Articles

Synthesis, Structure, and Reactivity of $(^tBu_2PC_2H_4P^tBu_2)Ni(CH_3)_2$ and $\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}H)_2$[†]

Ingrid Bach, Richard Goddard, Carsten Kopiske, Klaus Seevogel, and
Klaus-Richard Pörschke*

Max-Planck-Institut für Kohlenforschung, D-45466 Mülheim an der Ruhr, Germany

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Oxidative addition of CH_3I to $(d^tbpe)Ni(C_2H_4)$ ($d^tbpe = {}^tBu_2PC_2H_4P^tBu_2$) affords $(d^tbpe)Ni(I)CH_3$ (**1**). The reaction of $(d^tbpe)NiCl_2$ or **1** with the stoichiometric quantity of $(tmeda)Mg(CH_3)_2$ yields $(d^tbpe)Ni(CH_3)_2$ (**2**). $(d^tbpe)Ni(I)CD_3$ (**1**-d_3) and $(d^tbpe)Ni(CD_3)_2$ (**2**-d_6) have been prepared analogously. Thermolysis of **2** in benzene affords $\{(d^tbpe)Ni\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ (**4**). The reaction of either **2** or **4** with hydrogen (H_2, HD, D_2) gives $\{(d^tbpe)Ni\}_2(\mu\text{-}H)_2$ (**3**) and the isotopomers $\{(d^tbpe)Ni\}_2(\mu\text{-}H)(\mu\text{-}D)$ (**3**-d) and $\{(d^tbpe)Ni\}_2(\mu\text{-}D)_2$ (**3**-d_2). According to the NMR spectra, the structure of **3** is dynamic in solution. The crystal structures of **2** and **3** have been determined by X-ray crystallography. Solution thermolysis of **2** or reduction of $(d^tbpe)NiCl_2$ with Mg* in the presence of alkanes probably involves σ-complex-type intermediates $[(d^tbpe)Ni(\eta^2\text{-}R'H)]$ ($R' =$ e.g. C_2H_5, **A**). While the nonisolated $[(d^tbpe)Ni^0]$ σ-complexes **A** are exceedingly reactive intermediates, isolated **3** and **4** represent easy to handle starting complexes for $[(d^tbpe)Ni^0]$ reactions. Partial protolysis of **2** with CF_3SO_3H affords $(d^tbpe)Ni(CH_3)(OSO_2CF_3)$ (**5**). Complex **5** reacts slowly with 2 equiv of ethene to give equimolar amounts of $[(d^tbpe)Ni(C_2H_5)]^+(OSO_2CF_3^-)$ (**6**) and propene. The reaction is thought to be initiated by an insertion of ethene into the Ni−CH_3 bond of **5** to form the intermediate $[(d^tbpe)Ni(C_3H_7)(OSO_2CF_3)]$ (**G**), followed by elimination of propene to give the hydride intermediate $[(d^tbpe)Ni(H)(OSO_2CF_3)]$ (**H**), which on insertion of ethene into the Ni−H bond affords **6**.

Introduction

Increasing the size of ligands attached to metal centers can have a marked influence on reactivity. For example, Brookhart et al. have recently shown that cationic Ni^{II}− and Pd^{II}−methyl complexes containing bulky diimine ligands represent highly active catalysts for the polymerization of ethene and α-olefins.[1] For some time we have been interested in Ni^0 and Pd^0 complexes in which the metal center is ligated by the bidentate phosphane ${}^tBu_2PC_2H_4P^tBu_2$ (d^tbpe).[2−5] The combination of an exceedingly bulky phosphane ligand and the relatively small size of Ni confers interesting properties on the Ni^0 metal center. Hence, whereas the somewhat smaller ${}^iPr_2PC_2H_4P^iPr_2$ ligand allows the formation of tetrahedral (*T*-4) *and* trigonal-planar (*TP*-3) Ni^0−alkene complexes,[6] $(d^tbpe)Ni^0$−alkene complexes are exclusively *TP*-3.[3−5] Thus, for polyene ligands such as butadiene, 1,5-cyclooctadiene,[3] and cyclooctatetraene[5] only one C═C bond is coordinated to the $[(d^tbpe)Ni^0]$ fragment. Interestingly, Spencer et al. have reported that protolysis of $(d^tbpe)Ni(C_2H_4)$ by HBF_4 affords $[(d^tbpe)Ni(C_2H_5)]^+(BF_4^-)$ in which the C_2H_5 substituent is β-agostic.[7]

As part of our studies into the reactivity of the $[(d^tbpe)Ni^0]$ complexes, we were interested in investigating the properties of $(d^tbpe)Ni^{II,I}$−alkyl and −hydride complexes. In particular, we wished to establish whether they could be used to generate $[(d^tbpe)Ni^0]$ moieties directly *in situ*. Here we report the synthesis, structure, and properties of the title compounds, $(^tBu_2PC_2H_4P^tBu_2)Ni(CH_3)_2$ and $\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}H)_2$.[8]

[†] Abbreviations: bipy, 2,2′-bipyridine; d^tbpe, ${}^tBu_2PC_2H_4P^tBu_2$, bis(di-*tert*-butylphosphino)ethane; OTf, OSO_2CF_3, trifluoromethanesulfonate; tmeda, *N,N,N′,N′*-tetramethyl-1,2-ethanediamine.

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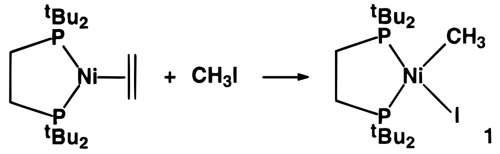
Results

($^tBu_2PC_2H_4P^tBu_2$)Ni(I)Me (1) and ($^tBu_2PC_2H_4P^tBu_2$)NiMe$_2$ (2). (d^{t}bpe)NiI$_2$ and (d^{t}bpe)NiCl$_2$ were prepared as possible starting materials for the syntheses of **1** and **2**. When NiCl$_2$ suspended in methanol is stirred with d^{t}bpe, large red needles of (d^{t}bpe)NiCl$_2$ crystallize at −78 °C. Treating yellow (d^{t}bpe)Ni(C_2H_4)[3] with 1,2-diiodoethane in THF results in evolution of ethene and precipitation of blue microcrystals of (d^{t}bpe)NiI$_2$ (0 °C). The yields are about 80%. While (d^{t}bpe)NiCl$_2$ is stable to 282 °C, solid (d^{t}bpe)NiI$_2$ decomposes at 90 °C. In the EI mass spectrum of (d^{t}bpe)NiCl$_2$ the molecular ion is observed, whereas for (d^{t}bpe)NiI$_2$ the largest ion observed is [(d^{t}bpe)NiI]$^+$. Both complexes are almost insoluble in pentane and diethyl ether, but (d^{t}bpe)NiI$_2$ dissolves in THF. Paramagnetism (NMR) indicates the presence of *T*-4 Ni^{II} centers.[9]

As far as we can ascertain, **1** cannot been synthesized from (d^{t}bpe)NiI$_2$ by partially substituting iodide for methyl. Instead, the reaction of (d^{t}bpe)Ni(C_2H_4) with CH_3I (neat, 1 h) yields large brown crystals of **1** (77%; eq 1). In a similar reaction using CD_3I, partially deuterated (d^{t}bpe)Ni(I)CD_3 (**1**-*d*$_3$) has also been prepared.

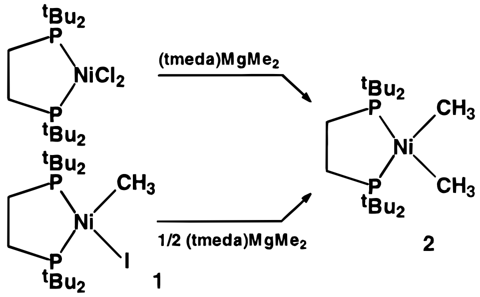


(1)

Solid **1** (mp 223 °C) is thermally surprisingly stable.[10] In the EI mass spectrum the molecular ion (*m*/*e* 518; 15%) is observed, which fragments by successive cleavage of methyl ([(d^{t}bpe)NiI]$^+$, base ion) and iodine to produce [(d^{t}bpe)Ni]$^+$, corresponding to a formal CH_3I elimination from [**1**]$^+$. Complex **1** dissolves well in THF. However, at ambient temperature the solutions decompose over the course of several days with elimination of ethane (NMR). Decomposition is presumably initiated by a metathesis reaction of **1** to give (d^{t}bpe)NiI$_2$ and **2**, which then eliminates ethane (see below). In the IR spectrum of **1** a CH-stretching mode (3026 cm^{-1}), a CH_3-*sym*-deformation mode (1126 cm^{-1}), and a CH_3-rocking band (752 cm^{-1}) can be assigned by comparison with **1**-*d*$_3$.[11] In the ^{1}H and ^{31}P NMR spectra the d^{t}bpe ligand of **1** shows signals for inequivalent $CH_2P^tBu_2$ parts; the coupling ^2J(PP) = 3 Hz is smaller than expected for a five-membered ($R_2PC_2H_4PR_2$)Ni ring.[12,13b] The signal for the NiCH_3 protons occurs at δ_H 0.55.

Attempts to synthesize (d^{t}bpe)Ni(H)CH_3 by reacting **1** with hydridic reagents such as LiAlH^{i}Bu$_3$ or NaBHEt$_3$ in diethyl ether or THF resulted in the formation of the dinuclear Ni^I−hydride **3** as the main product. It seems likely that (d^{t}bpe)Ni(H)CH_3 is formed as an intermediate but that it decomposes into **3**, similar to the solution thermolysis of **2** (see below). Thus, whereas *trans*-L$_2$Ni(H)CH_3 complexes have been known for a long time,[14] complexes of the type *cis*-L$_2$Ni(H)CH_3 remain elusive.

When the red suspension of (d^{t}bpe)NiCl$_2$ in diethyl ether is stirred with 1 equiv of (tmeda)Mg(CH_3)$_2$ at −30 °C, a yellow-orange solution is formed from which, after ($C_4H_8O_2$)$_2$MgCl$_2$ is precipitated with dioxane, yellow cubes of **2** (69%) crystallize at −78 °C. Similarly, (d^{t}bpe)NiCl$_2$ reacts with (tmeda)Mg(CD_3)$_2$ to give (d^{t}bpe)Ni(CD_3)$_2$ (**2**-*d*$_6$). Complex **2** can also be obtained from the reaction of **1** with the stoichiometric amount of (tmeda)Mg(CH_3)$_2$ (eq 2). Surprisingly, no reaction occurs between (tmeda)Ni(CH_3)$_2$ and d^{t}bpe, although the tmeda ligand can be displaced by $Me_2PC_2H_4PMe_2$ (−30 °C) to give ($Me_2PC_2H_4PMe_2$)Ni(CH_3)$_2$.[15] Complex **2**, which is best stored at −30 °C, melts at 124 °C with decomposition. Slow decomposition at 110 °C affords elimination of a mixture of ethane (55%), methane (23%), and ethene (16%). The ^{31}P NMR spectrum of the residue indicates the formation of several species, among which (d^{t}bpe)Ni(C_2H_4)[3,7] has been identified.



(2)

In the EI mass spectrum (110 °C) of **2** the molecular ion (*m*/*e* 406, 2%) is observed, which fragments by a stepwise loss of methyl groups to afford the ions [(d^{t}bpe)NiCH_3]$^+$ (8%) and [(d^{t}bpe)Ni]$^+$ (74%). Complex **2** dissolves well in diethyl ether and THF. The solutions slowly decompose above 0 °C and are only stable below −20 °C for long periods. In the NMR spectra (−30 °C) **2** displays, besides the signals of the d^{t}bpe ligand, for the NiCH_3 groups multiplets at δ_H −0.08 (AA′XX′; A, A′ = ^{31}P; X, X′ = ^{1}H) and δ_C 1.8 (AA′X; X = ^{13}C).

Crystal Structure of 2. The molecular structure of **2** has been determined by single-crystal X-ray structure analysis (Figure 1). The molecule is characterized by a square-planar (*SP*-4) Ni^{II} center coordinated to a chelating d^{t}bpe ligand and two methyl groups in cis positions. Conformational folding of the ethylene bridge between the two P atoms confers approximate C_2 symmetry on the molecule. The C_2 symmetry extends as far as the methyl groups, which do not lie exactly in the P1,P2,Ni plane but are arranged such that one methyl group is displaced above and the other below the plane (dihedral

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(9) Schröder, M. In *Encyclopedia of Inorganic Chemistry*; Wiley: Chichester, U.K., 1994; Vol. 5, p 2392.

(10) The complexes *trans*-(Me_3P)$_2$Ni(I)CH_3[10a] and *trans*-($^iPr_3P$)$_2$Ni(I)CH_3[10b] melt below 100 °C with decomposition: (a) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1972**, *105*, 2628. Klein, H.-F.; Karsch, H. H.; Buchner, W. *Chem. Ber.* **1974**, *107*, 537. Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524. (b) Green, M. L. H.; Smith, M. J. *J. Chem. Soc. A* **1971**, 639.

(11) For the IR characterization of [CH_3NiH] and [CD_3NiD], which are reported to be formed by the reaction of Ni atoms with methane (11−14 K), see: Chang, S.-C.; Hauge, R. H.; Billups, W. E.; Margrave, J. L.; Kafafi, Z. H. *Inorg. Chem.* **1988**, *27*, 205.

(12) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(13) (a) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 8094. (b) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436. (c) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449.

(14) For *trans*-{(*c*-C_6H_{11})$_3$P}$_2$Ni(H)CH_3, see: Jonas, K.; Wilke, G. *Angew. Chem.* **1969**, *81*, 534; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 519.

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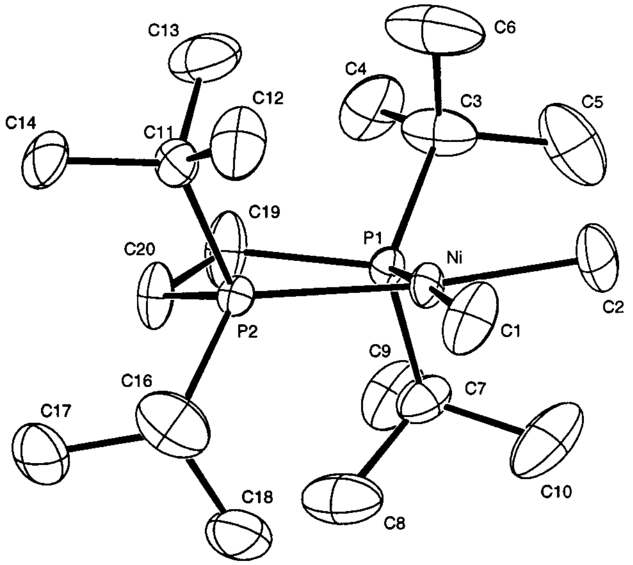


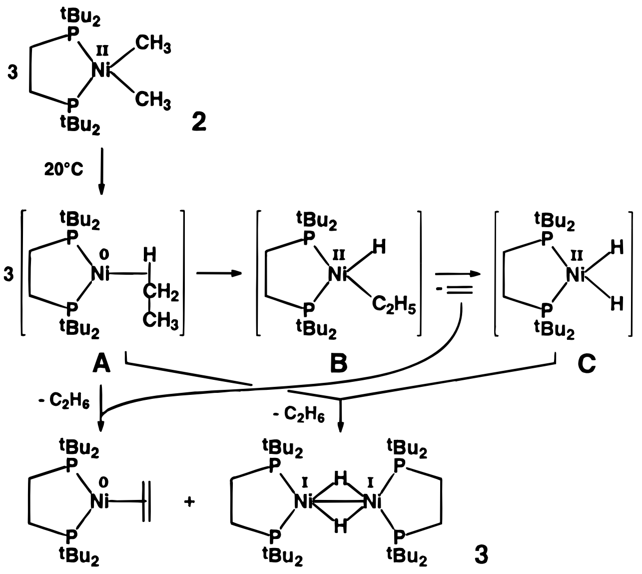
Figure 1. Molecular structure of **2**. Selected bond distances (Å) and angles (deg): Ni–C1 = 1.977(5), Ni–C2 = 1.965(5), Ni–P1 = 2.213(1), Ni–P2 = 2.209(1); P1–Ni–P2 = 90.44(4), C1–Ni–C2 = 83.7(2).

angle P1,P2,Ni/C1,C2,Ni 9°). Several short intramolecular distances indicate this is a result of steric interactions with the d^{t}bpe methyl groups. The C–Ni–C angle (83.7°) is also smaller than expected for *SP*-4 coordination even though the P1–Ni–P2 angle is 90.4°, and this can be attributed to the same cause. The Ni–C bond distance at 1.97(1) Å (mean) is nevertheless normal and lies within the expected range for C trans to P. In the isoelectronic (bipy)Ni(CH_3)$_2$[16] the N–Ni–N angle of 81.4(1)° is accompanied by a C–Ni–C angle of 86.6(2)° and a shorter Ni–C distance of 1.923(4) Å associated with C trans to N.[17,18]

Solution Thermolysis of 2. When a yellow solution of **2** in THF-d_8 is maintained at 20 °C for a few days, the color changes to dark red. In the ^{31}P NMR spectrum (**2**: δ_P 78.5) new signals are observed for (d^{t}bpe)Ni(C_2H_4) (δ_P 92.7) and **3** (δ_P 94.6) with relative intensities 1:2. After about 1 week the singlet from **2** completely disappears. In the ^{1}H NMR spectrum, in addition to the overlapping signals of various d^{t}bpe ligands, the signal of the ethene ligand in (d^{t}bpe)Ni(C_2H_4) (δ_H 1.84), a very narrow signal of ethane (δ_H 0.85), and a high-field quintet for the hydride ligand in **3** (δ_H −10.6) of approximate relative intensities 4:12:2 are observed. According to these observations, complex **2** decomposes in solution (20 °C) to yield equimolar amounts of (d-^{t}bpe)Ni(C_2H_4) and dinuclear **3**, concomitant with the elimination of 2 equiv of C_2H_6 (Scheme 1). The hydride in **3** arises from NiCH_3, since no deuterium has been abstracted from the solvent (cf. **3**-d_2, see below). Methane is apparently only formed to a small extent.

The mechanism of the solution thermolysis of **2**, therefore, is suggested to occur through oxidative coupling of the methyl groups in **2**, which generates the intermediate Ni^0–σ-ethane complex [(d^{t}bpe)Ni(η^2-H–C_2H_5)] (**A**). If neither a suitable π-ligand nor H_2 is present, intermediate **A** presumably undergoes an oxidative addition of the ethane C–H bond to Ni^0 to form a further intermediate, [(d^{t}bpe)Ni(H)C_2H_5] (**B**),[19] from which, by β-H elimination and formation of ethene, a third intermediate, [(d^{t}bpe)NiH_2] (**C**), results. We tentatively assign a weak ^{31}P NMR singlet at δ_P 72.4 to this intermediate (or its structural isomer **F**; cf. Schemes 2 and 3). A subsequent reaction of intermediate **A** with the generated ethene would produce (d^{t}bpe)Ni(C_2H_4) and 1 equiv of C_2H_6, whereas a combination of intermediates **A** and **C** would be expected to afford the dinuclear hydride complex **3** and 1 equiv more of C_2H_6.

Scheme 1



Similar results are obtained in the solution thermolysis of **2**-d_6 in THF-d_8. In addition to the ^{31}P singlet of (d^{t}bpe)Ni(C_2D_4) (δ_P 92.8) and the quintet of **3**-d_2 (δ_P 94.6; see below), a further, now quite intense, signal is observed at δ_P 72.6, which we attribute to [(d^{t}bpe)NiD_2] (**C**-d_2 or **F**-d_2).[20]

When the thermolysis of **2** (20 °C) is carried out in the presence of *ethene*, equimolar amounts of (d^{t}bpe)Ni(C_2H_4) and ethane, but no Ni^{I}–hydride **3**, is formed. The rate of the thermolysis of **2** is apparently unaffected by the amount of ethene added. These results support the view that for the reactions shown in Scheme 1 oxidative coupling of the methyl groups in **2** is rate-determining and that intermediate **A** is long-lived with respect to the subsequent reaction **A** → **B**; i.e., displacement reactions of the presumed σ-ethane ligand are faster than a C–H oxidative addition. This mechanism explains also the thermolysis of **2** in *benzene*, which produces mononuclear (d^{t}bpe)Ni(η^2-C_6H_6) in solution, from which dinuclear {(d^{t}bpe)Ni}$_2$(μ-η^2:η^2-C_6H_6) (**4**) is isolated.[4]

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(16) Wilke, G.; Herrmann, G. *Angew. Chem.* **1966**, *78*, 591; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 581.

(17) Tucci, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 6489.

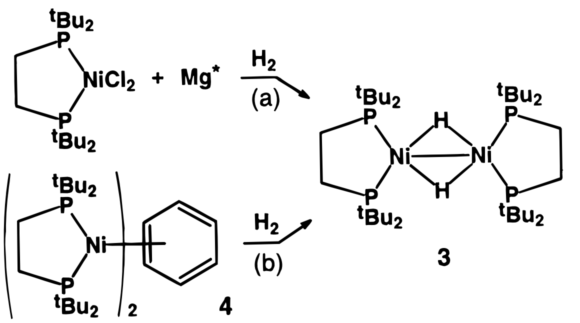
(18) For other structurally characterized (bipy)NiR_2 complexes, see: (a) Binger, P.; Doyle, M. J.; McMeeking, J.; Krüger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1977**, *135*, 405. (b) Binger, P.; Doyle, M. J.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34*, 1289.

(19) As pointed out by a reviewer, **2** may alternatively undergo an α-elimination of H to generate a nickel methyl methylene hydride intermediate, which then forms **B** by migration of the methyl group to the methylene carbon. However, for such a mechanism one would also expect the formation of methane, but the amount is negligible in solution.

(20) Experiments are in progress which are aimed at the synthesis and isolation of intermediates **C** (**C**-d_2) and **F** (**F**-d_2), respectively.

The chemistry of C−H activation reactions and metal−σ-alkane complexes is now well-established.[21] A precedent for the chemistry shown in Scheme 1 is provided by thermolysis of $(R_2PC_2H_4PR_2)Pt(H)(CH_2{}^tBu)$ ($R = c\text{-}C_6H_{11}$), which is reported to result in formation of the $[(R_2PC_2H_4PR_2)Pt^0]$ moiety.[13,22] In the presence of CH_4 or $c\text{-}C_6H_{12}$ additional $(R_2PC_2H_4PR_2)Pt(H)(R')$ complexes ($R' = CH_3$, $c\text{-}C_6H_{11}$) were obtained. Moreover, it has been reported that reduction of $(Ph_2PC_2H_4PPh_2)PtCl_2$ with Na/Hg in THF affords the $[(Ph_2PC_2H_4PPh_2)Pt^0]$ fragment, which reacts with the solvent to yield $(Ph_2PC_2H_4PPh_2)PtH_2$.[22a,23] It has also been suggested that the related species $[({}^iPr_2PC_2H_4P{}^iPr_2)Ni^0]$ is formed upon reduction of $({}^iPr_2PC_2H_4P{}^iPr_2)NiCl_2$ with activated magnesium (Mg*).[22a,24]

$\{({}^tBu_2PC_2H_4P{}^tBu_2)Ni\}_2(\mu\text{-}H)_2$ (3). As we have seen, thermolysis of **2** in an inert solvent leads to partial formation of the dinuclear Ni^I−hydride **3** (Scheme 1). Since the yield is relatively small, we were interested in obtaining a more efficient synthesis of **3**. When the red suspension of $(d^tbpe)NiCl_2$ in THF is stirred with Mg*[25a] under H_2 gas between −40 and 20 °C,[25b] an intensively colored dark red solution is obtained. When the temperature is lowered to −78 °C, dark crystals of **3**, exhibiting a green metallic sheen, precipitate (eq 3a).



(3)

Although the formation of **3** utilizing this route is almost quantitative (NMR), the resulting isolated yield remains only about 50% because of the high solubility of **3** in THF and the problem of avoiding cocrystallization of the $(THF)_4MgCl_2$ present.[26]

An improved synthesis of **3** is provided by stirring an ethereal solution of the $(d^tbpe)Ni^0$−benzene complex **4** with hydrogen gas between −60 and 20 °C (eq 3b). The red color of the solution intensifies immediately, and microcrystalline **3** precipitates in 80% yield. Larger crystals of **3** can be obtained by exposing a THF solution of **4** to hydrogen without stirring (20 °C). The reaction of **4** with D_2 affords the Ni^I−deuteride $\{(d^tbpe)Ni\}_2(\mu\text{-}D)_2$ (**3**-d_2). Similarly, the reaction of **4** with HD at −40 °C yields the pure mixed Ni^I−hydride−deuteride $\{(d^tbpe)Ni\}_2(\mu\text{-}H)(\mu\text{-}D)$ (**3**-d). When this reaction is carried out at 20 °C, however, **3**-d is still the main product, but the isotopomers **3** and **3**-d_2 are also formed due to a subsequent H/D exchange reaction of **3**-d with HD.

Solid **3** is thermally very stable and melts at 218 °C without decomposition. In the EI mass spectrum (175 °C) the molecular ion appears at m/e 754 (61%). Degradation of the $Ni_2(\mu\text{-}H)_2$ moiety is accompanied by cleavage and partial fragmentation of the d^tbpe ligands, but $[(d^tbpe)NiH]^+$ (377, 5%) and $[(d^tbpe)Ni]^+$ (376, 4%) are also detected. An analogous mass spectrum (160 °C) is obtained for **3**-d_2 (M^+: m/e 756, 9%). On the whole, the results indicate that the $Ni_2(\mu\text{-}H)_2$ moiety is remarkably stable. In the IR spectra of **3** and **3**-d_2 the Ni−H (1280 cm^{-1}) and Ni−D (920 cm^{-1}) absorption bands[27] are broad and weak, and the maxima were located by numerical subtraction of one spectrum from the other.

In the ^1H NMR spectrum (300 MHz, 27 °C) of **3**, the d^tbpe ligand gives rise to single signals for the PCH_2 and P^tBu_2 protons with poorly resolved J(PH) couplings. For the hydridic H atoms a sharp A_4X_2 quintet ($A = {}^{31}P$, $X = {}^1H$) is observed at δ_H −10.6 ($J(PH) = 21.6$ Hz). The $^{31}P\{^1H\}$ NMR spectrum displays a sharp singlet (δ_P 94.6). According to the spectra the four $CH_2P^tBu_2$ subunits of **3** are equivalent on the NMR time scale. The spectra are essentially unchanged at −80 °C.

In the ^1H NMR spectrum (27 °C) of **3**-d, the $Ni_2(\mu\text{-}H)(\mu\text{-}D)$ moiety also gives rise to a quintet at δ_H −10.6 ($J(PH) = 22$ Hz), the lines of which are furthermore 3-fold split[28] due to coupling to deuterium. The signal lies at slightly lower field (0.02 ppm) relative to that of nondeuterated **3**, which is best discernible when a solution contains both species. The small coupling $^2J(HD) \approx 1.5$ Hz corresponds to a geminal dihydride; i.e., no direct H···D interaction is present.[29] In the $^{31}P\{^1H\}$ NMR spectrum (27 °C) of **3**-d an apparent singlet is observed at δ_P 95.6, which is at 1 ppm lower field than for **3**.

For the $Ni_2(\mu\text{-}D)_2$ complex **3**-d_2 the ^{31}P NMR signal (27 °C) is at δ_P 94.6 and therefore comes at the same

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[21] (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Bergmann, R. G. *Science* **1984**, *223*, 902. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (d) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (e) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (f) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley-Interscience: New York, 1986; p 229. (g) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (h) Crabtree, R. H. *Angew. Chem.* **1993**, *105*, 828; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (i) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987.

[22] (a) No intermediates of the type $[(R_2PC_2H_4PR_2)M^0]$ ($M = Ni$, Pt; $R = C_6H_5$, ${}^iPr$, $c\text{-}C_6H_{11}$) have yet been isolated or spectroscopically characterized. In light of the present knowledge on the properties of *bent* $[L_2M^0]$ fragments and on metal−σ-alkane complexes[21] it appears most likely that monomeric $[(R_2PC_2H_4PR_2)M^0]$ species in solution are in fact the σ-alkane complexes $[(R_2PC_2H_4PR_2)M^0(\sigma\text{-}R'H)]$ ($M = Ni$, Pt). (b) Upon generation of $[\{R_2P(CH_2)_nPR_2\}Pd^0]$ ($n = 1, 2$; $R = {}^iPr$, $c\text{-}C_6H_{11}$) the chelate ring opens to afford the dinuclear complexes $Pd_2\{\mu\text{-}R_2P(CH_2)_nPR_2\}_2$ with formally linear $L{-}Pd^0{-}L$ geometries: Pan, Y.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 3842. Döhring, A.; Goddard, R.; Hopp, G.; Jolly, P. W.; Kokel, N.; Krüger, C. *Inorg. Chim. Acta* **1994**, *222*, 179. (c) In $[\{{}^tBu_2P(CH_2)_3P{}^tBu_2\}Pt^0]_2$ each bidentate phosphane chelates a *TP*-3 Pt^0 center with a relatively large P1−Pt−P2 angle of 102.6°. The L_2Pt^0 moieties are coordinated to each other via an unsupported $d^{10}{-}d^{10}$ $Pt^0{-}Pt^0$ bond (2.76 Å).[61]

[23] Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191.

[24] Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113.

[25] (a) Bartmann, E.; Bogdanovic, B.; Janke, N.; Liao, S.; Schlichte, K.; Spliethoff, B.; Treber, J.; Westeppe, U.; Wilczok, U. *Chem. Ber.* **1990**, *123*, 1517. (b) The activity of Mg* varies from batch to batch. The low-temperature reduction of $(d^tbpe)NiCl_2$ is feasible with the most active Mg*.

[26] Partial formation of **3** is also observed (NMR) when $(d^tbpe)NiCl_2$ is reduced by Mg* in the absence of molecular hydrogen. Here the hydridic H atoms of **3** presumably result from the reaction of the generated $[(d^tbpe)Ni^0]$ fragment with the solvent, i.e., either by attack of a THF C−H bond or, more likely, by protonation from inevitable amounts of moisture. A corresponding reactivity has been reported for the postulated $[({}^tBu_2PC_3H_6P{}^tBu_2)Pt^0]$, giving rise to $({}^tBu_2PC_3H_6P{}^tBu_2)PtH_2$.[23]

[27] For a terminal Ni−H group an intense IR stretching band is expected between 1950 and 1800 cm^{-1}.

[28] Multiplicity $2nI + 1$: for **3**-d, $I = 1$, $n = 1$; for **3**-d_2, $I = 1$, $n = 2$.

[29] (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

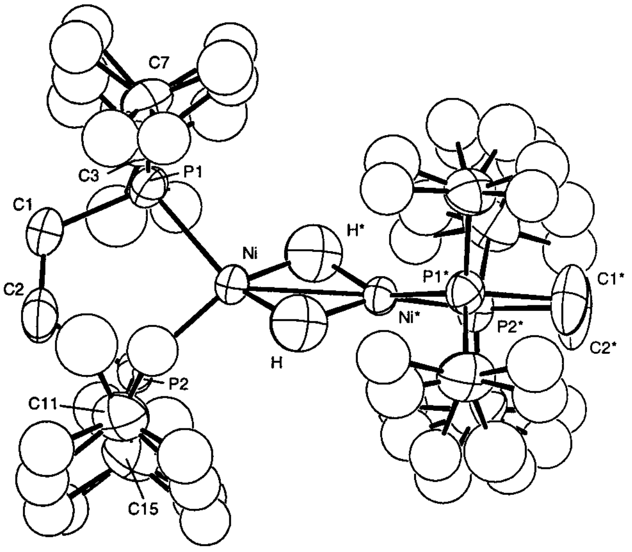

Figure 2. Molecular structure of **3**. Selected bond distances (Å) and angles (deg): Ni−Ni* = 2.433(1), Ni−P1 = 2.165(1), Ni−P2 = 2.158(1), Ni−H1 = 1.58(4), H1···H1* = 2.02(7); P1−Ni−P2 = 93.42(4), H1−Ni−H1* = 79(2), Ni−H−Ni* = 101(3).

field as that for **3** (sharp singlet), but it occurs as a quintet due to coupling to two equivalent deuterium nuclei (J(PD) = 3.4 Hz).[28] The isotopomers **3**, **3**-d, and **3**-d_2 are thus clearly distinguishable from each other on the basis of their ^{1}H and ^{31}P NMR spectra.

The NMR spectra of **3** are indicative of a structural dynamic process and will be discussed following a description of the molecular structure in the crystal.

Molecular Structure of 3. The molecular structure of **3** has been determined by a single-crystal X-ray structure analysis, which confirms the dimeric nature of the molecule. Two [(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni^I] moieties are bridged by two H atoms, forming a central planar Ni(μ-H)$_2$Ni four-membered ring (Figure 2). The structure of **3** is closely related to those of {(R$_2$PC$_3$H$_6$PR$_2$)Ni^I}$_2$(μ-H)$_2$ (R = c-C$_6$H$_{11}$ (**3a**),[30] ^{i}Pr (**3b**)[31a]),[31b] and it is convenient to compare it with them. Extended Hückel calculations on the sterically unhindered (P$_2$Ni)$_2$(μ-H)$_2$ moiety predict a completely square-planar dimeric D_{2h} ground-state structure (Figure 3a).[30c]

In **3** and **3a,b** the Ni centers are, however, not square planar, but the molecules are twisted about the Ni−Ni axis such that the two NiP$_2$ planes lie on either side of the Ni(μ-H)$_2$Ni ring with the result that the (P$_2$Ni)$_2$(μ-H)$_2$ core adopts D_2 symmetry. If we define the angle θ as the dihedral angle between the planes through the two NiP$_2$ units, then we find that θ is 80° for **3** while it is 63° for **3a** and 75° for **3b**. In **3** the planes P1,P2,Ni and P1*,P2*,Ni* are thus almost perpendicular to one another. It follows that θ/2, i.e., the distortion from the square-planar coordination at the Ni centers (P,P,Ni/Ni,H,H), is a large 40°.

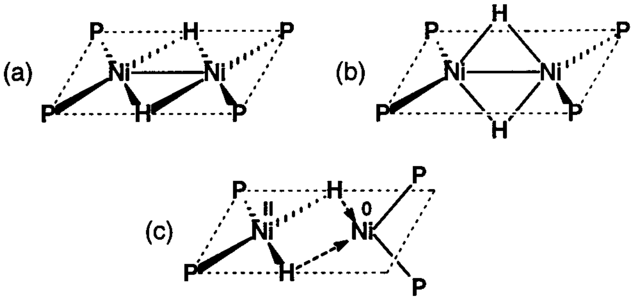

Figure 3. Discussed geometries of the (P$_2$Ni)$_2$(μ-H)$_2$ core of **3** and derivatives: (a) calculated "square-planar dimer" D_{2h} ground state; (b) energetically forbidden "tetrahedral dimer" D_{2h} state; (c) suggested C_{2v} transition state for the structural dynamics.

Since the substituents at P are more bulky in the case of **3**, the distortions from θ = 0° would appear to be the result of minimization of steric strain.[32] A direct comparison of **3** with **3a,b** is, however, complicated by the fact that the P(CH$_2$)$_n$PNi chelate complexes have different ring sizes, resulting in different bite angles of the P ligands at Ni (P1−Ni−P2 for **3** (n = 2) is 93.4(1)° and for **3a,b** (n = 3) is 103°) and in a change of not only the steric but also the electronic situation. Indeed, the Ni−Ni bond length of 2.433(1) Å in **3**, although typical for a Ni^I−Ni^I bond, is slightly shorter than that found in **3a,b** (2.44 Å), whereas an elongation might have been expected from steric arguments.

The Ni−P bond length in **3** (2.161(5) Å, mean) is longer than that for **3a** (2.13 Å, mean) and **3b** (2.14 Å, mean) but significantly less than that for the (d^{t}bpe)Ni^{II} complex **2** (2.211(3) Å, mean). The H atoms are symmetrically bound to both Ni centers (Ni−H 1.58(4) Å, mean), as is also the case for **3a,b** (within the limits of the experimental error). The large H1···H1* distance in the Ni(μ-H)$_2$Ni moiety (2.02(7) Å) precludes direct bonding between the H atoms.

Structural Dynamics of 3. The NMR spectra of **3** indicate the equivalence of the four CH$_2$P^{t}Bu$_2$ moieties and, within these, the equivalence of the PCH$_a$H$_b$ and P^{t}Bu$_a$^{t}Bu$_b$ protons. If the structure of **3** in solution were the same as that in the crystal (D_2 symmetry) and static with regard to the (P$_2$Ni)$_2$(μ-H)$_2$ core, one should observe separate ^{1}H NMR signals for the PCH$_a$H$_b$ and P^{t}Bu$_a$^{t}Bu$_b$ protons, which is not the case. Other possible rigid solution structures of **3** include the calculated "square-planar dimer" D_{2h} ground state (Figure 3a),[30c] but the (P$_2$Ni)$_2$(μ-H)$_2$ hydrogen atoms are expected to give rise to an A$_2$A′$_2$XX′ multiplet due to different couplings to cis- and trans-positioned ^{31}P nuclei, which is at variance with the observed A$_4$X$_2$ multiplet. The spectra fit a "tetrahedral dimer" D_{2h} structure (Figure 3b), but this arrangement is unlikely on the basis of the MO calculations, which predict a very high energy for this geometry.[30c] A rapid reversible dissociation of **3** into the monomer [(d^{t}bpe)Ni^{I}H] can be ruled out because of the extraordinary thermal stability of the complex and the A$_4$X$_2$ coupling of the hydride resonance.

Thus, the ^{1}H NMR spectrum of **3** in solution (−80 to 27 °C) is best explained by a *dynamic structure*, repre-

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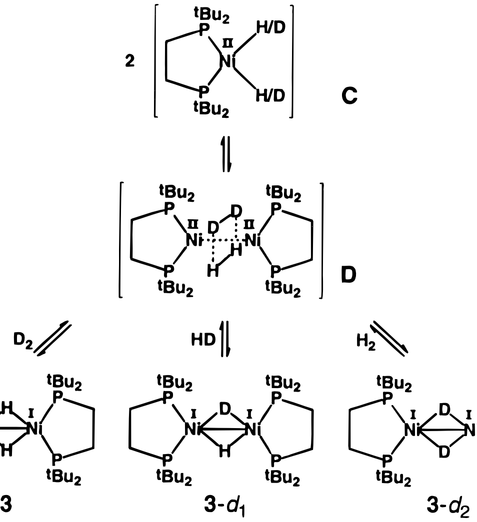
(30) (a) Jonas, K.; Wilke, G. *Angew. Chem.* **1970**, *82*, 295; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 312. Jonas, K. *J. Organomet. Chem.* **1974**, *78*, 273. (b) Krüger, C. *Angew. Chem.* **1972**, *84*, 412; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 387. (c) Barnett, B. L.; Krüger, C.; Tsay, Y.-H.; Summerville, R. H.; Hoffmann, R. *Chem. Ber.* **1977**, *110*, 3900. Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

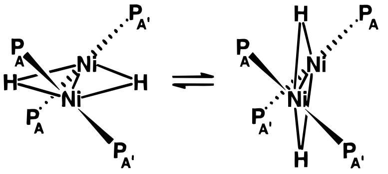
(31) (a) Fryzuk, M. D.; Clentsmith, G. K. B.; Leznoff, D. B.; Rettig, S. J.; Geib, S. J. *Inorg. Chim. Acta* **1997**, *265*, 169. (b) Further derivative: {(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni}$_2$(μ-H)$_2$ (**3c**): Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855.

(32) The extreme steric congestion in **3** can also be deduced from the fact that neither Ni(d^{t}bpe)$_2$ nor {(d^{t}bpe)Ni}$_2$(μ-d^{t}bpe) nor Ni$_2$(μ-d^{t}bpe)$_2$ is formed.[3]

Scheme 2



sented by a rotation of the $Ni_2(\mu\text{-}H)_2$ and P,P,Ni planes relative to each other. How could this rotation proceed? With the solid-state D_2 structure of the $(P_2Ni)_2(\mu\text{-}H)_2$ core as a starting point, a libration through the square-planar dimer D_{2h} structure will not give rise to the A_4X_2 quintet, and a libration through the tetrahedral dimer D_{2h} state is probably energetically forbidden. In addition, these transformations would imply a significant reorientation of the phosphorus atoms, which seems unlikely in view of the bulk of the phosphorus ligands and the ease with which the dynamics occur (−80 °C). We therefore think that the spectra are best described by a motion whereby both P,P,Ni planes take up an approximately perpendicular arrangement (resulting from a distortion of the ground-state planar D_{2h} structure by strain imposed by the phosphorus ligands) and this is maintained in the course of the dynamic process, while the central $Ni_2(\mu\text{-}H)_2$ plane rotates in steps of 90° (eq 4).

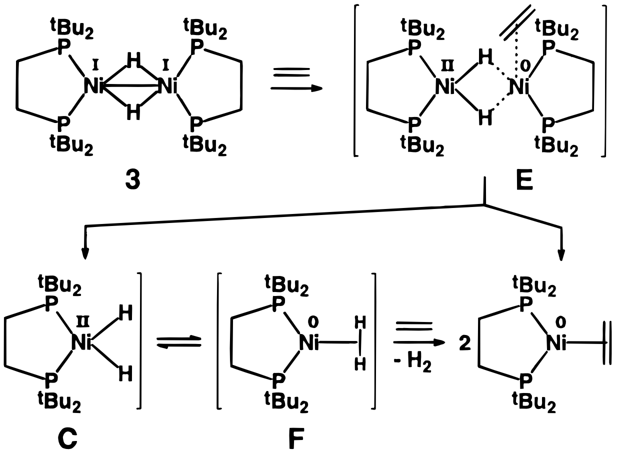


(4)

After a rotation of 45°, the complex passes through a C_{2v} transition state, in which one Ni center has attained *SP*-4 coordination geometry and the other *T*-4 geometry. This transition state implies a formal disproportionation of the $Ni^I_2(\mu\text{-}H)_2$ group into *T*-4 Ni^0 and *SP*-4 $Ni^{II}H_2$ moieties held together by hydride bridges (Figure 3c).[33] Hence, the structural dynamics are mechanistically closely related to the suggested formation of **3** from intermediates **A** [Ni^0] and **C** [Ni^{II}] (Scheme 1).

Reactivity of 3. We have already mentioned that the mixed Ni^I−hydride−deuteride **3**-*d* undergoes (slow) H/D scrambling with additional HD to give **3** and **3**-d_2 (20 °C). Similarly, when a solution of **3** in THF-d_8 is stirred under D_2 at 20 °C for 30 min, the ^{31}P NMR spectrum displays, besides the singlet of residual **3** (δ_P 94.6), as the main signal the quintet of **3**-d_2 (δ_P 94.6) and furthermore the singlet of **3**-*d* (δ_P 95.6). In the corresponding ^1H NMR spectrum the hydride quintets of **3** and **3**-*d* (δ_H −10.6) are observed. Thus, the bridging hydride substituents of the $(P_2Ni)_2(\mu\text{-}H)_2$ moiety are exchanged by D_2 predominantly as a H_2 unit (H_2/D_2 exchange), but slow H/D scrambling also occurs. The mechanisms of the H_2/D_2 exchange and H/D scrambling reactions[33] are apparently related to one another. Since H_2 dissociation from **3** is unlikely and does not explain the formation of **3**-*d*, it is suggested that **3** *associatively* reacts with D_2 to give the dinuclear tetrahydride/deuteride intermediate $\{(d^tbpe)Ni\}_2(\mu\text{-}H_2D_2)$ (**D**), formally a dimer of the Ni^{II}−dihydride **C** (Scheme 2). For **D** a principal structure may be envisaged in which the original H atoms have gained close contact while the incoming D_2 is not yet fully split. Intermediate **D** is related to a series of ionic complexes $[(L_2M)_2H_3]^+$ (M = Ni, Pt)[34a] and $[(L_2Pt)_2(\mu\text{-}H)_2]^{2+}$ [34b] (L_2 = bidentate phosphane) by formal hydride addition to the latter. The formation of **D** explains both the preferred H_2/D_2 exchange **3** → **3**-d_2 and the H/D scrambling **3** → **3**-*d* upon addition of D_2 (respectively H/D scrambling **3**-*d* → **3** + **3**-d_2 with HD).

Scheme 3



Complex **3** reacts with alkenes or alkynes by displacement of the H_2 moiety to afford the corresponding (d^{t}bpe)Ni^0−alkene and −alkyne complexes; a similar reactivity has been noted previously for **3a**[30a] and related complexes.[35] For example, when ethene is added to an ethereal solution of **3** at 20 °C, the color changes from red to yellow within 20 min and (d^{t}bpe)Ni(C_2H_4)[3] is isolated. When ethyne is added to a THF-d_8 solution of **3** at −60 °C, the color lightens in about the same time, and the ^1H and ^{31}P NMR spectra display the signals of (d^{t}bpe)Ni(C_2H_2)[3] but no signals for C_2H_4, (d^{t}bpe)Ni(C_2H_4), or C_2H_6. Thus, in these reactions ethene and ethyne cleanly displace H_2 without hydrogenation or formation of NiC_2H_5 or $NiCH{=}CH_2$ groups. As for the H_2/D_2 exchange reaction, we suggest for the mechanism of these H_2 displacement reactions (Scheme 3) that dinuclear **3** reacts *associatively* with the substrates. Coordination of the π-ligand to one Ni center in di-

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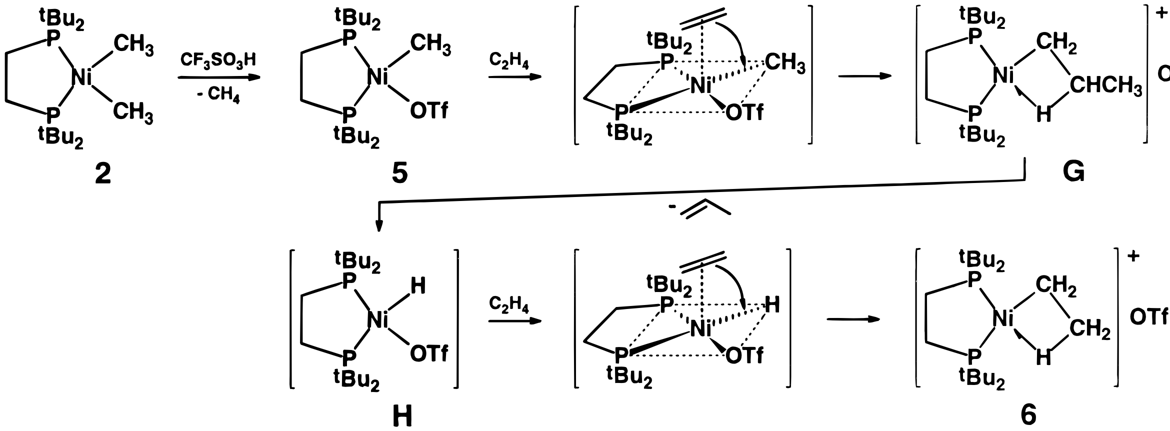
[33] For (d^{t}bpe)Pt(H)-Pt(H)(d^{t}bpe),[64] which is stoichiometrically analogous to **3** but structurally quite different (see Discussion), different mechanisms are suggested for the structural dynamics and the H/D scrambling process encountered there.

[34] (a) Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1996**, 1305 and literature cited therein. (b) Mole, L.; Spencer, J. L.; Litster, S. A.; Redhouse, A. D.; Carr, N.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 2315.

[35] Bennett, B. L.; Roddick, D. M. *Inorg. Chem.* **1996**, *35*, 4703.

Scheme 4



nuclear **3** initiates the disproportionation Ni^I(μ-H)$_2$Ni^I → [Ni^{II}H$_2$/Ni^0] (**E**). While the Ni^0–π-ligand complex is formed directly, coupling of the H substituents in the resulting **C** presumably affords the Ni^0–σ-H$_2$ intermediate **F,** from which H$_2$ is displaced by further substrate. The reaction is closely related to both the H$_2$/D$_2$ exchange reaction (Scheme 2) and the structural dynamics of **3** via the C_{2v} symmetrical transition state. Upon addition of an excess of PMe$_3$ to **3** (THF-d_8, 20 °C) all ligands are displaced to form Ni(PMe$_3$)$_4$ (δ_P −21.0). In conclusion, although **3** is spectroscopically and structurally best regarded as a Ni^I complex, chemically it acts as a Ni^0 source.

While **3** reacts with ethene and ethyne by displacing H$_2$ from the [(d^{t}bpe)Ni^0] fragment, it can, on the other hand, be synthesized from the Ni^0–benzene complex **4** by displacing benzene with H$_2$ (eq 3b). In turn, the Ni^0–σ-complex **A**, generated by thermolysis of **2**, is a likely common intermediate in the synthesis reactions of **4**,[4] the Ni^I–hydride **3**, and (d^{t}bpe)Ni(C$_2$H$_4$) (Scheme 1). We have no indication that a hot ligand-free [(d^{t}bpe)Ni^0] fragment has a reasonable lifetime as a strongly bent L$_2$Ni^0 complex in solution. Instead, we rather assume that it forms σ-R′H complexes with either the solvent (THF, benzene), ethane (when generated from **2**), or other potential substrates containing C–H bonds.[22] Thus, complexes [(d^{t}bpe)Ni^0(η^2-R′H)] such as **A** which may be generated by various routes (thermolysis of **2**; reduction of (d^{t}bpe)NiCl$_2$ with Mg* in THF) can be considered to be the most reactive *nonisolated* [(d^{t}bpe)-Ni^0] species and serve to synthesize all isolable derivatives. Nevertheless, the benzene complex **4** is the most reactive *isolated* [(d^{t}bpe)Ni^0] complex and provides the best starting material for the synthesis of further complexes. The Ni^I–hydride **3** is less reactive than **4** but markedly more reactive than (d^{t}bpe)Ni(C$_2$H$_4$), for which a low reactivity has already been stated.[3] When the various [(d^{t}bpe)Ni^0] sources are arranged according to the relative reactivities, a cascade of displacement reactions may be carried out, as depicted in Figure 4.

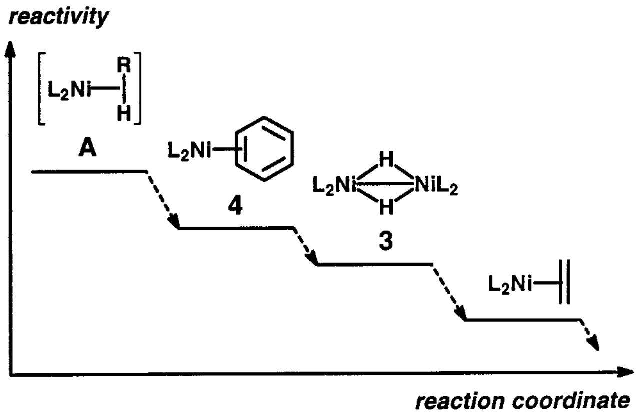


Figure 4. Relative reactivity of various [(d^{t}bpe)Ni^0] sources.

(d^{t}bpe)Ni(CH$_3$)(OSO$_2$CF$_3$) (5) and [(d^{t}bpe)Ni-(C$_2$H$_5$)]$^+$(OSO$_2$CF$_3$)$^-$ (6). When the ethereal solution of **2** is reacted with 1 mol equiv of CF$_3$SO$_3$H at −30 to 20 °C, ocher microcrystals of **5** precipitate in 75% yield (route a). Further synthetic routes to **5,** which, however, have not been optimized, are (b) oxidative addition of MeOTf to **2** via a Ni^{IV} intermediate, (c) oxidative addition of MeOTf to the Ni^0–benzene complex **4**, and (d) halide substitution in **1** with AgOTf. As for **1**, solid **5** (mp 180 °C) is rather stable. Both complexes are almost insoluble in pentane and only sparingly soluble in diethyl ether but dissolve well in THF. A very slow solution decomposition of **5** with evolution of ethane (20 °C) is explained by a metathesis reaction to afford (d-^{t}bpe)Ni(OTf)$_2$ and **2**, which decomposes as described. The NMR and EI-MS data of **5** are unexceptional. Since **5** does not contain additional Et$_2$O, the anion CF$_3$SO$_3^-$ is most likely coordinated to the *SP*-4 Ni^{II} center.

In contrast to **1**, complex **5** in THF solution reacts slowly at 20 °C with 2 equiv of ethene to give equimolar amounts of **6** and propene[36] (Scheme 4). As monitored by ^{1}H and ^{31}P NMR, the reaction is complete after 3 days. The ^{1}H and ^{31}P NMR data of **6** (THF-d_8, 27 °C) agree with those reported for [(d^{t}bpe)Ni(C$_2$H$_5$)]$^+$(BF$_4$)$^-$ (**6a**) (CD$_2$Cl$_2$),[7] which features an agostic β-proton interaction of the ethyl substituent with the *SP*-4 Ni^{II} center (X-ray). In the ^{1}H NMR spectrum **6** displays (besides the d^{t}bpe signals) a characteristic multiplet at δ_H −1.13 for the NiC$_2$H$_5$ methyl protons, while the signal of the NiCH$_2$ protons is obscured by d^{t}bpe signals. The high-field shift of the (coalesced) β-proton signal is due to the agostic Ni–H interaction of one of the three protons.[7] In the ^{31}P NMR spectrum complex **6** exhibits a pair of doublets at δ_P 102.0 and 96.6 with ^2J(PP) = 13.4 Hz. We assume that the structure of **6** (which has not been isolated so far) is ionic, as for **6a**.

As far as the mechanism of the formation of **6** and propene is concerned, we suggest that complex **5** reacts

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[36] ^{1}H NMR of propene (THF-d_8): δ_H 5.79 (=CH–), 4.98 (=CH$_Z$H), 4.89 (=CHH$_E$), 1.70 (CH$_3$).

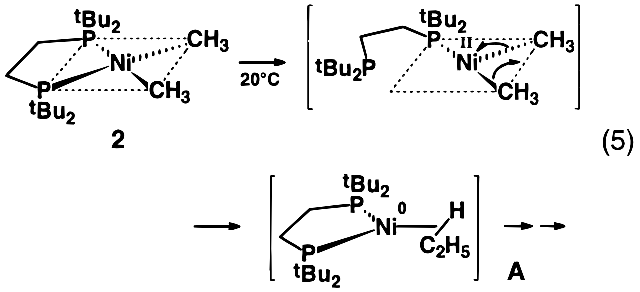
with ethene by insertion into the Ni−CH_3 bond (rate-determining step) to form the intermediate [(d^{t}bpe)Ni(C_3H_7)(OSO_2CF_3)] (**G**), which is structurally related to **6** and **6a**. Intermediate **G**, as a result of β-H activation, eliminates propene to give the Ni^{II}−hydride intermediate [(d^{t}bpe)Ni(H)(OSO_2CF_3)] (**H**), which rapidly inserts ethene into the Ni−H bond to yield **6** (Scheme 4).[37]

Discussion

The [(d^{t}bpe)Ni] fragment displays interesting features due to the combination of an exceedingly bulky chelating ligand and the smallest metal center of the homologous series Ni, Pd, Pt. One consequence is that typical (d^{t}bpe)Ni^0−alkene complexes (alkene: e.g. ethene, 1,5-hexadiene, *trans,trans,trans*-1,5,9-cyclododecatriene) have unexpectedly low kinetic reactivities. For example, when it is dissolved in undiluted butadiene or cyclooctatetraene, (d^{t}bpe)Ni(η^2-$C_{12}H_{18}$) is inert (20 °C, 24 h) and (d^{t}bpe)Ni(C_2H_4) reacts only very slowly to give (d^{t}bpe)Ni(η^2-C_4H_6)[3] and (d^{t}bpe)Ni(η^2-C_8H_8),[3,5] respectively. The low reactivity is in sharp contrast to the otherwise facile displacement of alkene ligands from Ni^0 centers. It follows that complexes such as (d^{t}bpe)Ni(C_2H_4) are not suited for the ready generation of [(d^{t}bpe)Ni^0] as a reactive intermediate for reactions with, e.g., H_2, N_2, or CH_4.

Two aspects concerning the properties of the title complexes are particularly noteworthy.

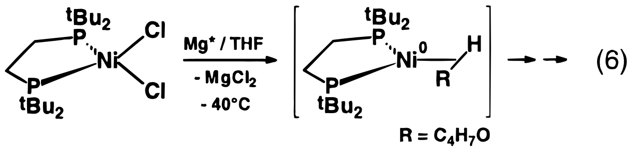
A. As has been shown here and in the concurrent report on **4**,[4] an *access to highly reactive [(d^{t}bpe)Ni^0] complexes* is provided both by solution thermolysis of **2** and by Mg* reduction of (d^{t}bpe)NiCl_2. Thermolysis of **2** in solution (0 °C) proceeds under conditions markedly milder than those in the solid state and leads mainly to the elimination of ethane with only negligible amounts of methane. In agreement with the mechanism suggested for elimination reactions from *SP*-4 M^{II} centers (M = Pd, Pt),[38] it seems likely that also for M = Ni the C−C coupling step to form ethane is initiated by lowering the coordination number from 4 to 3 by a reversible ring-opening of the (d^{t}bpe)Ni chelate complex (eq 5),[13b] a process which, for obvious reasons, proceeds more readily for the dissolved complex than for the solid. The ring-opening step is presumably supported by steric repulsion between the P^{t}Bu$_2$ groups and the rest of the complex. It apparently proceeds more readily at the *SP*-4 Ni^{II} than at the *TP*-3 Ni^0 center, and consequently, reduction to Ni^0 supports the reverse ring closure. The proposed primary product from the C−C coupling step is the intermediate [(d^{t}bpe)Ni^0(σ-H−C_2H_5)] (**A**). The σ-ethane ligand in **A** may be displaced by suitable substrates (C_2H_4, H_2, C_6H_6), or otherwise, **A** undergoes a C−H activation reaction (Scheme 1). The supposed C−H activation step results from the strong dπ donor capability of bent 14e L_2M^0 (M = Ni, Pd, Pt) complex fragments.[23] Correspondingly, reduction of (d^{t}bpe)NiCl_2 with Mg*/THF (−40 °C) likely generates the initial intermediate [(d^{t}bpe)Ni^0(σ-R′H)] (R′H = C_4H_8O), from which the further products arise (eq 6).



2

(5)

A



(6)

In addition to **2** there are numerous *trans*- and *cis*-$L_2Ni(CH_3)_2$ complexes that are known, e.g., *trans*-(Me_3P)$_2$NiMe_2,[10a] {(Ph-2-C_6H_4O)$_3$P}$_2$NiMe_2,[16] (bipy)-NiMe_2,[16,39a] (ArN=CHCH=NAr)NiMe_2 (Ar = 2,6-^{i}Pr$_2C_6H_3$),[40] (tmeda)NiMe_2,[15] and ($Me_2PC_2H_4PMe_2$)NiMe_2.[15] Early detailed studies on the parameters that determine reductive elimination reactions have been carried out for (bipy)NiR_2 (R = Me, Et, Pr, ^{n}Bu)[39a] and {$Ph_2P(CH_2)_n$-PPh_2}NiMe_2.[39b]

B. The profound interest in *Ni−hydride complexes* arises from the function of Ni as a heterogeneous[41] or possibly homogeneous[42] hydrogenation catalyst,[43] the likely occurrence of Ni−hydride intermediates in catalytic reactions,[44] and also the function of NiFe hydrogenase.[45] For Ni^{II}, a variety of neutral 16e [*trans*-(Cy_3P)$_2$Ni(H)X][14,46−49] and 18e [(Ph_3P)$_3$Ni(H)Br][50] com-

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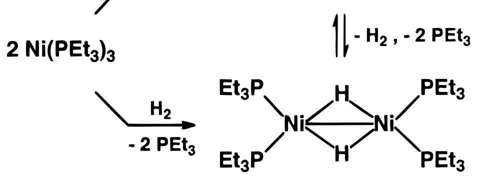
plexes and also ionic 18e $[L_4NiH]^+X^-$ [51−53] complexes have been described, whereas initial reports on "NiH_2"[54a] have been questioned.[54b] In seminal studies Jonas and Wilke have shown that $\{R_2P(CH_2)_nPR_2\}Ni^{II}Cl_2$ and $\{R_2P(CH_2)_nPR_2\}Ni^{I}Cl$ ($R = c\text{-}C_6H_{11}$, $n = 2-4$) react with $NaHBMe_3$ and $\{R_2P(CH_2)_nPR_2\}Ni^0$−arene with H_2 to afford the formal Ni^I−hydrides $[\{R_2P(CH_2)_nPR_2\}Ni^I]_2(\mu\text{-}H)_2$ (cf. **3a**).[30,31] Isolable Ni^I−hydrides are so far confined to those stabilized by bidentate phosphane ligands, whereas the corresponding complexes with monodentate ligands are labile. Thus, for a solution of $Ni(PEt_3)_3$ pressurized with H_2 (10 bar; −63 °C) two high-field ^1H NMR signals have been observed, which are attributed to $\{(Et_3P)_2Ni^I\}_2(\mu\text{-}H)_2$ (δ_H −11.9, quintet; **3d**) and $(Et_3P)_3NiH_2$ (δ_H −13.3, quartet; $(Et_3P)_3Ni^0(\eta^2\text{-}H_2)$ or *trans*-$(Et_3P)_3Ni^{II}H_2$) in slow equilibrium (eq 7).[52b,55] Similarly, photolysis of $Ni(CO)_4$ in an H_2/Ar matrix (<4.4 K) is reported to produce labile $(CO)_3Ni(\eta^2\text{-}H_2)$.[56]



(7)

It is evident that complex **3** is closely related to **3a**−**d**. A further relationship is found in Pd and Pt analogues which have been synthesized in recent times.[57] Regarding *palladium*, $\{^iPr_2P(CH_2)_3P^iPr_2\}PdI_2$ has been reacted with $KHBEt_3$ to afford $[\{^iPr_2P(CH_2)_3P^iPr_2\}Pd^I]_2(\mu\text{-}H)_2$.[58] This complex displays a nearly planar $P_4Pd_2H_2$ core (θ = 24°). Interestingly, the Pd^I-Pd^I bond is relatively long (2.82 Å) and the hydride ligands are *semibridging* the Pd^I centers (Pd1−H1 1.67 Å; Pd2−H1 2.11 Å). Similar to what is observed for **3** and **3a**, H_2 is displaced by ethene without the latter becoming hydrogenated. No stable mononuclear complexes *cis*-$L_nPd(H_2)$ are known,[59] but *trans*-$L_2Pd^{II}H_2$ ($L_2 = {}^tBu_2P(CH_2)_3\text{-}p\text{-}C_6H_4(CH_2)_3P^tBu_2$) has been synthesized.[23] Regarding *platinum*, *cis*-L_2Pt^{II}−dihydrides such as $(^tBu_2PCH_2\text{-}o\text{-}C_6H_4CH_2P^tBu_2)PtH_2$,[60] $\{RR'P(CH_2)_nPRR'\}PtH_2$ ($R, R' = {}^tBu$, Men, Ph; $n = 2, 3$),[61] and $\{R_2P(CH_2)_nPR_2\}PtH_2$ ($n = 2-4$; $R = c\text{-}C_6H_{11}$)[62] are readily accessible.[63] Although the coordination of the hydride in these complexes is static on the ^1H NMR time scale (the hydride substituents couple with cis and trans P atoms),[60,61] they undergo a (slow) H_2/D_2 exchange, indicative of a $Pt^{II}H_2 \rightleftharpoons Pt^0(\eta^2\text{-}H_2)$ equilibrium.[61,62] Purging a solution of $(d^tbpe)PtH_2$[61] with N_2 (90 °C) affords H_2 elimination and formation of $\{(d^tbpe)Pt^IH\}_2$[64] as the Pt analogue to **3**. Structurally the Pt complex is a dimer of *SP*-4 $(d^tbpe)Pt^IH$ moieties with *terminal* hydride substituents and is connected by an unsupported Pt−Pt bond (2.61 Å). In solution (^1H NMR), the ^{31}P nuclei equilibrate via a $L_2Pt(\mu\text{-}H)_2PtL_2$ transition state. Upon addition of H_2 (20 °C) mononuclear $(d^tbpe)PtH_2$ is recovered. Thus, there is the further equilibrium $2L_2Pt^{II}H_2 \rightleftharpoons \{L_2Pt^IH\}_2 + H_2$.[64,65] Both types of complexes react with electron-poor alkenes[61] and alkynes[62] with elimination of H_2 to yield the corresponding Pt^0 complexes.[65a]

On the basis of the properties of **3** and the results cited above the following general characteristics of the system L_2M^0/H_2 (M = Ni, Pd, Pt; $L_2 = 2\ PR_3$, $R_2P(CH_2)_nPR_2$) can be established.

(a) In the dinuclear $\{L_2M^IH\}_2$ complexes short M^I-M^I bonds are encountered for M = Ni, Pt, while the Pd^I-Pd^I bond is long. The hydride bridges are symmetrical and strong for $L_2Ni(\mu\text{-}H)_2NiL_2$ but unsymmetrical and weaker for $L_2Pd(\mu\text{-}H)_2PdL_2$ (semibridging hydride), whereas the hydride is terminally bound in $L_2Pt(H)-Pt(H)L_2$.

(b) The di- and mononuclear complexes form the equilibrium

$$\{L_2M^IH\}_2 + H_2 \rightleftharpoons 2L_2M^{II}H_2$$

This equilibrium is shifted to the side of the mononuclear complexes in the series Ni < Pd < Pt and with an increasing bulk of the L_2 ligand. Thus, for the combination Pt/d^tbpe the preferred complex is mononuclear $(d^tbpe)PtH_2$, whereas for Ni the equilibrium is still on the side of dinuclear **3**, despite the bulk of the d^tbpe ligand. However, it follows from the above that the mononuclear Ni derivative $L_2Ni^{II}H_2$ (cf. **C**; Schemes 1−3) should possibly be accessible for d^tbpe (in contrast to the situation for smaller bidentate phosphanes) by

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increasing the concentration of H_2. Corresponding experiments are in progress.[66]

(c) From the above it is to be expected that for the series of dinuclear Ni complexes $[\{R_2P(CH_2)_nPR_2\}Ni^I]_2(\mu\text{-}H)_2$ (R = e.g. Me, Et, *c*-C_6H_{11} (**3a**), ^{i}Pr (**3b**), ^{t}Bu (**3**)), concomitant with an increasing distortion θ from the calculated ground-state D_{2h} symmetry, (i) a lowering of the energy barrier of the structural dynamics according to eq 4, (ii) a lowering of the energy barrier for H_2/D_2 exchange reactions (Scheme 2), and (iii) a more facile generation of the formal $[L_2Ni^0]$ fragments (e.g. Scheme 3) take place. While this hypothesis still has to be tested for the smaller homologues of the given series, it explains the ready generation of the formal $[(d^tbpe)Ni^0]$ fragment in solution, as shown in Figure 4.

Experimental Section

All reactions and manipulations were performed using Schlenk-type techniques under an inert atmosphere of argon. Solvents were dried by distillation from $NaAl(C_2H_5)_4$. d^{t}bpe,[3] $(d^tbpe)Ni(C_2H_4)$,[3] $\{(d^tbpe)Ni\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)$ (**4**),[4] and (tmeda)$Mg(CH_3)_2$ and (tmeda)$Mg(CD_3)_2$[67] were prepared as reported. Microanalyses were performed by the Mikroanalytisches Labor Kolbe, Mülheim, Germany. ^{1}H 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, 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. The solvent for solution NMR was THF-d_8. EI mass spectra (the data refer to ^{58}Ni) were recorded at 70 eV on a Finnigan MAT 8200 and IR spectra on a Nicolet 7199 FT-IR instrument.

$(^tBu_2PC_2H_4P^tBu_2)NiCl_2$. A suspension/solution of $NiCl_2$ (259 mg, 2.00 mmol) and d^{t}bpe (637 mg, 2.00 mmol) in methanol (40 mL) was stirred at 40 °C for 10 h. Large red needles crystallized from the resulting deep red solution at −78 °C. The product was separated from the mother liquor, washed with cold pentane, and dried under vacuum (20 °C): yield 700 mg (78%); dec pt 282 °C. The complex is paramagnetic; hence, no NMR signals were observed. EI-MS (210 °C): *m/e* (%) 446 (7) M$^+$, 354 (4) $[(^tBu_2PC_2H_4P^tBu)NiCl]^+$, 261 (88) $[^tBu_2PC_2H_4P^tBu]^+$. Anal. Calcd for $C_{18}H_{40}Cl_2NiP_2$ (448.1): C, 48.25; H, 9.00; Cl, 15.83; Ni, 13.10; P, 13.83. Found: C, 48.10; H, 9.28; Cl, 15.81; Ni, 13.11; P, 13.76.

$(^tBu_2PC_2H_4P^tBu_2)NiI_2$. 1,2-Diiodoethane (311 mg, 1.1 mmol) was added at 20 °C to a yellow solution of $(d^tbpe)Ni(C_2H_4)$ (405 mg, 1.00 mmol) in THF (50 mL). The color of the solution changed to dark green, and a dark blue microcrystalline precipitate formed. After completion of the crystallization at 0 °C the product was isolated by filtration, washed with pentane, and dried under vacuum (20 °C): yield 430 mg (78%); mp 90 °C dec. The complex is paramagnetic. EI-MS (150 °C): *m/e* (%) 503 (48) $[(d^tbpe)NiI]^+$, 447 (21) $[(^tBu_2PC_2H_4P(H)^tBu)NiI]^+$, 391 (27) $[(^tBu(H)PC_2H_4P(H)^tBu)NiI]^+$, 335 (39) $[(^tBu(H)PC_2H_4PH_2)NiI]^+$, 279 (12) $[(H_2PC_2H_4PH_2)NiI]^+$. Anal. Calcd for $C_{18}H_{40}I_2NiP_2$ (631.0): C, 34.26; H, 6.39; I, 40.23; Ni, 9.30; P, 9.82. Found: C, 34.19; H, 6.45; I, 40.16; Ni, 9.36; P, 9.78.

$(^tBu_2PC_2H_4P^tBu_2)Ni(I)CH_3$ (1). $(d^tbpe)Ni(C_2H_4)$ (810 mg, 2.00 mmol) was reacted with neat methyl iodide (3 mL) at 20 °C for 1 h, whereupon the color of the mixture changed from yellow to red-brown. After diethyl ether was added (30 mL) and the solvent was discarded, large brown crystals remained, which were washed with pentane and dried under vacuum (20 °C): yield 800 mg (77%); mp 223 °C. EI-MS (140 °C): *m/e* (%) 518 (15) M$^+$, 503 (100) $[(d^tbpe)NiI]^+$, 376 (74) $[(d^tbpe)Ni]^+$. IR (KBr, 20 °C): 3026 ($\nu(CH_3)$), 1126 ($\delta_s(CH_3)$), 752 ($\rho_r(CH_3)$) cm^{-1} ($NiCH_3$). ^{1}H NMR (400 MHz, 27 °C): δ 1.91, 1.71 (each m, 2H, PCH_2 and $P'CH_2$), 1.48, 1.44 (each d, 18H, P^tBu_2 and P'^tBu_2), 0.55 (m, 3H, $NiCH_3$). ^{31}P NMR (81 MHz, 27 °C): δ 86.3, 72.7 ($^2J(PP) = 3.0$ Hz). Anal. Calcd for $C_{19}H_{43}INiP_2$ (519.1): C, 43.96; H, 8.35; Ni, 11.31; P, 11.93; I, 24.45. Found: C, 43.91; H, 8.31; Ni, 11.36; P, 11.98; I, 24.34.

$(^tBu_2PC_2H_4P^tBu_2)Ni(I)CD_3$ (1-*d*$_3$). The synthesis was carried out as for **1**, but by using CD_3I. IR (KBr): 2255/2204, 2096/2038 ($\nu(CD_3)$), 866 ($\delta_s(CD_3)$) cm^{-1} ($NiCD_3$). ^{1}H NMR (d^{t}bpe part): as for **1**. ^{31}P NMR (81 MHz, 27 °C): δ 86.5, 72.8 ($^2J(PP)$ = 3.4 Hz).

$(^tBu_2PC_2H_4P^tBu_2)Ni(CH_3)_2$ (2). (a) $(d^tbpe)NiCl_2$ (896 mg, 2.00 mmol) suspended in diethyl ether (30 mL) was reacted with (tmeda)$Mg(CH_3)_2$ (436 mg, 2.10 mmol) at −30 °C until a clear solution had formed. After addition of dioxane (0.35 mL, 4.2 mmol) colorless $(C_4H_8O_2)_2MgCl_2$ precipitated, which was separated by filtration and washed with ether. Yellow cubes crystallized from the orange yellow filtrate at −78 °C and were freed from the mother liquor, washed with cold pentane, and dried under vacuum at −30 °C: yield 566 mg (69%).

(b) A suspension of $(d^tbpe)Ni(I)CH_3$ (**1**; 519 mg, 1.00 mmol) and (tmeda)$Mg(CH_3)_2$ (102 mg, 0.50 mmol) in diethyl ether was stirred at −30 °C until all **1** was dissolved. The precipitate of MgI_2 was filtered off, and yellow crystals were obtained from the remaining solution at −30 °C. The mother liquor was discarded, and the product was washed with cold pentane and dried under high vacuum at −30 °C: yield 155 mg (40%); mp 124 °C dec. EI-MS (110 °C): *m/e* (%) 406 (2) M$^+$, 391 (8) $[(d^tbpe)NiCH_3]^+$, 376 (74) $[(d^tbpe)Ni]^+$. IR (KBr, 20 °C): 1116 ($\delta_s(CH_3)$), 735 ($\rho_r(CH_3)$) cm^{-1} ($NiCH_3$); all CH stretching bands are obscured by phosphane vibrations. ^{1}H NMR (400 MHz, −30 °C): δ 1.69 (m, $J(PH) = 10$ Hz, 4H, PCH_2), 1.32 (d, $^3J(PH) = 11$ Hz, 36H, CCH_3), −0.08 (m, 6H, $NiCH_3$). ^{13}C NMR (100.6 MHz, 27 °C): δ 36.1 (4C, CCH_3), 31.2 (12C, CCH_3), 23.8 (2C, PCH_2), 1.80 (2C, AA′X spin system, $^2J(PC) = 71$ Hz, $^2J(P'C) = -17.6$ Hz, $^2J(PP) = 17.6$ Hz, $NiCH_3$). ^{31}P NMR (81 MHz, −30 °C): δ 78.5. Anal. Calcd for $C_{20}H_{46}NiP_2$ (407.2): C, 58.99; H, 11.39; Ni, 14.41; P, 15.21. Found: C, 58.91; H, 11.42; Ni, 14.48; P, 15.20.

$(^tBu_2PC_2H_4P^tBu_2)Ni(CD_3)_2$ (2-*d*$_6$). The synthesis was carried out as for **2**, route a, but by using (tmeda)$Mg(CD_3)_2$. IR (KBr): 2213/2183, 2083/2048 ($\nu(CD_3)$), 863sh, ($\delta_s(CD_3)$) cm^{-1} ($NiCD_3$). ^{1}H NMR (d^{t}bpe part): as for **2**. ^{31}P NMR (81 MHz, 27 °C): δ 79.6.

$\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu\text{-}H)_2$ (3). (a) The red solution of **4** (833 mg, 1.00 mmol) in diethyl ether (20 mL) was kept under hydrogen without stirring for 1 h (20 °C). Thereafter the color intensified to dark red and dark green crystals separated. After completion of the crystallization at −78 °C the mother liquor was removed by means of a capillary and the product was washed with cold pentane and dried under vacuum at 20 °C: yield 620 mg (82%).

(b) Stirring a red suspension of $(d^tbpe)NiCl_2$ (448 mg, 1.00 mmol) and Mg* (50 mg, excess) in THF (40 mL) under H_2 gas for several hours at 20 °C afforded a deep red solution. When the solution was cooled to −78 °C, dark green crystals precipitated, which were isolated as described: yield 200 mg (53%); mp 218 °C. IR (KBr): ~1280vw cm^{-1} (broad, $\nu(NiH)$). EI-MS (175 °C): *m/e* (%) 754 (61) M$^+$, 377 (5) $[(d^tbpe)NiH]^+$, 376 (4) $[(d^tbpe)Ni]^+$, 261 (100) $[^tBu_2PC_2H_4P^tBu]^+$. ^{1}H NMR (300 MHz, 27 °C): δ 1.67 (m, 8H, PCH_2), 1.28 (m, 72H, CCH_3), −10.6 (quint, 2H, $^2J(PH) = 22$ Hz, $Ni(\mu\text{-}H)_2Ni$). ^{31}P NMR (121 MHz, 27 °C): δ 94.6. Anal. Calcd for $C_{36}H_{82}Ni_2P_4$ (756.3): C,

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[66] The ^{31}P NMR spectrum of a THF-d_8 solution of **3** saturated with H_2 shows a weak singlet at δ_P 108 in addition to the singlet of **3** (δ_P 94.6). The extremely low field location of the new signal is indicative of oxidation of the Ni center, and thus the signal is tentatively attributed to either $[(d^tbpe)Ni^{II}H_2]$ (**C**) or $[(d^tbpe)Ni^{IV}H_4]$. The formation of the latter would also explain (together with the process described in Scheme 2) the slow H/D scrambling that is observed in the H_2/D_2 exchange reaction of **3**.

[67] (a) Coates, G. E.; Heslop, J. A. *J. Chem. Soc. A* **1966**, 26. (b) Kaschube, W.; Pörschke, K.-R.; Angermund, K.; Krüger, C.; Wilke, G. *Chem. Ber.* **1988**, *121*, 1921.

57.17; H, 10.93; Ni, 15.52; P, 16.38. Found: C, 57.28; H, 10.67; Ni, 15.58; P, 16.35.

$\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu$-H)($\mu$-D) (3-*d*). The reaction was carried out as for **3**, route a, but by using HD and stirring the mixture at −40 °C. For NMR data, see text. $C_{36}H_{81}DNi_2P_4$ (757.3).

$\{(^tBu_2PC_2H_4P^tBu_2)Ni\}_2(\mu$-D$)_2$ (3-d_2). Synthesis was as for **3**, route a, but by using D_2 instead of H_2. IR (KBr): ~920vw cm^{-1} (broad, ν(NiD)). EI-MS (160 °C): *m/e* (%) 756 (9) M^+, 376 (2) $[(d^tbpe)Ni]^+$, 261 (79) $[^tBu_2PC_2H_4P^tBu]^+$. ^1H NMR spectrum (d^{t}bpe part): as for **3**. For ^{31}P NMR spectrum, see text. $C_{36}H_{80}D_2Ni_2P_4$ (758.3).

(d^{t}bpe)Ni(CH$_3$)(OSO$_2$CF$_3$) (5). CF_3SO_3H (0.09 mL, 1.0 mmol) was slowly added to a stirred yellow solution of **2** (407 mg, 1.00 mmol) in diethyl ether (30 mL) at −30 °C. When the mixture was warmed to 20 °C, the color darkened to ocher and a microcrystalline precipitate formed. After completion of the crystallization at −78 °C, the product was freed of the mother liquor by means of a capillary, washed with cold pentane, and dried under vacuum at 20 °C: yield 405 mg (75%); mp 180 °C dec. EI-MS (140 °C): *m/e* (%) 540 (7) M^+, 525 (62) $[(d^tbpe)Ni(OTf)]^+$, 469 (35) $[(^tBu(H)PC_2H_4P^tBu_2)Ni(OTf)]^+$, 413 (27) $[(^tBu(H)PC_2H_4P(H)^tBu)Ni(OTf)]^+$, 357 (22) $[(H_2PC_2H_4P(H)^tBu)Ni(OTf)]^+$. ^1H NMR (300 MHz, 27 °C): δ 1.97, 1.58 (each m, 2H, PCH_2 and $P'CH_2$), 1.46, 1.42 (each d, 18H, P^tBu_2 and P'-$^tBu_2$); 0.22 (dd, 3H, $NiCH_3$). ^{13}C NMR (75.5 MHz, 27 °C): δ 38.6, 35.7 (each d, 2C, $\mathit{C}CH_3$), 31.6, 31.0 (each d, 6C, $C\mathit{C}H_3$), 27.8, 26.6 (each m, 1C, PCH_2 and $P'CH_2$); 19.1 (m, 1C, $NiCH_3$); CF_3 not detected. ^{31}P NMR (81 MHz, 27 °C): δ 79.5, 71.2 (^2J(PP) = 12 Hz). Anal. Calcd for $C_{20}H_{43}F_3NiO_3P_2S$ (541.3): C, 44.38; H, 8.01; Ni, 10.84; P, 11.45; F, 10.53; O, 8.87; S, 5.92. Found: C, 44.48; H, 8.12; Ni, 10.06; P, 11.42; F, 10.04.

Crystal Data for 2: $C_{20}H_{46}NiP_2$, M_r = 407.2, yellow crystal, size 0.46 × 0.60 × 0.88 mm, a = 13.702(2) Å, b = 14.661(2) Å, c = 22.648(3) Å, V = 4550(1) Å^3, T = 100 K, Z = 8, D_{calcd} = 1.19 g cm^{-3}, μ = 0.99 mm^{-1}, orthorhombic, space group *Pbca* [No. 61], Enraf-Nonius CAD4 diffractometer, λ = 0.710 69 Å, $\omega-2\theta$ scan, 10 116 reflections, 5174 independent, 3568 observed ($I > 2\sigma(I)$), $[(\sin\theta)/\lambda]_{max}$ = 0.65 Å^{-1}, no absorption correction, direct methods (SHELXS-97),[68a] least-squares refinement on F_o^2 (SHELXL-97),[68b] H riding, 210 refined parameters, R1 = 0.061 (obsd data), wR2 = 0.157 (Chebyshev-weights), final shift/error 0.001, residual electron density +1.56 e Å^{-3}.

Crystal Data for 3: $C_{36}H_{82}Ni_2P_4$, M_r = 756.3, black crystal, size 0.39 × 0.39 × 0.39 mm, a = 11.5188(3) Å, b = 16.4946(6) Å, c = 22.9190(8) Å, V = 4354.6(2) Å^3, T = 293 K, Z = 4, D_{calcd} = 1.15 g cm^{-3}, μ = 2.60 mm^{-1}, orthorhombic, space group *Pbcn* [No. 60], Enraf-Nonius CAD4 diffractometer, λ = 1.541 78 Å, $\omega-2\theta$ scan, 4494 reflections, 3615 observed ($I > 2\sigma(I)$), $[(\sin\theta)/\lambda]_{max}$ = 0.63 Å^{-1}, ψ-scan absorption correction, direct methods (SHELXS-97),[68a] least-squares refinement on F_o^2 (SHELXL-97),[68b] H atom isotropic, remaining H atoms riding, Me groups disordered (50:50) isotropic, 182 refined parameters, R1 = 0.059 (obsd data), wR2 = 0.159 (Chebyshev weights), final shift/error 0.001, residual electron density +0.413 e Å^{-3}.

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Supporting Information Available: Tables of data collection information, anisotropic displacement parameters, hydrogen atom coordinates, and bond lengths and angles for **2** and **3** (9 pages). Ordering information is given on any current masthead page.

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