer-controlled diffractometer equipped with a graphite-incident beam monochromator. Crystal data: C$_{42}$H$_{86}$Ni$_2$P$_4$, M_r = 832.4 g mol^{-1}, monoclinic, space group *C*2/*c*, *a* = 25.953(5) Å, *b* = 11.440(1) Å, *c* = 15.553(2) Å, β = 98.80(1)°, *V* = 4563.5(11) Å^3, *Z* = 4, D_{calcd} = 1.21 g cm^{-1}, *F*(000) = 1816, μ(Mo Kα) = 9.92 cm^{-1}. A total of 11 179 unique reflections[48] were obtained by using ω−2θ scan technique with a scan rate of 1−5° min^{-1} (in ω). The structure was solved by SHELXS-86[49] on the basis of heavy-atom methods and refined by SHELXL-93[50] (on F_o^2, H3−H5 refined isotropically, otherwise H atoms riding) to a final *R* value of 0.030, with w*R* = 0.072 (observed data). Final difference Fourier: 0.64 eÅ^{-3}.

Crystal Structure Determination of 5. A crystal (orange/yellow plate) of dimensions 0.03 × 0.12 × 0.25 mm was used for X-ray crystallography. Preliminary examination and data collection were performed at 20 °C with Cu Kα radiation (λ = 1.541 78 Å) on an Enraf-Nonius CAD4 computer-controlled diffractometer equipped with a graphite-incident beam monochromator. Crystal data: C$_{24}$H$_{40}$F$_6$NiP$_2$, M_r = 563.2 g mol^{-1}, monoclinic, space group *C*2/*c*, *a* = 20.146(1) Å, *b* = 9.032(1) Å, *c* = 30.442(1) Å, β = 101.39(1)°, *V* = 5429.9(4) Å^3, *Z* = 8, D_{calcd} = 1.38 g cm^{-1}, *F*(000) = 2368, μ(Cu Kα) = 26.07 cm^{-1}, analytical absorption correction (min, 1.155, max, 1.976).[48] A total of 5568 unique reflections were obtained by using ω−2θ scan technique with a scan rate of 1−5° min^{-1} (in ω). The structure was solved by SHELXS-86[49] on the basis of heavy-atom methods and refined by SHELXL-93[50] (on F_o^2, H atoms riding) to a final *R* value of 0.064, with w*R* = 0.177 (observed data). Final difference Fourier: 0.60 eÅ^{-3}.

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Supporting Information Available: Tables of data collection information, anisotropic thermal parameters, atom coordinates and *U* values, and bond lengths and angles for **2** and **5** (10 pages). Ordering information is given on any current masthead page.

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