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Basicities of Nickel and Allyl in $[Ni(\eta^3\text{-}C_3H_5)(PhP(CH_2CH_2PPh_2)_2]^+$ and Comparison of the Effects of Allyl and Methyl on the Basicity of Nickel

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Kinetic studies on the reaction between $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ (triphos = $\{Ph_2PCH_2CH_2\}_2$-PPh) and $[lutH]^+$ (lut = 2,6-dimethylpyridine) in MeCN show that initial protonation of the nickel or allyl is followed by equilibration of the proton between the two sites. Analysis of the data allows calculation of the basicities of the nickel and allyl sites. This, together with earlier work on $[NiMe(triphos)]^+$, shows the nickel site is (2.5−79) × 10^6 times more basic when coordinated to allyl than to methyl.

Introduction

The protonation of transition metal complexes containing coordinated hydrocarbon residues is a fundamental reaction of importance in industrial processes[1] and in the action of certain metalloenzymes.[2] In general, protonation at both the metal and carbon-based ligands can be slow,[3,4] and establishing which is the initial site of protonation is often complicated by the ability of protons to move between adjacent carbon and metal sites. Depending on the complex, initial protonation at the metal or the carbon-based ligand has been observed,[5] and there is currently no reliable method of predicting the kinetically or thermodynamically preferred site of protonation.

Before it is possible to confidently predict whether protonation is at the metal or hydrocarbon ligand, it is necessary to understand (i) the factors that control the rates of protonation and (ii) the relative basicities of the two sites. We report herein kinetic studies on the equilibrium protonation of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ {triphos = $PhP(CH_2CH_2PPh_2)_2$} with $[lutH]^+$ (lut = 2,6-dimethylpyridine) in MeCN, which allows us to calculate the difference in basicities of the nickel and η^3-allyl sites. These results (together with those of earlier studies[6] on $[NiMe(triphos)]^+$) allow us to show that allyl and methyl ligands have markedly different effects on the basicity of the nickel site.

Experimental Section

All manipulations in the synthetic and kinetic aspects of this work were performed under an atmosphere of dinitrogen using Schlenk and syringe techniques, as appropriate. Triphos, lutidine, $NaBPh_4$, C_3H_5MgBr, and $NiCl_2{\cdot}6H_2O$ were purchased from Aldrich and used as received.

All solvents were dried and distilled under dinitrogen immediately prior to use. MeCN was distilled from CaH_2, thf from Na/benzophenone, CH_2Cl_2 from P_2O_5, and diethyl ether from Na. $[lutH]BPh_4$ was prepared by the method reported in the literature.[7]

Preparation of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]BPh_4$. To a suspension of $[NiCl(triphos)]BPh_4$ (0.75 g, 0.79 mmol) in thf (10 mL) was added C_3H_5MgBr (2.0 mL of 2 M solution in thf; 4.0 mmol). The solution turned dark red almost immediately and was stirred overnight at room temperature. The next day any excess Grignard reagent was destroyed by dropwise addition of methanol. All volatiles were then removed in vacuo, and the residue was dissolved in a minimum of CH_2Cl_2, then filtered through Celite to remove insoluble material. Slow diffusion of methanol into the solution produced red needles of the product, which were removed by filtration, washed with methanol, and then dried in vacuo. Yield = 0.26 g; 35%. Anal. Calcd for $C_{61}H_{58}BNi\,P_3$: C, 76.8; H, 6.1. Found: C, 76.5; H, 6.0. $^{31}P\{^1H\}$ NMR (THF): 112.1 (t, J_{PP} = 48.6 Hz, central P); 48.2 (d, J_{PP} = 48.6 Hz, terminal P). ^1H NMR ($CDCl_3$): 6.3−7.9 (m, 45, *Ph* of triphos and BPh_4^-); 5.0 (quin, 1, J_{HH} = 8 Hz, $CH_2C\mathit{H}CH_2$); 3.3 (d, 4, J_{HH} = 8 Hz, $C\mathit{H_2}CHC\mathit{H_2}$); 2.6, 2.4 (br, 8, $-C\mathit{H_2}C\mathit{H_2}-$). The positions, multiplicities, and coupling constants attributable to the η^3-C_3H_5 ligand are fully in accord with values in the literature for Ni(η^3-allyl) complexes.[8]

Kinetic Studies. All kinetic studies were performed on an Applied Photophysics stopped-flow SX.18V spectrophotometer, modified to handle air-sensitive solutions. The temperature was maintained at 25.0 °C using a Grant LTD6G recirculating thermostat tank.

The kinetics were studied in dry MeCN under pseudo-first-order conditions with $[lutH^+]$ and [lut] in at least a 10-fold excess over the concentration of complex. Mixtures of [lutH]-

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[1] Elschenbroich, C.; Salzer, A. *Organometallics, A Concise Introduction,* 2nd ed.; VCH: Weinheim, 1992; Chapter 17, and references therein.

[2] Evans, D. J.; Henderson, R. A.; Smith, B. E. In *Bioinorganic Catalysis*, 2nd ed.; Reedijk, J., Bouwman, E., Eds.; Marcel Dekker: New York, 1999; Chapter 7, p 153, and references therein.

[3] Kramarz, K. W.; Norton, J. R. *Prog. Inorg. Chem*. **1994**, *42*, 1, and references therein.

[4] Henderson, R. A. *Angew Chem., Int. Ed.* **1996**, *35*, 946, and references therein.

[5] Åkermark, B.; Martin, J.; Nyström, J.-E.; Strömberg, S.; Svensson, M.; Zetterberg, K.; Zuber, M. *Organometallics* **1998**, *17*, 5367, and references therein.

[6] Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Chem. Commun.* **1999**, 2271.

[7] Grönberg, K. L. C.; Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Dalton Trans.* **1998**, 3093.

[8] Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Chapter VI, p 335, and references therein.

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BPh_4 and lut were prepared from stock solutions of the two reagents. All solutions were used within 1 h of preparation.

Under all the conditions described herein the absorbance−time curves were a single exponential, with an initial absorbance which is that of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ and a final absorbance corresponding to the equilibrium mixture of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ and $[NiH(\eta^3\text{-}C_3H_5)(triphos)]^{2+}$. The associated rate constants (k_{obs}) were determined by a computer fit to the exponential absorbance−time curve. In all cases the curve was an exponential for more than 4 half-lives. The dependence of k_{obs} on $[lutH^+]$ and [lut] was determined graphically, as presented in the Results and Discussion section.

X-ray Crystal Structure Determination of [Ni(SPh)(triphos)]BPh₄. Crystallographic data for $[Ni(\eta^3\text{-}C_3H_5)(triphos)]BPh_4$: $a = 11.8500(5)$ Å, $b = 14.2338(6)$ Å, $c = 15.9500(7)$ Å, $\alpha = 80.287(2)°$, $\beta = 69.588(2)°$, and $\gamma = 80.221(2)°$ with $Z = 2$ in space group $P1$. $R1(F) = 0.0298$ for 8829 reflections with $I > 2\sigma(I)$, and $R_w(F^2) = 0.0769$ for all 10 316 unique data and 616 parameters; GOF = 1.023 on F^2. The data collection and structure determination followed standard procedures, with a Bruker AXS SMART CCD diffractometer and Mo Kα radiation ($\theta_{max} = 28.6°$, 44 882 reflections measured, 23 463 unique, semiempirical absorption corrections based on symmetry-equivalents), direct methods, and full matrix least squares refinement on all unique F^2 values. Programs were Bruker SMART (data collection), SAINT (integration), and SHELXTL (structure solution).

Results and Discussion

Structure of [Ni(η³-C₃H₅)(triphos)]⁺. $[Ni(\eta^3\text{-}C_3H_5)(triphos)]BPh_4$ was prepared, in modest yield (ca. 30%), by the route shown in eq 1.

$$\begin{array}{l} NiCl_2{\cdot}6H_2O \xrightarrow[NaBPh_4]{triphos} [NiCl(triphos)]BPh_4 \\ \qquad\qquad\qquad\qquad \downarrow LiSPh \\ \qquad\qquad\qquad [Ni(SPh)(triphos)]BPh_4 \\ \qquad\qquad\qquad\qquad \downarrow C_3H_5MgBr \\ \qquad\qquad\quad [Ni(\eta^3\text{-}C_3H_5)(triphos)]BPh_4 \end{array} \qquad (1)$$

The structure of the cation in crystals of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]BPh_4$ is shown in Figure 1. The coordination geometry of the nickel is best considered as a distorted tetrahedron comprising the three phosphorus atoms and the central carbon of the $\eta^3\text{-}C_3H_5$ residue. The important bond lengths and angles are listed in Figure 1 and show that there is nothing unusual about the structure.[9]

The crystal structure confirms the presence of the $\eta^3\text{-}C_3H_5$ ligand that was indicated by the ^1H NMR spectrum. The angle C(35)−C(36)−C(37) = 118° is in the normal range,[10] and the Ni−C distances are close to the mean values reported for $\eta^3\text{-}C_3H_5$ ligands.[11]

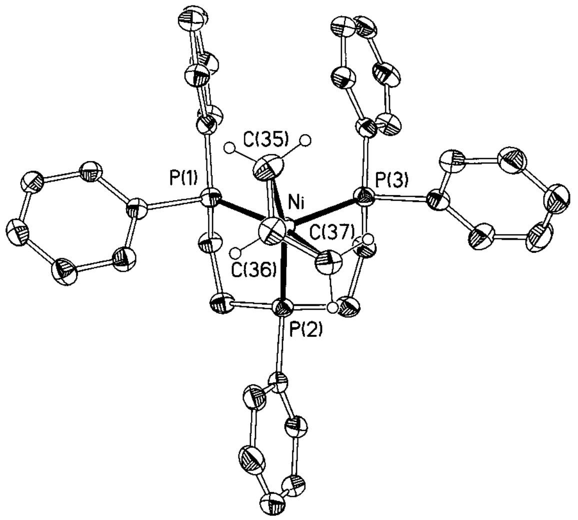

Figure 1. Structure of the cation in $[Ni(\eta^3\text{-}C_3H_5)(triphos)]BPh_4$ with 50% probability ellipsoids; triphos H atoms are omitted. Important bond distances (Å) and angles (deg): Ni−P(1) = 2.1897(4), Ni−P(2) = 2.1830(4), Ni−P(3) = 2.2935(4); Ni−C(36) = 1.9898(15), Ni−C(35) = 2.0618(16), Ni−C(37) = 2.0853(16); P(1)−Ni−P(2) = 88.490(16), P(1)−Ni−P(3) = 104.448(17), P(2)−Ni−P(3) = 90.154(16), P(1)−Ni−C(36) = 116.59(5), P(2)−Ni−C(36) = 118.90(5), P(3)−Ni−C(36) = 128.75(6).

Reaction of [Ni(η³-C₃H₅)(triphos)]⁺ with [lutH]⁺. The reaction between $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ and an excess of $[lutH]^+$ and lut in MeCN is an equilibrium process. This is most evident when the reaction is studied on a stopped-flow apparatus. The absorbance−time curves are exponential, but, most notably, the magnitude of the curves increases with increasing $[lutH^+]/[lut]$ (up to a maximum value when $[lutH^+]/[lut]$ = ca. 2), as progressively more $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ is protonated. It is important to stress that the choice of acid is crucial in ensuring that an equilibrium reaction is observed. Use of stronger acids associated with conjugate bases that can coordinate (e.g., anhydrous HCl) results in evolution of propene and formation of $[NiCl(triphos)]BPh_4$, probably because of coordination of Cl^- and/or addition of more than one proton to the allyl complex.

The exponential shape of the curves indicates that the reaction exhibits a first-order dependence on the concentration of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$. This is confirmed by experiments in which the concentration of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ was varied from 0.05 to 0.25 mmol dm^{-3} while keeping the concentrations of $[lutH]^+$ (10 mmol dm^{-3}) and lut (5 mmol dm^{-3}) constant. Under these conditions the observed rate constant did not vary, $k_{obs} = 0.05\ s^{-1}$.

The dependence of k_{obs} on the concentrations of $[lutH]^+$ and [lut] is complicated. Analysis of the kinetic data is accomplished by considering two conditions: (i) the variation of k_{obs} with $[lutH^+]/[lut]$ at constant $[lutH^+]$ (Figure 2, main) and (ii) variation of k_{obs} with $[lutH^+]$ at constant $[lutH^+]/[lut]$ (Figure 2, inset). Analysis of these data gives the rate law in eq 2.

$$\frac{-d[Ni(\eta^3\text{-}C_3H_5)(triphos)^+]}{dt} = \frac{\{(2.1\pm0.3)\times10^2[lutH^+] + (1.0\pm0.2)\}[Ni(\eta^3\text{-}C_3H_5)(triphos)^+]}{(8.0\pm0.3)\times10^3[lutH^+] + (4.0\pm0.2)\times10^2[lut]} \qquad (2)$$

The rate law shown in eq 2 is too complicated for a single equilibrium protonation, but rather corresponds to two coupled equilibria:[12] the first step is protonation of $[Ni(\eta^3\text{-}C_3H_5)(triphos)]^+$ and the second a unimolecular rearrangement of the protonated species as shown in

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(9) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Chapter VI, p 331, and references therein.

(10) Cotton, F. A.; Luck, R. L. *Inorg. Chem*, **1989**, *28*, 3210.

(11) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. C.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, 51.

(12) Wilkins R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinheim, 1991; p 34.

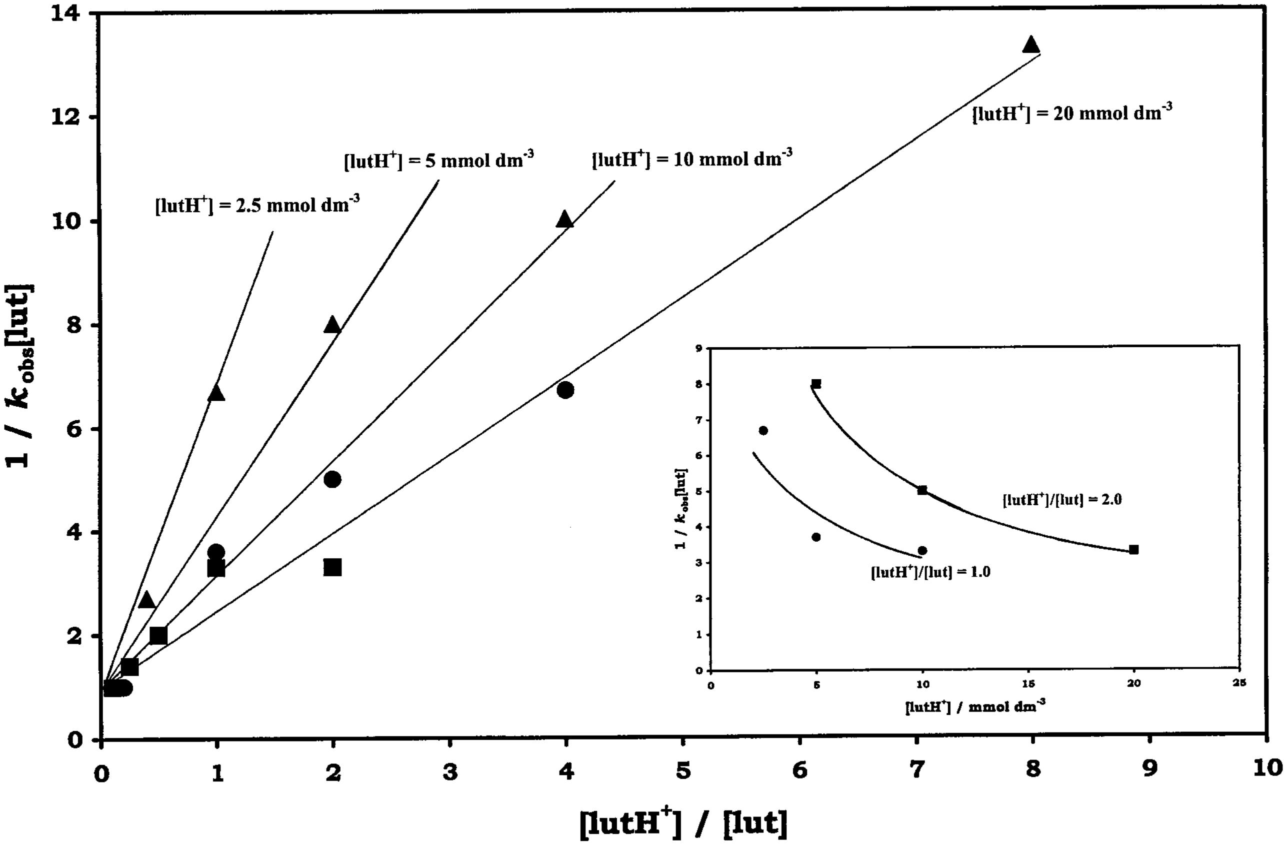

Figure 2. Kinetics for the reaction of [Ni(η^3-C_3H_5)(triphos)]$^+$ with mixtures of [lutH]$^+$ and lut in MeCN at 25.0 °C. All kinetics were measured at λ = 350 nm. Main figure: dependence of $1/k_{obs}$[lut] on [lutH$^+$]/[lut] at constant [lutH$^+$]. Data corresponds to [lutH$^+$] = 1−20 mmol dm^{-3}, [lut] = 2.5 mmol dm^{-3} (▲); [lutH$^+$] = 1−20 mmol dm^{-3}, [lut] = 5.0 mmol dm^{-3} (●); [lutH$^+$] = 1−20 mmol dm^{-3}, [lut] = 10.0 mmol dm^{-3} (■). Inset: dependence of $1/k_{obs}$[lut] on [lutH$^+$] at constant [lutH$^+$]/[lut]. Data points correspond to [lutH$^+$]/[lut] = 1.0 (●) and [lutH$^+$]/[lut] = 2.0 (■). Lines and curves are those defined by eq 2.

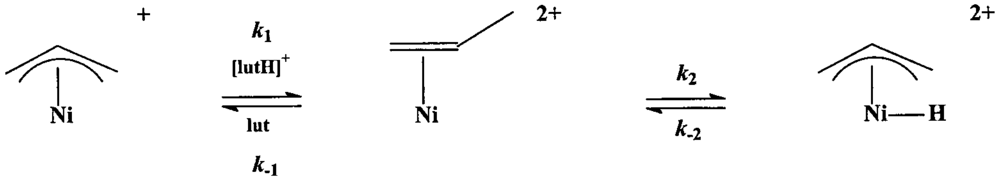

Figure 3. Mechanism for the protonation of [Ni(η^3-C_3H_5)(triphos)]$^+$ with [lutH]$^+$ in MeCN.

Figure 3. The rate law associated with this mechanism is shown in eq 3, when $k_{-2} > k_2$.

$$-\frac{d[\mathrm{Ni}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{triphos})^+]}{dt} = \frac{\{k_1k_2[\mathrm{lutH^+}] + (k_2 + k_{-2})\}[\mathrm{Ni}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{triphos})^+]}{k_1[\mathrm{lutH^+}] + k_{-1}[\mathrm{lut}]} \tag{3}$$

Comparison of eqs 2 and 3 yields $k_2 = 0.03 \pm 0.01$ s^{-1}, $k_{-2} = 0.97 \pm 0.01$ s^{-1}, $k_1 = (8.0 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1}, and $k_{-1} = (4.0 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1}. The equilibrium constants $K_1 = k_1/k_{-1} = 20$ and $K_2 = k_2/k_{-2} = 3.1 \times 10^{-2}$ are simply calculated from these rate constants. Unfortunately, the relatively poor solubility of [Ni(η^3-C_3H_5)(triphos)]$^+$ means we have been unable to confirm the values of K_1 and K_2 using NMR spectroscopy.

The kinetics described above do not allow us to distinguish between the mechanism shown in Figure 3 and the alternative in which initial protonation of nickel is followed by proton transfer to carbon. Studies on the protonation of a variety of alkene, alkyne,[5,13,14] and η^3-allyl[15,16] complexes show that no generalizations can be made about whether the metal or ligand is protonated first. Nonetheless, the study on [Ni(η^3-C_3H_5)(triphos)]$^+$ still allows us to calculate the difference in basicities of the nickel and carbon sites.

Basicities of the Nickel and η^3-Allyl Sites. The p$K_a{}^1$ of the protonated complex can be calculated directly. In MeCN, the p$K_a{}^{\mathrm{lutH}}$ of [lutH]$^+$ is 15.4,[17] and since $K_1 = K_a{}^{\mathrm{lutH}}/K_a{}^1$, p$K_a{}^1$ = 16.7 can be calculated. Our mechanism proposes that this is the pK_a of coordinated

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(13) Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Chem. Commun.* **1991**, 584.

(14) Oglieve, K. E.; Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3295.

(15) Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Dalton Trans.* **1994**, 767.

(16) Henderson, R. A.; Hughes, D. L.; Macdonald, C. J.; Oglieve, K. E. *Inorg. Chim. Acta* **1997**, *259*, 107, and references therein.

(17) Cauquis, G.; Deronzier, A.; Serve, D.; Vieil, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 205.

propene. We can calculate the $pK_a{}^3$ for the protonation at the other site (Ni). Although we do not observe the direct protonation of this site, the unobserved protolytic equilibrium constant K_3, as defined by eq 4, is related to K_1 and K_2 by the simple relationship $K_3 = K_1K_2 = 0.62$, and thus $pK_a{}^3 = 15.2$.

$$[\mathrm{Ni}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{triphos})^+] + [\mathrm{lutH}^+] \underset{}{\overset{K_3}{\rightleftharpoons}} [\mathrm{Ni}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{triphos})]^{2+} + \mathrm{lut} \quad (4)$$

Thus, the difference in the basicities of the nickel and η^3-allyl is only ca. 30-fold. That this difference must be small is self-evident since the proton can move between the two sites. Indeed, a small difference in the basicities of metal and ligand must be a general feature of all complexes that show such proton-transfer processes.

One further feature from this study is that, irrespective of whether K_1 or K_3 corresponds to protonation of the η^3-C_3H_5 group, it is clear that upon coordination to the {Ni(triphos)} site propene becomes at least a 10^{33} stronger acid.

The results of these studies allow us to compare the effect that η^3-C_3H_5 and Me groups have on the basicity of the nickel. Recently,[6] we showed that the reaction of $[\mathrm{NiMe(triphos)}]^+$ with anhydrous HCl ($pK_a = 8.9$) in MeCN involves initial protonation of the nickel to form the spectroscopically detectable $[\mathrm{Ni(H)Me(triphos)}]^{2+}$. Analysis of the data gives $pK_a{}^{\mathrm{Ni}} = 8.8$ for $[\mathrm{NiH(Me)(triphos)}]^{2+}$. *Comparison with the results presented herein shows that the nickel in* $[\mathrm{Ni}(\eta^3\text{-}C_3H_5)(\mathrm{triphos})]^+$ *is* $(2.5-79) \times 10^6$ *times more basic than in* $[\mathrm{NiMe(triphos)}]^+$. Clearly, $[\mathrm{NiH}(\eta^3\text{-}C_3H_5)(\mathrm{triphos})]^{2+}$ is a closed shell complex, while $[\mathrm{Ni(H)Me(triphos)}]^{2+}$ is a 16-electron species. Nonetheless, the difference in pK_a's for structurally so similar complexes is noteworthy.

Although the acidities of metal-hydrides have been determined in MeCN, this is the first time that the influence of different hydrocarbon residues on the acidities has been quantified. It is useful to put the results presented herein into context.[18] The effect of formally replacing a Me group for η^3-C_3H_5 is similar to (i) changing a CO for PPh_3 in $[\mathrm{MnH(CO)_5}]$ ($pK_a = 14.2$) and $[\mathrm{MnH(CO)_4(PPh_3)}]$ (20.4) or $[\mathrm{CoH(CO)_4}]$ (8.4) and $[\mathrm{CoH(CO)_3(PPh_3)}]$ (15.4); (ii) replacing C_5H_5 by C_5Me_5 in $[\mathrm{FeH}(\eta^5\text{-}C_5H_5)(\mathrm{CO})_2]$ (19.4) and $[\mathrm{FeH}(\eta^5\text{-}C_5Me_5)(\mathrm{CO})_2]$ (26.3); and (iii) changing the metal as in $[\mathrm{FeH_2(CO)_4}]$ (11.4) and $[\mathrm{RuH_2(CO)_4}]$ (18.7) or $[\mathrm{PdH\{P(OMe)_3\}_4}]^+$ (10.6) and $[\mathrm{PtH\{P(OMe)_3\}_4}]^+$ (18.5).

The large difference in basicities observed in $[\mathrm{NiR(triphos)}]^+$ (R = Me or η^3-C_3H_5) stands in stark contrast to the effect methyl and allyl residues have in organic molecules. As illustrated by the following aqueous pK_a's, methyl and allyl groups have a similar affect on the acidities[19] of adjacent carboxylate {$MeCO_2H$ (4.8) and $CH_2{=}CHCO_2H$ (4.2)} and amine groups {$MeNH_3{}^+$ (10.7) and $CH_2{=}CHCH_2NH_3{}^+$ (9.5)}. It seems most likely that the η^3-coordination of the allyl group in the metal complex is the origin of the increased basicity of the nickel site in $[\mathrm{Ni}(\eta^3\text{-}C_3H_5)(\mathrm{triphos})]^+$. Obviously this binding mode is unavailable to organic molecules. Interestingly, if this proposal is correct, then it follows that the metal site in a complex containing an η^1-allyl ligand would be ca. 10^6 times less basic than the analogue containing an η^3-allyl ligand.

Kinetic studies on the equilibrium protonation reaction of $[\mathrm{Ni}(\eta^3\text{-}C_3H_5)\{(\mathrm{Ph_2PCH_2CH_2})_2\mathrm{PPh}\}]^+$ with $[\mathrm{lutH}]^+$ (lut = 2,6-dimethylpyridine) shows that the basicities of the nickel and allyl sites differ by less than 30. Furthermore, comparison of $[\mathrm{NiR}\{(\mathrm{Ph_2PCH_2CH_2})_2\mathrm{PPh}\}]^+$ (R = Me or η^3-C_3H_5) shows that η^3-allyl makes the nickel site ca. 10^6 times more basic than methyl.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Kristjansdottir, S. S.; Norton, J. R. *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9, and references therein.

[19] Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry* OUP: Oxford, 2000; Chapter 8.