π-Allyl Nickelate(II) and Palladate(II) Complexes†

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The homoleptic M−π-allyl complexes M(η^3-C_3H_5)$_2$ (M = Ni, Pd) react with LiC_3H_5 and $Li_2C_4H_8$ in the presence of tmeda to give the ionic π-allyl nickelates(II) and palladates(II) [Li(tmeda)$_2$]$^+$[(η^3-C_3H_5)M(η^1-C_3H_5)$_2$]$^-$ (M = Ni, **3a**; M = Pd, **3b**) and [Li(tmeda)$_2$]$^+$[(η^3-C_3H_5)M(C_4H_8)]$^-$ (M = Ni, **4a**; M = Pd, **4b**). Complexes **3a**,**b** are formed by reversible addition of a further allyl group, while the formation of **4a**,**b** occurs by replacement of one allyl group by the chelating dianionic butane-1,4-diyl ligand. The solid nickel complexes **3a** and **4a** are temporarily stable at ambient temperature, whereas the palladium derivatives **3b** and **4b** decompose above 0 °C. All the complexes are ionic, with square-planar metalate(II) anions containing one π-allyl and two σ-organyl ligands, and there is no direct interaction between the Li atom and the anion, as exemplified by low-temperature X-ray structure analyses of **3a** and **4a**. CP-MAS ^{13}C NMR spectroscopy shows that the structure of **3a** is fluxional in the solid state above −93 °C.

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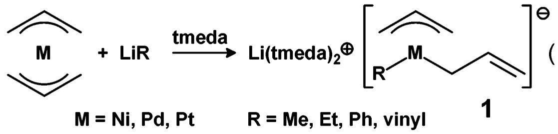
Introduction

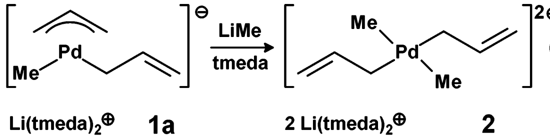
It has long been known that the homoleptic square-planar d^8 complexes M(η^3-C_3H_5)$_2$ (M = Ni, Pd) react with monodentate phosphanes to form addition compounds. In the case of Ni(η^3-C_3H_5)$_2$, a small and strong donor such as PMe_3 adds to give the formally five-coordinate 18e adduct (η^3-C_3H_5)$_2$Ni(PMe_3), in which both allyl groups have remained π-bound.[1] In contrast, the related reaction of Pd(η^3-C_3H_5)$_2$ with monodentate phosphanes affords square-planar 16e complexes (η^3-C_3H_5)Pd(η^1-C_3H_5)(PR_3), in which one of the allyl ligands remains π-bound and the other becomes σ-bound, consistent with the propensity of palladium to retain the 16e configuration.[1a,2−4] Similarly, Pd(η^3-C_3H_5)$_2$ reacts with bidentate phosphanes $R_2PC_2H_4PR_2$ (R = ^{i}Pr, ^{t}Bu) to give ($R_2PC_2H_4PR_2$)Pd(η^1-C_3H_5)$_2$ complexes, containing two cis σ-allyl ligands.[3c,5]

In a completely different type of reaction, appropriate Ni^{II} and Pd^{II} compounds react with an excess of lithium organyl, as a source of carbanions, to give tetraorganylnickelate(II) and palladate(II) complexes, such as [(THF)$_n$$Li_2NiMe_4$]$_2$ (n = 1, 2),[6] {(tmeda)Li}$_2$Ni(C_4H_8)$_2$,[7] Li_2PdMe_4,[8] and {(THF)$_2$Li}$_2$Pd(C_4H_8)$_2$.[9] These mono- or dinuclear, formally dianionic complexes consist of square-planar d^8 metal centers coordinated by four alkyl substitutents, the latter being bridged by partially solvated lithium ions.

Combining both these ideas, Jolly et al.[3c,10] reacted M(η^3-C_3H_5)$_2$ (M = Ni, Pd, Pt) with lithium organyls LiR (R = Me, Et, Ph, vinyl) and obtained the substituted π/σ-allylmetalates(II) [Li(tmeda)$_2$]$^+$[(η^3-C_3H_5)M(η^1-C_3H_5)-R]$^-$ (**1**) (eq 1a). The palladium derivative **1a** (R = Me) was shown to react with further LiMe to give the dianionic complex [Li(tmeda)$_2$]$^+_2$[Me_2Pd(η^1-C_3H_5)$_2$]$^{2-}$ (**2**), containing two trans σ-allyl ligands. No allyl replacement occurs in the formation of this complex (eq 1b).



1 (1a)



1a **2** (1b)

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† Dedicated to Professor M. T. Reetz on the occasion of his 60th birthday.

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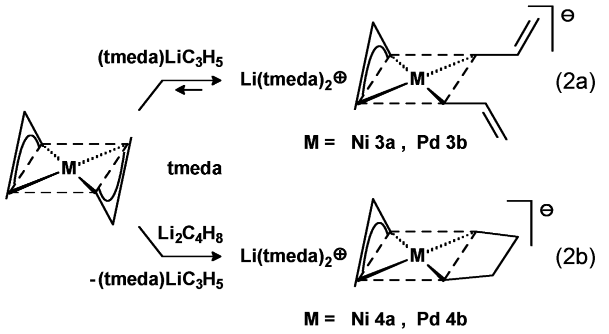
We were intrigued to know what would occur if R was itself an allyl group or a dicarbanion. Here we describe the reactions of $M(\eta^3\text{-}C_3H_5)_2$ (M = Ni, Pd) with lithium allyl to give the first homoleptic π-allyl bis-σ-*allyl* metalates(II) $Li[(\eta^3\text{-}C_3H_5)M(\eta^1\text{-}C_3H_5)_2]$ (**3**), and with dilithium butane-1,4-diyl to afford, by substitution of just one allyl ligand, the π-allyl bis-σ-*alkyl* metalates(II) $Li[(\eta^3\text{-}C_3H_5)M(C_4H_8)]$ (**4**).[11,12]

Results and Discussion

Reaction of yellow $M(\eta^3\text{-}C_3H_5)_2$ (M = Ni, Pd) with 1 equiv of the likewise yellow LiC_3H_5 in diethyl ether affords a red (Ni) or intense yellow (Pd) solution. Addition of an excess of *N*,*N*′-tetramethylethylenediamine (tmeda) yields the crystalline trisallylmetalates(II) **3a** (red; dec 55 °C) and **3b** (yellow; dec 0 °C). The reaction has to be started at low temperature (−30 °C) because of the thermal instability of $M(\eta^3\text{-}C_3H_5)_2$. The solutions are markedly stabilized after addition of LiC_3H_5, but the overall reaction is an equilibrium that is driven to the product side by coordination of the tmeda ligands to the Li cation (eq 2a). Isolated **3a** (the most stable compound that will be described in this paper) is only temporarily stable at ambient temperature and should be stored in the cold (−78 °C). IR bands at 1640 and about 1580 cm^{-1} are attributed to the σ-C_3H_5 ligands of **3a**,**b**. No meaningful solution NMR spectra were observed between 20 and −80 °C for the two compounds, which may be explained by both their fluxionality (see solid state NMR below) and dissociation in solution. The only distinct signals were those from isomeric $M(\eta^3\text{-}C_3H_5)_2$ (M = Ni, Pd)[13] and tmeda.



Attempts to react $Ni(\eta^3\text{-}C_3H_5)_2$ under similar conditions with 2 equiv of LiMe to obtain $Li_2[(\eta^1\text{-}C_3H_5)_2NiMe_2]$ (which would be analogous to **2**) or under LiC_3H_5 elimination to obtain $Li[(\eta^3\text{-}C_3H_5)NiMe_2]$ (the parent complex of **3a**,**b**) resulted in a mixture of compounds that presumably included Li_2NiMe_4. Since $Li[(\eta^3\text{-}C_3H_5)NiMe_2]$ appeared not to be a particularly stable compound, we tried to synthesize a derivative in which the two σ-alkyl functions were part of a chelating butane-1,4-diyl ligand.

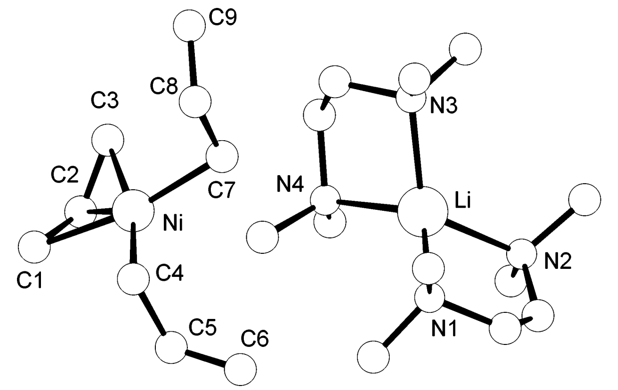


Figure 1. Structure of **3a**. Selected bond distances (Å), angles (deg), torsion angles (deg), and dihedral angles (deg): Ni−C1 = 2.032(5), Ni−C3 = 2.031(4), Ni−C4 = 1.979(3), Ni−C7 = 1.953(4); C1−Ni−C3 = 73.1(2), C4−Ni−C7 = 93.2(2); C4−Ni−C7−C8 = −86(2), C7−Ni−C4−C5 = −97(2), Ni−C4−C5−C6 = 103(2), Ni−C7−C8−C9 = −106(2); C1,Ni,C3/C4,Ni,C7 = 10(2).

The reaction of $M(\eta^3\text{-}C_3H_5)_2$ with 1 equiv of $Li_2C_4H_8$ proceeds by elimination of $(tmeda)LiC_3H_5$ to give the likewise monoanionic π-allyl bis-σ-alkylmetalates **4a** (orange; dec 20 °C) and **4b** (yellow; dec 0 °C), in which one π-allyl ligand is retained and the butane-1,4-diyl ligand is coligated (eq 2b). The Pd complexes (**3b**, **4b**) are generally less stable than the Ni homologues (**3a**, **4a**), and the π-allyl bis-σ-*alkyl* metalates (**4a**,**b**) are less stable than the corresponding π-allyl bis-σ-*allyl* metalates (**3a**,**b**). The color of the compounds lightens from red (**3a**) over orange (**4a**) to yellow (**3b**, **4b**) in the same sequence as decreasing thermal stability. Interestingly, no dianionic cis bis-σ-allyl complex $Li_2[(C_4H_8)M(\eta^1\text{-}C_3H_5)_2]$ is formed, corresponding to **2** (trans isomer) or $(R_2PC_2H_4PR_2)Pd(\eta^1\text{-}C_3H_5)_2$.[5] Reaction of $M(\eta^3\text{-}C_3H_5)_2$ with 2 equiv of $Li_2C_4H_8$ and tmeda affords the previously known $\{(tmeda)Li\}_2M(C_4H_8)_2$.[7,9,14]

The solution ^1H and ^{13}C NMR spectra of **4a**,**b** in THF-d_8 are sharp and temperature independent between −80 and 20 °C,[15] in contrast to those of **3a**,**b**. The allyl protons give rise to an AM_2X_2 spin system. The ^1H and ^{13}C allyl resonances of monoanionic **4a**,**b** are all shifted to higher field compared with homoleptic $M(\eta^3\text{-}C_3H_5)_2$,[13] and this shift is most pronounced for the terminal methylene groups (up to 2 ppm for the syn protons). The ^{13}C resonances of the butane-1,4-diyl ligand are very similar for both **4a**,**b** and the dianionic $Li_2[M(C_4H_8)_2]$.[7,9] The MCH_aH_b protons of **4a** (δ(H) 1.23, 0.82) and **4b** (δ(H) 1.82, 1.50) are deshielded by 1−1.5 ppm compared to the corresponding $Li_2[M(C_4H_8)_2]$ (M = Ni, δ(H) −0.21;[9] Pd, δ(H) 0.30). The splitting of the resonances is due to an exo or endo location of the protons on the allyl ligand. The inner CH_aH_b protons are isochronous, and the shift is about the same for all the compounds (δ(H) ≈ 1.4). The spectra indicate that the ligands in **4a**,**b** are rigidly coordinated on the NMR time scale; that is, the π-allyl ligand undergoes neither π-allyl rotation nor π−σ-allyl isomerization.

Molecular Structures of 3a and 4a. The crystal structures of the Ni complexes **3a** (Figure 1) and **4a**

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[14] It has been previously shown that $NiCp_2$ reacts with 2 equiv of $Li_2C_4H_8$ to yield $Li_2[Ni(C_4H_8)_2]$.[7a]

[15] The ambient-temperature spectra of **4a**,**b** may be obtained if quickly recorded.

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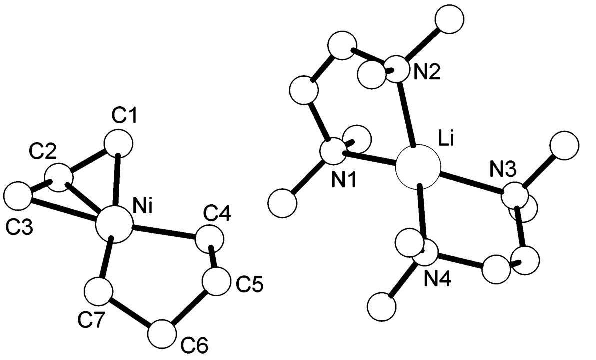

Figure 2. Structure of **4a**. Selected bond distances (Å), angles (deg), and dihedral angles (deg): Ni−C1 = 2.049(7), Ni−C3 = 2.010(7), Ni−C4 = 1.932(6), Ni−C7 = 1.910(7); C1−Ni−C3 = 74.4(3), C4−Ni−C7 = 86.5(3); C1,Ni,C3/C4,Ni,C7 = 8(2).

(Figure 2) at low temperature have been determined by X-ray crystallography. They are the first examples of structurally characterized π-allylmetalate(II) complexes. The complexes are clearly ionic, with the Li cations tetrahedrally coordinated by two tmeda ligands, and the square-planar Ni centers are coordinated by the terminal C atoms of a π-allyl ligand and two σ-bonded substituents, rendering the Ni complexes overall monoanionic. In **3a** the σ-substituents are also allyl groups, giving rise to a homoleptic π/σ-allyl nickelate(II) anion, while in **4a** they represent the terminal atoms of a butane-1,4-diyl ligand, which chelates the nickel center. The X-ray analysis of **3a** shows that in **3a**,**b** one of the allyl ligands is π-bound while the other two are σ-bound at the square-planar metal center.

The Ni(η^1-C_3H_5)$_2$ moiety in **3a** does not have local C_2 symmetry, but despite an unsymmetrical environment around the anion in the crystal, the C1−C2 bonds of σ-C_3H_5 groups are bent out of the nickel coordination plane by approximately the same angle (C4−Ni−C7−C8 −86(2)°, C7−Ni−C4−C5 −97(2)°). In the crystal structure of bis(σ-allyl)-(1,2-bis(dicyclohexylphosphine)ethane-*P*,*P*′)platinum(II) the corresponding angles are both −72°.[3c]

For **3a** the C4−Ni−C7 angle between the σ-allyl substituents at 93.2(2)° is relative large in comparison with the values observed for (bipy)Ni(C_4H_8) (C−Ni−C = 83.8°),[16a] ($^iPr_2PC_2H_4P^iPr_2$)Ni(CH_2SiMe_2Ph)$_2$ (89.0°),[16b] (bipy)NiMe_2 (86.6°),[16c] and ($^tBu_2PC_2H_4P^tBu_2$)NiMe_2 (83.7°).[16d] It is tempting to suggest that the large C4−Ni−C7 angle is the result of compensation for the small bite angle of the allyl ligand (C1−Ni−C3 = 73.1(2)°). The Ni−C4 and Ni−C7 bond lengths at 1.97(2) Å, however, lie within the range found for these compounds (1.92−2.01 Å). For **4a** the corresponding mean Ni−C bond length at 1.92(1) Å is rather small and is close to the lower limit of the normal range of Ni−C bond lengths. The value should, however, be treated with caution in view of the relatively high errors associated with the bond lengths in this structure. In the crystal structure of {(THF)$_2$Li}$_2$Ni(C_4H_8)$_2$ the average Ni−C distance is 2.00 Å, but this may be due to the close proximity of the lithium cations to the carbon atoms.[7b] In all the other known crystal structures of nickel and palladium metalates, [(THF)$_n$Li$_2$NiMe$_4$]$_2$ (n = 1, 2),[6b] {-(tmeda)Li}$_2$Ni($C_4H_4Me_4$)$_2$,[7d] and {(THF)$_2$Li}$_2$Pd(C_4H_8)$_2$,[9] the lithium ions are also intimately bound up in the complex. The C−Ni−C angle in the Ni-butane-1,4-diyl chelate ring of **4a**, C4−Ni−C7 = 86.5(3)°, is larger than the comparable one in (bipy)Ni(C_4H_8) and {(THF)$_2$-Li}$_2$Ni(C_4H_8)$_2$. As in the case of **3a**, this is probably due to the small bite angle of the coligating π-allyl ligand.

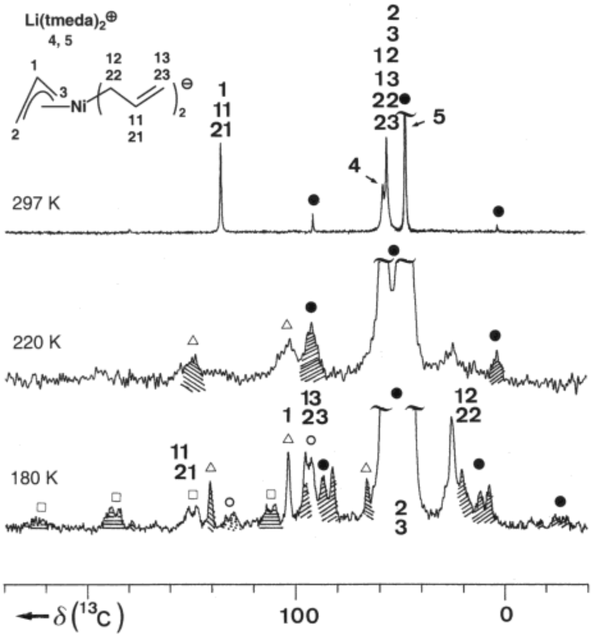

Figure 3. Variable-temperature ^{13}C CP-MAS NMR spectra of **3a**. Top trace (297 K. R_0 = 3.3 kHz, 900 scans, 10 s repetition delay): ● marks NMe signal of the tmeda ligand (only partial intensity given) and corresponding spinning sidebands (ssb). Middle trace (220 K, R_0 = 3.3 kHz, 320 scans, 4 s rep. delay): The spectrum was recorded close to the coalescence temperature, and only a few and broad lines were observed. △ denotes the rising signal for C1 with one visible ssb of the π-allyl ligand. Lower trace (180 K, R_0 = 2.8 kHz, 1000 scans, 3 s rep. delay): □ labels signals of the central C atoms C11 and C21 of the σ-allyl ligands and their ssb; ○ marks the terminal olefinic C atoms C13 and C23 of the σ-allyl ligands and their ssb. The signals of the terminal C atoms of the π-allyl ligand, C2 and C3, expected at $\delta \approx 49$, are obscured. The ssb's of respective signals have been hatched accordingly.

Solid State ^{13}C CP-MAS NMR Spectra of 3a. Since no meaningful solution NMR spectra were observable for **3a**, we decided to look at its variable-temperature solid state ^{13}C CP-MAS NMR spectra (Figure 3). At 24 °C a rather simple spectrum was obtained, comprising two lines for the central and terminal allyl C atoms at δ(C) 135.2 (C1, C11, C21) and 55.9 (C2, C12, C22, C3, C13, C23), and two lines for the tmeda NCH_2 and NMe_2 groups (δ(C4) 57.9, δ(C5) 47.2). Interestingly, the low-field shift of the central allyl carbon atoms is intermediate between the shifts expected for the central C atoms of Ni−σ- (140−150) and π-C_3H_5 ligands (100−120) (cf. Li[(η^3-C_3H_5)Ni(η^1-C_3H_5)Me], **A**),[10] indicating a dynamic structure.

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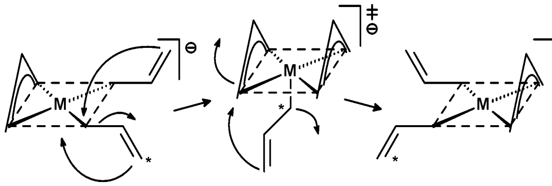
When the temperature is lowered, the allyl resonances become broad and coalesce around −53 °C. At −93 °C six of the nine allyl resonances are resolved. Two lines at δ(C) 150.5 and 147.0, which display the typical spinning sideband patterns of olefinic carbon atoms, can be attributed to the central C atoms C11 and C21 of σ-allyl ligands, while the narrow line at δ(C) 102.9 can be assigned to the meso C atom of a π-allyl ligand, C1. The calculated mean of these resonances (133.5) corresponds to the chemical shift found at ambient temperature. On the basis of the data of **A**, two signals at δ(C) 94.7 and 92.1 are assigned to the terminal $=CH_2$ carbon atoms C13 and C23, and a high-field signal at δ(C) 25.1 to the (isochronous) $NiCH_2$ carbons C12 and C22 of two σ-C_3H_5 ligands. The resonances of the terminal C atoms C2 and C3 of the π-allyl ligand, expected from the coalesced signal of all the terminal carbon atoms (δ(C) 55.9) at δ ~49, seem obscured by the tmeda signals. The spectral changes are reversible within this temperature range.[17]

Thus, the spectra show that the solid state structure of **3a** is static and C_1 symmetric at −93 °C, with the nickel atom bearing one π-C_3H_5 and two inequivalent σ-C_3H_5 ligands, in agreement with the result from the X-ray structure determination, while at 25 °C it is fluxional, leading to an equilibration of the σ- and π-allyl ligands, possibly according to the mechanism suggested in eq 3.[18]



(3)

Conclusions

$Ni(\eta^3\text{-}C_3H_5)_2$ and $Pd(\eta^3\text{-}C_3H_5)_2$ react with LiC_3H_5 and $Li_2C_4H_8$ in the presence of tmeda to give the elusive ionic π-allyl nickelates(II) and palladates(II) $[Li(tmeda)_2]^+[(\eta^3\text{-}C_3H_5)M(\eta^1\text{-}C_3H_5)_2]^-$ (M = Ni, **3a**; M = Pd, **3b**) and $[Li(tmeda)_2]^+[(\eta^3\text{-}C_3H_5)M(C_4H_8)]^-$ (M = Ni, **4a**; M = Pd, **4b**). The solid nickel complexes **3a** and **4a** are only temporarily stable at ambient temperature, while the palladium derivatives **3b** and **4b** decompose around 0 °C. Solid state ^{13}C CP-MAS NMR investigations reveal that **3a** becomes dynamic in the solid state above −93 °C.

The crystal structures of **3a** and **4a** show that the compounds exist as separate $Li(tmeda)_2$ cations and monoanionic π-allyl complex anions. The metalate complexes of **3a**,**b** and **4a**,**b** thus appear to be much less basic toward the Li cation than similar metalates hitherto studied. Partial delocalization of the negative charge of the metalate ions into the π-allyl ligand can be concluded from the high-field shift of the ^1H and ^{13}C allyl resonances. Similarly, the marked deshielding of the MCH_aH_b resonances can be attributed to withdrawal of charge, if one neglects a possible anisotropic effect caused by the π-allyl ligand. Such a charge delocalization into the π-allyl ligand as well as the formation of the LiC_3H_5 contact ion pair is seen as the reason that initially possibly formed $Li_2[(C_4H_8)M(\eta^1\text{-}C_3H_5)_2]$ is stabilized by LiC_3H_5 elimination to give **4a**,**b**.

The properties of **3a**,**b** and **4a**,**b** are in stark contrast to those of the thermally rather stable tetraorganylnickelate(II) and palladate(II) complexes such as $\{(tmeda)Li\}_2Ni(C_4H_8)_2$ (dec 182 °C) and $\{(tmeda)Li\}_2Pd(C_4H_8)_2$ (dec 169 °C), in which the Li atom is intimately bound to both the methylene groups and the transition metals (contact ion pairs). Exploratory experiments have shown that the Pt derivatives of **3a**,**b** and **4a**,**b** are also accessible, but they are about as unstable as the Pd compounds and were not studied further.

Experimental Part

All manipulations were carried out under argon with Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$. $Ni(\eta^3\text{-}C_3H_5)_2$ and $Pd(\eta^3\text{-}C_3H_5)_2$ were prepared according to the literature. LiC_3H_5 (obtained by reaction of C_3H_5MgCl with lithium metal and purified by repeated crystallizations)[19] and $Li_2C_4H_8$[20] were used as 1 M diethyl ether solutions (these should be kept at −30 °C for stabilization). Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. ^1H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra at 75.5 MHz (both relative to $SiMe_4$) on Bruker AMX-300 and DPX-300 instruments for THF-d_8 solutions. Solid state ^{13}C CP-MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer, equipped with a double bearing probe and a Bruker B-VT 1000 temperature control unit. 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. 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).

$[Li(tmeda)_2]^+[(\eta^3\text{-}C_3H_5)Ni(\eta^1\text{-}C_3H_5)_2]^-$ (3a). When a yellow ethereal solution (10 mL) of $Ni(\eta^3\text{-}C_3H_5)_2$ (704 mg, 5.00 mmol) was combined with 5 mL of a 1 M solution of $Li(C_3H_5)$ (5.00 mmol) in diethyl ether at −30 °C, the color turned red. After addition of tmeda (2 mL, 13.4 mmol) a yellow precipitate of $(tmeda)LiC_3H_5$ was formed, which largely dissolved when the mixture was warmed to ambient temperature. The reaction solution was filtered and cooled to −40 °C to give red needles, which were freed from the mother liquor by means of a capillary, washed with a small volume of cold pentane, and dried under vacuum (20 °C): yield 1.64 g (78%); dec 55 °C. Anal. Calcd for $C_{21}H_{47}LiN_4Ni$ (421.3): C, 59.88; H, 11.25; Li, 1.65; N, 13.30; Ni, 13.93. Found: C, 60.75; H, 11.10; Li, 1.68; N, 12.88; Ni, 13.52. IR (KBr): 3064 (−CH=), 1640, 1577, 1492 (C=C) cm^{-1}. ^1H and ^{13}C NMR (300 MHz): between 20 and −80 °C only the resonances for *trans*/*cis*-$Ni(\eta^3\text{-}C_3H_5)_2$[13] and tmeda were detected. For ^{13}C CP-MAS NMR, see text and Figure 3.

X-ray Crystal Structure Analysis of 3a. $[C_{12}H_{32}N_4Li]^+[C_9H_{15}Ni]^-$: M_w = 421.28, yellow-orange needle, crystal size 0.03 × 0.06 × 0.42 mm, a = 19.0995(3) Å, b = 13.0036(2) Å, c = 10.9698(2) Å, β = 110.033(1)°, U = 2559.6(1) Å^3, T = 100 K, monoclinic, $P2_1/n$ [No. 14], Z = 4, d_{calcd} = 1.09 g cm^{-3}, λ = 0.71073 Å, μ(Mo Kα) = 0.769 mm^{-1}, Nonius KappaCCD diffractometer, 4.14° < θ < 30.05°, absorption correction (T_{max}

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[17] Line shape analysis of the solid state NMR spectra has not been feasible. From the Eyring equation the activation barrier of the exchange process can be estimated to be in the range of 9 kcal/mol.

[18] In eq 3 the depicted square pyramidal geometry of the five-coordinate transition state of **3a**,**b** is in accord with the crystal structure of $(\eta^3\text{-}C_3H_5)_2Ni(PMe_3)$.[1] However, in the light of recent results on five-coordinate Ni−π-allyl complexes a formally trigonal bipyramidal geometry cannot be ruled out. Gemel, C.; Bühl, M.; Goddard, R.; Rufińska, A.; Pörschke, K.-R. To be submitted.

[19] Jonas, K. Unpublished results.

[20] Schöllkopf, U. In *Methoden der Organischen Chemie*, 4th ed.; Houben, Weyl, Müller, Eds.; Thieme: Stuttgart, 1970; Vol. 13/1, p 147.

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= 0.97445, $T_{\min}$ = 0.97437), 20 993 measured, 7439 independent reflections, 4751 with $I > 2\sigma(I)$. The structure was solved by the heavy atom method and refined by least-squares[21] using Chebyshev weights on F_o^2 to R_1 = 0.076 [$I > 2\sigma(I)$], wR_2 = 0.229, 244 parameters, H atoms riding, S = 1.024, Δ/σ = 0.001, residual electron density +1.072/−0.965 e Å^{-3}, 0.93/0.70 Å from Ni.

[Li(tmeda)$_2$]$^+$[(η^3-C$_3$H$_5$)Pd(η^1-C$_3$H$_5$)$_2$]$^-$ (3b). The synthesis was as described for **3a** but starting from Pd(η^3-C$_3$H$_5$)$_2$ (943 mg, 5.00 mmol). Addition of Li(C$_3$H$_5$) (5.00 mmol) gave an intense yellow solution, to which tmeda (2 mL, 13.4 mmol) was added (−30 °C). The precipitated (tmeda)LiC$_3$H$_5$ was largely dissolved at 0 °C, and the mixture was filtered. Cooling to −40 °C gave yellow rods, which were separated as described and dried under vacuum at −30 °C: yield 1.76 g (75%); dec 0 °C. Anal. Calcd for C$_{21}$H$_{47}$LiN$_4$Pd (469.0): C, 53.78; H, 10.10; Li, 1.48; N, 11.95; Pd, 22.69. Found: C, 53.80; H, 9.88; Li, 1.58; N, 11.61; Pd, 22.58. IR (KBr): 3070 (H$_2$C=), 1640, 1585, 1500 (C=C) cm^{-1}. ^{1}H and ^{13}C NMR (300 MHz, −80 °C): the spectra showed mainly the signals of *trans/cis*-Pd(η^3-C$_3$H$_5$)$_2$[13] and tmeda.

[Li(tmeda)$_2$]$^+$[(η^3-C$_3$H$_5$)Ni(C$_4$H$_8$)]$^-$ (4a). The synthesis was as described for **3a** by reacting yellow Ni(η^3-C$_3$H$_5$)$_2$ (704 mg, 5.00 mmol) with 5 mL of a 1 M solution of Li$_2$C$_4$H$_8$ (5.00 mmol) in diethyl ether at −30 °C. To the subsequently orange solution was added tmeda (2 mL, 13.4 mmol) (0 °C). The precipitated (tmeda)LiC$_3$H$_5$ was removed by filtration. Cooling to −40 °C gave orange clusters, which were isolated as described and dried under vacuum (−30 °C): yield 1.17 g (59%); dec 20 °C. Anal. Calcd for C$_{19}$H$_{45}$LiN$_4$Ni (395.2): C, 57.74; H, 11.48; Li, 1.76; N, 14.18; Ni, 14.85. Found: C, 57.77; H, 11.34; Li, 1.81; N, 14.16; Ni, 14.82. IR (KBr): No characteristic bands assignable. ^{1}H NMR (300 MHz, 20 °C): δ 4.15 (tt, 1H, meso), 1.76 (d, J(HH) = 7.2 Hz, 2H, syn), 1.01 (d, J(HH) = 13 Hz, 2H, anti), allyl; 1.35 (4H, −CH$_a$H$_b$−), 1.23, 0.82 (each m, 2H, NiCH$_a$H$_b$), NiC$_4$H$_8$; 2.34 (8H, NCH$_2$), 2.18 (24H, NCH$_3$), tmeda. ^{13}C NMR (75.5 MHz, 20 °C): δ 103.4 (1C), 43.2 (2C), allyl; 38.1 (2C, −CH$_2$−), 19.2 (2C, NiCH$_2$), NiC$_4$H$_8$; 58.6 (4C, NCH$_2$), 46.3 (8C, NCH$_3$), tmeda.

X-ray Crystal Structure Analysis of 4a. [C$_{12}$H$_{32}$N$_4$Li]$^+$-[C$_7$H$_{13}$Ni]$^-$: M_w = 395.24, yellow prism, crystal size 0.12 × 0.21 × 0.28 mm, a = 14.915(2) Å, b = 17.358(2) Å, c = 18.286(2) Å, U = 4734.2(10) Å^3, T = 100 K, orthorhombic, *Pbca* [No. 61], Z = 8, d_{calcd} = 1.11 g cm^{-3}, λ = 0.71073 Å, μ(Mo Kα) = 0.828 mm^{-1}, Siemens SMART diffractometer, 2.12° < θ < 23.26°, absorption correction ($T_{\max}$ = 0.88108, $T_{\min}$ = 0.88076), 17 296 measured, 3396 independent reflections, 1628 with $I > 2\sigma(I)$. Structure solved by direct methods and refined by least-squares[21] using Chebyshev weights on F_o^2 to R_1 = 0.063 [$I > 2\sigma(I)$], wR_2 = 0.174, 224 parameters. The ethylene moiety of the butane-1,4-diyl ligand is disordered over two positions (50:50), only one conformation is shown in Figure 2. H atoms riding, Δ/σ < 0.001, S = 0.966 residual electron density +0.562/−0.428 e Å^{-3}, 1.09/0.94 Å from Ni.

[Li(tmeda)$_2$]$^+$[(η^3-C$_3$H$_5$)Pd(C$_4$H$_8$)]$^-$ (4b). The synthesis was as described for **3a** but by reacting Pd(η^3-C$_3$H$_5$)$_2$ (943 mg, 5.00 mmol) with 5 mL of a 1 M solution of Li$_2$C$_4$H$_8$ (5.00 mmol) at −30 °C. No notable color change occurred. Tmeda (2 mL, 13.4 mmol) was added (0 °C), and the precipitated (tmeda)-LiC$_3$H$_5$ was removed by filtration. Cooling the solution to −60 °C gave a bright yellow precipitate, which was separated by filtration, washed with cold pentane, and dried under vacuum (−30 °C): yield 1.26 g (57%); dec 0 °C. Anal. Calcd for C$_{19}$H$_{45}$-LiN$_4$Pd (443.0): C, 51.52; H, 10.24; Li, 1.57; N, 12.65; Pd, 24.03. Found: C, 50.65; H, 9.78; Li, 1.49; N, 11.93; Pd, 25.44. ^{1}H NMR (300 MHz, 20 °C): δ 4.41 (tt, 1H, meso), 2.34 (d, J(HH) = 7.4 Hz, 2H, syn), 1.53 (d, J(HH) = 12.8 Hz, 2H, anti), allyl; 1.82, 1.50 (each m, 2H, PdCH$_a$H$_b$), 1.42 (4H, −CH$_a$H$_b$−), PdC$_4$H$_8$; 2.34 (8H, NCH$_2$), 2.18 (24H, NCH$_3$), tmeda. ^{13}C NMR (75.5 MHz, 20 °C): δ 113.1 (1C), 44.0 (2C), allyl; 38.5 (2C, −CH$_2$−), 20.6 (2C, PdCH$_2$), PdC$_4$H$_8$; 58.5 (4C, NCH$_2$), 46.3 (8C, NCH$_3$), tmeda.

Supporting Information Available: Tables of X-ray data collection information, atom coordinates and thermal parameters, and bond lengths and angles, together with CIF data, for **3a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030448J

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