Journal of Organometallic Chemistry, 359 (1989) 409–418
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

New η^6-arene complexes of nickel(II): polyarene and fused arene systems

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(Received May 11th, 1988)

Abstract

Two reactions schemes have been employed to prepare a series of polyarene and fused arene-$Ni(SiCl_3)_2$ complexes. The first method was based on arene $\rightleftarrows$ arene′ exchange equilibria, and the second employed the production of the $Ni(SiCl_3)_2$ moiety in the presence of the desired arene by the reaction of $(allyl)_2Ni$ derivatives with $HSiCl_3$. Arenes employed were biphenyl, 4,4′-dimethylbiphenyl, diphenylmethane, 1,2-diphenylethane, 4,4′-paracyclophane, naphthalene, and anthracene. Equilibria studies showed that the tendency to bind with the $Ni(SiCl_3)_2$ moiety was in the order 4,4′-paracyclophane $\gg$ toluene > diphenylmethane > 1,2-diphenylethane > -biphenyl > naphthalene ∼ anthracene > halobenzenes. Repeated attempts to bind two arene groups in the same molecule with two $Ni(SiCl_3)_2$ groups failed, as did attempts to prepare $(Cl_3Si)_2Ni$-arene-$Ni(SiCl_3)_2$ species.

Introduction

The synthesis of the first well characterized η^6-arenenickel complex (η^6-toluene)$Ni(C_6F_5)_2$ in 1978 [1] followed by analogous (arene)$Ni(SiCl_3)_2$ [2] and (arene)$Ni(SiF_3)_2$ [3] systems opened up new area of organonickel chemistry. Synthetic routes to these materials utilizing both metal atom methods and solution methods were developed [1–4]. These general procedures make a wide variety of arene-nickel(II) complexes available. Toluene bound in this way is very labile, so simple exchange reactions are possible:

$$(\eta^6\text{-toluene})NiR_2 + \text{arene} \rightleftarrows (\eta^6\text{-arene})NiR_2 + \text{toluene}$$

$$(R = C_6F_5,\ SiCl_3,\ SiF_3)$$

By removing toluene the equilibria can usually be shifted in the desired way. If this

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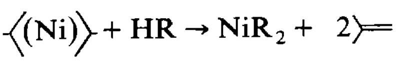
is not possible, the NiR_2 group can be generated in the presence of the desired arene:



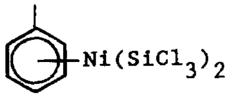
NiR_2 + arene → (η^6-arene)NiR_2

($R = SiCl_3$, SiF_3)

Further understanding of the arene–Ni^{II} bond is desirable. This consideration, and the opportunity to prepare a broader series of complexes, possibly even binuclear systems, led us to carry out the work described herein.

Results and discussion

Arenes employed included biphenyl, 4,4′-dimethylbiphenyl, diphenylmethane, 1,2-diphenylethane, 4,4′-paracyclophane, naphthalene, and anthracene. We were able to prepare complexes **3**–**7** from **1**, and **8** and **9** from **2** as discussed in the Introduction and Experimental sections.



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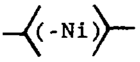

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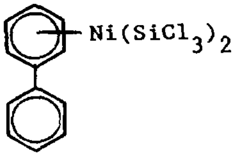

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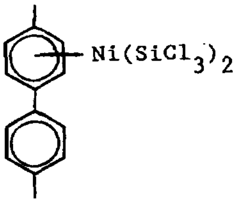

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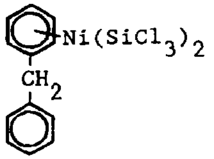

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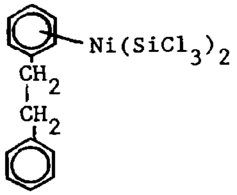

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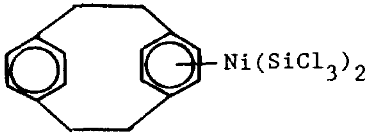

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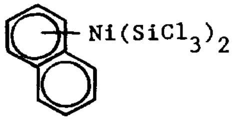

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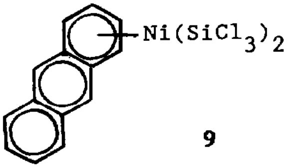

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We found that it was not possible to prepare **8** and **9** by the exchange method due to the very unfavorable equilibrium set up with toluene thus completely favoring **1**. Similar behavior was encountered when haloarenes (C_6H_5F, C_6H_5Cl, C_6H_5Br) were employed: no detectable amounts of haloarene-Ni compounds were formed even under forcing conditions of high concentrations [5*]. Nor was it possible to prepare binuclear complexes even where the two arene groups are relatively insulated, such as with 1,2-diphenylmethane. These results demonstrate the surprising sensitivity of the NiR_2 fragment for seeking out electron rich arene ligands. We have encountered similar behavior in studies of (arene)Co(C_6F_5)$_2$ systems [6]. Such extreme sensitivity to electron density is not encountered in more well known bisarene-chromium chemistry where many haloarene complexes are known [7,8]. However, it is interesting to note that in Cr-cyclophane complexes, only after six CH_2 groups were inserted between the arene rings, did the rings begin to behave independently [9].

In order to determine equilibrium constants for the measurable exchange reactions, a series of NMR studies were carried out. This was possible due to the substantial upfield shift of protons attached to complexed arenes and a similar although smaller shift of attached methyl substituents. These NMR data are collected in Table 1, and Fig. 1 and 2 illustrate spectra for two examples. The relative molar ratios of **1**: arene were varied from 0.4 to 2.3, and the relative concentrations of toluene-Ni, arene, arene-Ni, toluene were measured by ^1H NMR integration. The reaction mixtures were monitored after 15, 30, and 45 minutes and

$$\text{toluene-Ni} + \text{arene} \rightleftarrows \text{arene-Ni} + \text{toluene}$$

$$M = \frac{[\text{arene-Ni}][\text{toluene}]}{[\text{toluene-Ni}][\text{arene}]}$$

no changes occurred over this period, showing that the equilibria were established very quickly at room temperature. Several determinations in each case showed good reproducibility, and yielded: K(biphenyl) = 0.21 ± 0.05, (diphenylmethane) = 0.78 ± 0.01, (1,2-diphenylethane) = 0.31 ± 0.02, and (4,4′-paracyclophane) = 7600 ± 2600. (And recall that K for naphthalene and anthracene were too small to measure).

These results show that toluene is preferred over biphenyl, which is to be expected based on electron density in the arene ring. When a CH_2 is inserted between the rings, this toluene preference is dimininished significantly. However, upon adding another CH_2 group, toluene preference is enhanced again. It may be that steric factors start to become important, which would explain this trend.

Electronic factors and steric factors might be invoked as rationale for the striking behavior of 4,4′-paracyclophane. Obviously the near-by second ring exhibits a giant through space effect so that bonding to Ni($SiCl_3$)$_2$ is greatly favored.

And finally, the behavior of naphthalene and anthracene is also somewhat surprising, although naphthalene is known to be a more readily displaced ligand in arene-Cr complexes as well [10]. In that case an argument was made that this is due to an energetically favorable transition state. For a fused arene system, the arene $\eta^6 \rightarrow \eta^4$ bond shift in the transition state may restore the full aromaticity of the

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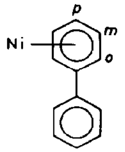
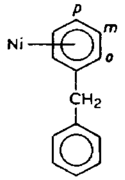
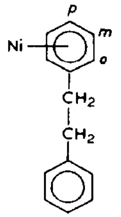
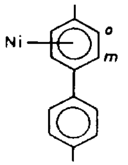
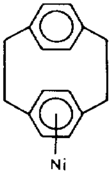
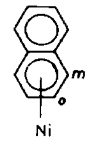
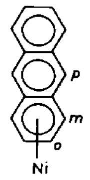
* Reference numbers with asterisks indicate notes in the list of references.

Table 1

^{1}H NMR chemical shifts

Arenes		Chemical shifts				
		free	bound	$\Delta\delta$	unbound	$\Delta\delta$
	**3**					
	o	7.43	6.90	−0.53	7.55	0.12
	m	7.58	7.02	−0.44	7.70	0.12
	p	7.30	7.43	0.13	7.45	0.15
	CH_2	none				
	**5**					
	o	7.20	6.56	−0.64	7.37	0.17
	m	7.27	6.72	−0.55	7.43	0.16
	p	7.20	7.22	0.02	7.37	0.17
	CH_2	4.00	4.30			
	**6**					
	o	7.17	6.57	−0.60	7.18	0.01
	m	7.27	6.72	−0.55	7.28	0.01
	p	7.17	7.20	0.03	7.18	0.01
	CH_2	2.90	3.20	0.30	3.10	0.20
	**4**					
	o	7.22	6.68	−0.54	7.34	0.12
	m	7.48	6.85	−0.53	7.56	0.08
	p					
	CH_2	2.39	2.70	0.31	2.47	0.08
	**7**					
	o	6.50	5.74	−0.76	6.78	0.28
	m					
	p					
	CH_2	3.10	3.32	0.22		
	**8**					
	o	7.52	7.13	−0.39	7.90	0.38
	m	7.85	7.25	−0.60	8.00	0.15
	**9**					
	o	7.45	7.16	−0.29	7.70	0.25
	m	8.00	7.36	−0.64	8.06	0.06
	p	8.40			8.49	0.09

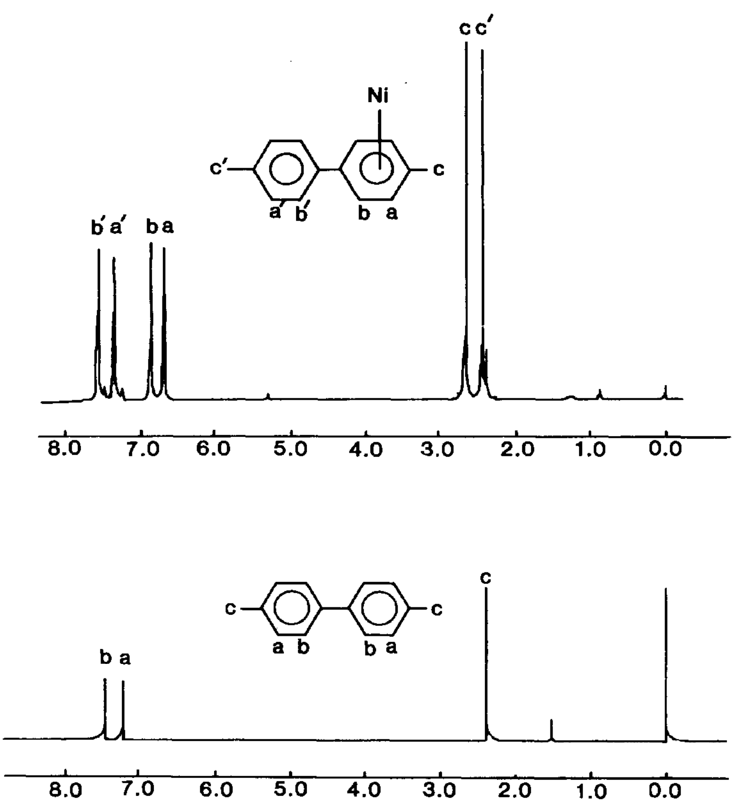


Fig. 1. NMR spectra for the 4,4'-dimethylbiphenyl system.

unbound ring. Though the fused arenes are more labile than mono-arenes in chromium complexes, still the arene exchange reactions require severe conditions. For example, arene exchange reactions did not occur for (η^6-naphthalene)Cr(CO)$_3$ and (η^6-anthracene)Cr(CO)$_3$ in benzene solvent at room temperature [10]. Note that for our corresponding nickel complexes, (η^6-naphthalene)Ni(SiCl$_3$)$_2$ and (η^6-anthracene)Ni(SiCl$_3$)$_2$, the arene exchange relations were complete within one minute under the same conditions.

Can our equilibria results be correlated with NMR chemical shifts? Since metal binding significantly effects chemical shifts, it might be presumed that the strength of interaction would be reflected in this way. Table 1 lists not only the chemical shifts for the free vs. metal complexed arene, but also vs. the attached non-complexed second arene ring. There does appear to be a rough correlation of K with $\Delta\delta$ for the *ortho*-hydrogens (most shifted) for the biphenyl, diphenylmethane, and 1,2-diphenylethane. However, the cyclophane is so far off scale that it cannot be properly compared or plotted. Likewise, naphthalene and anthracene are also not really comparable with the other systems. It would appear that if an arene-NiR$_2$ complex can be prepared and is stable, a significant NMR shift of 0.3–0.6δ can be expected for the metal bound ring protons. And depending on the arene structure, the non-metal bound second ring also experiences a significant chemical shift but in the opposite direction.

We conclude that the NiR$_2$ group is en electron demanding fragment. Upon complexation to the arene ring the ring current and aromaticity is disrupted, thus

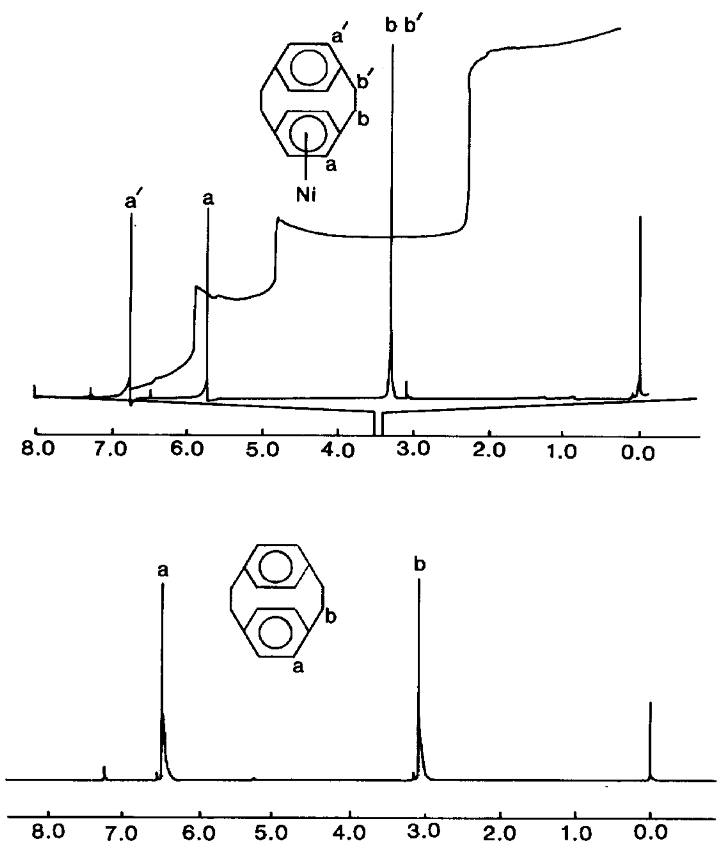


Fig. 2. NMR spectra for the cyclophane system.

destroying anisotropic shielding effects, and an upfield shift is observed. The attached second ring, however, donates electron density by a "through bond" mechanism if possible (note the smallest downfield shift for the unligated ring in 1,2-diphenylethane). If a "through space" effect is possible, as with the cyclophane, a large downfield shift of the non-ligated ring is exhibited.

Considering the naphthalene and anthracene ligands further, the NMR of **8** and **9** clearly show signals for complexed and non-complexed rings, which argues against any rapid (NMR time scale) ring switching process. Note from Table 1 that the upfield shift of the ligated ring in **8** is equaled by the downfield shift of the uncomplexed ring. The non-complexed ring is significantly perturbed, apparently. Also, the NMR data for **9** support an arene–Ni to the terminal ring rather than to the center ring. Note the small downfield shift of the protons on the bridge carbons (*p*), the large upfield shift of the *ortho* protons (*o*) and the moderate shift of the *meta* (*m*) as well. However, the *meta* protons of the non-complexed terminal ring shift downfield.

It can be concluded that equilibrium constants *K* and NMR chemical shift changes correlate in a qualitative way. Quantitative correlations cannot really be expected since the structural changes in the series of arenes studied preclude this. Still, this correlation is a very characteristic property of these complexes.

More quantitative comparisons are available if we look carefully at the shifts for *ortho*, *meta*, and *para* protons. For example, consider the NMR data for **3**. Large

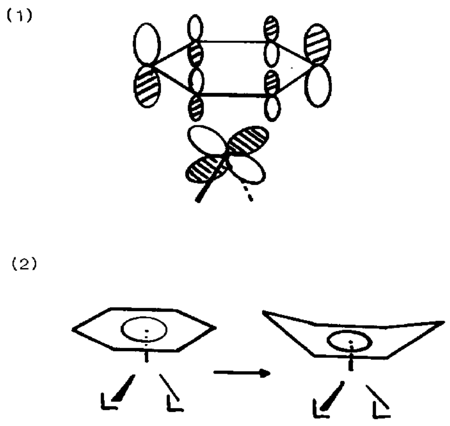


Fig. 3. The effect of antibonding interactions: (1) Antibonding orbital interactions between benzene b_1 orbital and NiL_2 fragment b_1 orbital; (2) resulting ring deformation.

shifts for *ortho* and *meta* protons were observed while that of *para* was relatively small. Thus, for free biphenyl the chemical shifts of *ortho, meta*, and *para* are 7.43, 7.58 and 7.30 ppm, respectively. But for the complexed biphenyl, the corresponding shifts are 6.90, 7.02, and 7.43 ppm. Note that *ortho* and *meta* shifted substantially upfield, while *para* shifted a small amount downfield.

Radonovich and Albright have constructed an MO energy diagram for benzene and the NiR_2 fragment [11,12,13]. From this model, it can be seen that there are three bonding orbitals in the benzene MO, which interact with the matching NiR_2 orbitals, $1a_1$, b_1, and b_2. The b_2 bonding MO of benzene is made up of $2p_z$ orbitals of C(2) and C(3) carbons which have a strong bonding interaction with the NiR_2 b_2 orbital, and the benzene b_1 orbital has bonding and antibonding interaction with the NiR_2 orbital and the resulting orbitals are filled. To reduce the antibonding interaction, the "*para*" carbons in benzene are bent away from the plane of the ring as shown in Fig. 3 [11]. Considering this, we might expect different NMR behavior of the *para* proton vs. the *ortho* and *meta* (if they could be labeled or distinguished from one another). In fact, the NMR data fit nicely with this concept when considering the biphenyl ligand. The data show the same trends for other ligands possessing *ortho*, and *para* protons, e.g. diphenylmethane and 1,2-diphenylethane.

Perhaps one might even expect the benzene complex itself to display this unusual NMR behavior. We did obtain the spectrum of (benzene)$Ni(SiCl_3)_2$, but only a singlet for the ^1H NMR of the complexed ring was observed. We assume that this is due to a low barrier for rotation.

Experimental

Materials

All chemicals, biphenyl, diphenylmethane, 1,2-diphenylethane, 4,4′-paracyclophane, naphthalene, and anthracene were purchased from Aldrich Chemical Co., and used without further purification. (η^6-toluene)$Ni(SiCl_3)_2$ was prepared as described earlier [3]. Toluene, pentane, and methylene chloride were dried by refluxing over CaH_2 under a nitrogen atmosphere. Diethyl ether was dried over benzophenone-sodium ketyl.

Table 2

Physical and Spectral Data for Complexes Prepared

	M.p. (°C)	IR (cm^{-1})	Analyses (Found (calcd.)(%))		
			C	H	Cl
3	153–157	470s,500m,540s,605w 690m,720w,730w,750m, 810m,910w,930w,980w, 1010w,1070w,1150w,1295w	28.84 (29.91)	2.22 (2.09)	43.29 (44.15)
4	131–150	470s,500m,540s,550s, 615w,720w,740w,820s, 840w,870s,910m,980w, 1010w,1040m,1070w,1310w, 1490s,3100w	not obtained		
5	135–137	470s,480s,495s,503s, 520s,535s,542s,610w, 708m,720w,747m,798m, 818w,900w,940w,1028m, 1073m,1425m	not obtained		
6	150–165	475s,508m,535s,545s, 695w,720w,740w,810m, 950m,1200m,1255m	not obtained		
7	185–190	470s,530s,550s,610w, 690w,720m,810w,900m, 1150w,1240w,1380m, 1430w,1490m,3025w	35.78 (35.80)	3.23 (3.00)	38.15 (39.69)
8	130–140	470s,490m,517m,530m, 590w,620w,720w,750m, 760w,780m,800w,840s, 920m,980m,1010w,1220w, 1230w,1260m	25.68 (26.35)	1.90 (1.77)	46.76 (46.67)

Apparatus and measurements

Most experiments were performed under nitrogen using typical Schlenk techniques. When necessary a vacuum atmospheres inert atmosphere glove box was used. The reaction products were examined mainly by NMR since the products showed characteristic NMR peaks. The NMR spectra were taken on a Bruker 400 multinuclear FT NMR Spectrometer. The IR spectra were taken on a Perkin–Elmer IR 1330 Spectrophotometer. The melting points were measured by using a Thomas Hoover capillary melting point apparatus. The elemental analyses were performed by Galbraith Laboratories, Inc., and equilibrium constants were calculated based on ^{1}H NMR peak areas.

Reactions

Preparation of (η^6-biphenyl)bis(trichlorosilyl)nickel(II) (3). Into a 200 ml Schlenk tube, 0.462 g (3 mmol) of biphenyl and 0.420 g (1 mmol) of (η^6-toluene)Ni($SiCl_3$)$_2$ (**1**) and 30 ml methylene chloride were added through a fine filter frit in the glove box. The resulting solution was red brown in color. After taking the Schlenk tube from the glove box, the solution was stirred for 20 min. Then the solvent was pumped off leaving a light brown solid. To this solid 30 ml of methylene chloride was added and the solid redissolved. After 5 min stirring the solvent was pumped off again and this process repeated twice for complete displacement of toluene by biphenyl. To the remaining light brown solid, 10 ml of methylene chloride was added and to the resulting red brown solution, 50 ml of pentane was added. By addition of pentane to the red brown solution, an orange brown solid was precipitated. The solution was filtered and the precipitate washed with another 50 ml pentane. Then the precipitate was redissolved with 20 ml methylene chloride and the resulting solution was filtered through a fine filter frit. After the solvent was evaporated 0.411 g of gold orange solid was left. Yield was 85%. The data for melting point NMR, IR, and elemental analyses are tabulated in Tables 1 and 2.

Preparation of (η^6-diphenylmethane)bis(trichlorosilyl)nickel(II) (5). Into a 200 ml Schlenk tube, 0.420 g (1 mmol) of (η^6-toluene)Ni($SiCl_3$)$_2$ and 30 ml of methylene chloride were added through a fine filter frit. To the resulting red brown solution, 0.5 ml (3 mmol) of diphenylmethane was added. The color of the solution became orange brown. After 20 min stirring, the solvent was pumped off. In the Schlenk tube some orange brown very viscous liquid remained. Then 20 ml of methylene chloride was added and stirred for 20 min, and the solvent was pumped off again. This process was repeated twice and then 10 ml of methylene chloride was added. To the resulting orange brown solution, 50 ml of pentane was added, causing precipitation of an orange solid. After the solution was filtered the remaining solid was washed with another 50 ml of pentane. Then the solid was redissolved with 20 ml of methylene chloride and the resulting orange solution was filtered through a fine filter frit. After drying the solvent 0.40 g of pale orange solid was left. Yield was 78%. See Tables 1 and 2.

Preparation of (η^6-bibenzyl)bis(trichlorosilyl)nickel(II) (6). The reaction procedure was similar with that for complex (3). Here we used 0.546 g (3 mmol) of 1,2-diphenylethane instead of biphenyl. Following the same procedure, 0.385 g of yellow orange product was obtained. Yield was 75%. See Tables 1 and 2.

Preparation of (η^6,4,4′-dimethylbiphenyl)bis(trichlorosilyl)nickel(II) (4). Using 0.182 g (1 mmol) of 4,4′-dimethylbiphenyl and 0.420 g (1.0 mmol) of (η^6-toluene)Ni($SiCl_3$)$_2$, and following the same procedure mentioned above, 0.425 g of orange brown solid was obtained. Yield 83%. See Tables 1 and 2.

Preparation of (η^6,4,4′-paracyclophane)bis(trichlorosilyl)nickel(II) (7). Using 0.210 g (1.0 mmol) of 4,4′-paracyclophane and 0.420 g (1.0 mmol) of (η^6-toluene)Ni($SiCl_3$)$_2$ following the same procedure as above, 0.487 g of pale orange solid was obtained. Yield 91%. See Tables 1 and 2.

Preparation of (η^6-naphthalene)bis(trichlorosilyl)nickel(II) (8). Into a 200 ml Schlenk tube, 0.532 g (4.0 mmol) of naphthalene and 30 ml pentane were added. The solution was degassed by freeze/thaw cycles. To the frozen solution 0.73 g (4.3 mmol) of bis(methylallyl)nickel was added by vacuum transfer and the mixture was allowed to warm. After the solution was melted all the bis(methylallyl)nickel was dissolved by shaking the Schlenk tube. The resulting homogeneous yellow solution was frozen again and to this solution 1.0 ml (5 mmol) of $HSiCl_3$ was added by vacuum transfer. The frozen mixture was placed in an isopropyl alcohol cold bath set at −40 °C. After the mixture was melted, it was stirred for 1 h, then the solution was allowed to reach room temperature without stirring. During this time some dark brown solid precipitated. After the solution was warmed to room temperature, it was filtered and the solid was redissolved in 20 ml of methylene chloride. The solution became red brown. Again, the solvent was pumped off and the resulting red brown solid redissolved in 5 ml of methylene chloride. To this solution 50 ml of pentane was added, causing a rust colored solid to precipitate. After the solvent was decanted and dried, 0.472 g of solid was left. Yield 25%. See Tables 1 and 2.

Preparation of (η^6-anthracene)bis(trichlorosilyl)nickel(II) (9). Using 0.178 g (1.0 mmol) of anthracene, 0.540 g (3.0 mmol) of bis(methylallyl)nickel and 1.0 ml (6.0 mmol) of $HSiCl_3$, and following the same procedure as above, an orange brown solid was obtained. Because of the difficulty in purification of the product only an NMR spectrum was obtained. See Table 1.

Preparation of samples for measurement of K

For these experiments the sample were prepared by the following procedure, using diphenylmethane as an example. In a 5 ml glass vial, 42 mg (0.1 mmol) of (η^6-toluene)$Ni(SiCl_3)_2$ was added and dissolved in 2.0 ml of $CDCl_3$. In another 5 ml glass vial, 18 mg (0.1 mmol) of diphenylmethane was added and dissolved in 2.0 ml of $CDCl_3$. To three other 2 ml glass vials were transferred 0.3, 0.5, and 0.7 ml of nickel complex solution prepared above, and to these three samples 0.7, 0.5, and 0.3 ml of diphenylmethane solution was added to make the total volume of each 1.0 ml. From these vials 0.6 ml of each solution was used for NMR analysis.

Measurement of equilbrium constants

For preliminary tests, we examine the relative intensities of the NMR peaks at 15, 30 and 45 min after the samples were mixed. In all cases there were no changes of relative intensities of peaks detected, which indicates that the equilibria were reached within 15 min. For each arene, two or three different samples were used to measure the constants. The concentration of each component was measured in arbitrary units and the *K* value was taken as an average of the measurements.

Acknowledgement

The support of the National Science Foundation is acknowledged with gratitude.

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