A route to thermally stable organonickel(II) complexes containing two C_{sp3}-Ni(II) bonds

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Dedicated to Professor Albert Padwa on the occasion of his 65th birthday (received 19 Mar 02; accepted 27 Jun 02; published on the web 05 Jul 02)

Abstract

The synthesis of an air- and thermally stable organonickel(II) complex possessing two C_{sp3} -Ni(II) bonds is reported. The NMR spectral data suggest that the carbanionic center in the complex carries a larger negative charge and reduced structural ring strain than the related Pd(II) and Pt(II) analogs.

Keywords: Carbon-metal bond, organometallic, bipyridine,P d(II)-complex, Pt(II)-complex, Ni(II)-complex

Introduction

We have been interested in the synthesis of stable organo-Pd(II) complexes ¹⁻³ possessing *cis*, *bis*-C_{sp3}-metal bonds,⁴⁻¹⁰ as potential anti-tumor agents¹¹ and catalysts.¹² This series has subsequently been expanded to include the corresponding platinum(II) counterparts.¹³⁻¹⁷ The similarities and differences between these complexes have led us to investigate the related Ni(II) members in order to determine the structural and chemical relationships within this triad family. Few meaningful series of organometallic complexes involving a complete triad have been reported;¹⁸⁻²¹ thus, this nickel complex would afford insight into potential relationships. To this end, we report herein the synthesis of the air- and thermally stable organonickel(II) complex **3a** containing two *cis*-C_{sp3}–Ni bonds, which are in contrast to the more common sp²-hybrids.²²⁻²⁴ These stable complexes also possess β -hydrogens, which when present, usually lead to facile elimination reactions.²⁵ Lastly, in general, organonickel(II) complexes are not noted for their thermal stability; in fact, the main interest relates to their ability to generate organic radicals, an artifact of their inherent instability.²⁶⁻²⁸

Results and Discussion

The insolubility of most nickel salts in organic solvents prevents the use of our normal procedure for Pd(II)-complex formation,⁴ since the one-pot mixture of ligand-soluble metal salt (*e.g.*, NiCl₂·6H₂O or NiBr₂), and K₂CO₃ in MeCN led to the quantitative precipitation of nickel carbonate. The methodology used in the synthesis of Pt(II) complexes⁵ seemed more amenable for entrée into the organonickel series. Addition of anhydrous NiBr₂ to bipyridine ligand **1** (Scheme 1) in either CH₂Cl₂ of CHCl₃ afforded (*ca.* 60 %) the initial *N,N*-complex **2a**, which could also be synthesized by refluxing a solution of anhydrous NiBr₂ and **1** in dry THF under argon for 18 h. This homogeneous procedure was cleaner and the work-up was easier than for our more traditional heterogeneous method.

An interesting feature of complex 2a is that the NMR spectra are nearly superimposable with that of the free ligand; however, its elemental analysis, visible purple chromophore, and X-ray crystallographic data ²⁹ support the assignment. Although its ¹H NMR spectrum was identical to that of the ligand, its ¹³C NMR showed a –2.9 ppm shift for *C*-2 while the remaining shift differences were in the –1.4 to –0.8 ppm range. The rationale for the minor shifts in the NMR data became apparent on the basis of its X-ray analysis,²⁹ in which the *N*,*N*-coordinated complex is tetrahedral; thus along with the lack of steric interactions, present in the square planar Pt(II) and Pd(II) analogs, the electronics of Ni(II) in this geometry are very comparable to Zn(II) in that it is effectively neutral.



Scheme 1. For Ni cyclometallation: (a) anhydrous NiBr₂, CH₂Cl₂, 25 °C; (b) *tert*-BuOK, anhydrous THF, 0 °C.

Despite the tetrahedral geometry of **2a** in the solid state, sufficient distortion must occur due to the electron pairing in solution,³⁰ since no evidence for paramagnetism was found in the NMR data.³¹ The geometry in **2a** is typical of such complexes,^{32, 33} in which Ni-N bond lengths of 1.981(4) and 2.004(4)Å and Ni-Br bond lengths of 2.336(1) and 2.322(1)Å are observed along with an 85° dihedral angle between the NiN₂ plane and the NiBr₂ planes. The Ni lies 0.154Å out of the least-squares plane of the bipyridine sub-unit and the two Br atoms lie 1.475 and 2.417Å above and below the plane, respectively. A more detailed presentation of the structural features of **2a** appears elsewhere.²⁹

Cyclometallation of 2a was difficult due to the ease of Ni(II) extraction. Use of various carbonates (*e.g.*, K or Cs) in different solvents led to the same result, quantitative recovery of the free ligand and the formation of NiCO₃. The first success was attained using 50% NaH and 2a in anhydrous THF at reflux for 4-6 h under argon; however, the yields of the desired product 3a were variable and the work-ups difficult. Thus, treatment of 2a with a slight excess (1.05 equiv.) of *tert*-BuOK in dry THF at 0 °C under argon caused an immediate color change (light purple to yellow) and the formation of the stable yellow microcrystalline 3a, whose ¹H NMR spectrum paralleled that of the Pd(II) and Pt(II) analogs, 3b and 3c, respectively.

In the ¹H NMR data (Table 1), *H*-5 showed a slight upfield shift (+0.06 ppm), while *H*-3 shifted downfield (-0.90 ppm) owing to conformational changes from the *anti* (ligand) to the *syn* (complex), and metal coordination. A shift of +0.07 ppm for *H*-4 was the smallest within the series (*cf*.: +0.20 for **3b** and +0.27 for **3c**). For **3a**, the alkyl portion was also supportive of cyclization, as indicated by a +0.35 ppm shift for the CH_2 moieties demonstrating that the 5.5.5-fused ring system is better suited to the smaller transition metal (*i.e.*, Ni) when compared to the +0.52 ppm shift for **3b** and **3c**. The ¹³C NMR spectrum for **3a** further verified the more efficient "fit" of the Ni(II) into this core since the CH_2 shift was +5.5 *vs*. +12.2 for **3b** and +14.2 ppm for **3c**. Shifts experienced with this signal have been mainly attributed to ring strain.¹⁵ Ligand-to-metal donation is supported by the upfield shift of *H*-4 in the ¹H NMR spectrum and the upfield shift (+2.6 ppm) for *C*-4 in the ¹³C NMR spectrum. The location of the ¹³C NMR signal (45.0 ppm) for the metallated carbon in **3a** indicated an increased electron density at the carbanionic centers compared to that of 47.4 for **3b** and 49.0 for **3c** ppm; these results were not surprising in view of the decreased electronegativity of Ni(II) as compared to Pd(II) and Pt(II).

Cpd.	Н-3	<i>H</i> -4	<i>H</i> -5	CH_2	CH	<i>C</i> -2	<i>C</i> -4	<i>C</i> -6	CH_2	C/CH
1	8.25d	7.69t	7.16d	3.50d	4.29t	156.6	136.8	155.0	35.8	50.4
2a	8.25d	7.68t	7.16d	3.50d	4.42t	153.7	135.8	155.1	34.3	48.7
2b	8.28dd	7.90t	7.24dd	4.12d	4.51t	157.1	140.9	164.8	36.9	52.0
2c	8.19d	8.01 ^a	7.21d	4.20d	4.57t					
3 a	7.35d	7.76t	7.22d	3.85s			139.4		41.3	45.0
3b	7.62d	7.89t	7.50d	4.02s		152.5	138.6	169.6	48.0	47.4
3c	7.53dd	7.96 ^a	7.44dd	4.00 ^b			137.6		50.0	49.0

 Table 1. ¹H/¹³C NMR Data for Ligand 1 and Complexes 2 and 3

Due to ¹⁹⁵Pt couplings: (a) Triplet/sextet. (b) Singlet/doublet.

Complex **3a** not only provides entrance into air- and thermally stable organonickel(II) complexes containing two C_{sp3} -Ni bonds, but also completes a series of complexes of the nickel triad, thus allowing comparisons of their respective chemical and spectral properties. The use of **3a** in potential anti-tumor activity is being explored.

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Experimental Section

General Procedures. Melting points were determined with an Electrothermal 9100 instrument and are uncorrected. ¹H- and ¹³C- NMR spectra were recorded on a Bruker DPX250 spectrometer using CDCl₃, except where noted. IR spectra were recorded on an ATI Matheson Genesis FTIR spectrophotometer. Absorption spectra were measured on a Hewlett Packard 8452A Diode Array spectrophotometer in MeCN solution at 25 °C.

Dibromo[dimethyl-*a*,*a*'-*bis*(methoxycarbonyl)(2,2'-dipyridine)-6,6'-di(propionate)]nickel(II) (2a). A solution of the bipyridinyl ligand ⁵ **1** in anhydrous CH_2Cl_2 was slurried with anhydrous $NiBr_2$ (1.05 equiv.) at 25 °C for at least 24 h. Filtration of the purplish-pink slurry, followed by concentration *in vacuo* gave the crude *N*,*N*-complex, which was chromatographed (SiO₂) eluting with CH_2Cl_2 , then 1% MeOH/CH₂Cl₂, followed by recrystallization (C₆H₆) to afford (60%) **2a**, as purple crystals: ²⁹ m.p. 183–185 °C (dec.); for NMR data, see Table. *Anal.* Calcd. for $C_{22}H_{24}N_2O_8NiBr_2\cdot0.5$ H₂O: C, 42.77; H, 3.88; N, 3.99. Found: C, 42.65; H, 4.01; N, 3.89.

[2,2'-Dipyridine]-6,6'-diyl-*bis*-[1,1-*bis*-(methoxycarbonyl)-2,1-ethanediyl]-*C*, *C'*, *N*, *N'*-nickel(II) (3a). An anhydrous THF solution of complex 2a was treated with *tert*-BuOK (2.05 eq.) at 0 °C under argon for 3 h. The resultant yellow solution was concentrated *in vacuo* then chromatographed (SiO₂), eluting with 10% MeOH/CH₂Cl₂ to give (83%) 3a, as yellow microcrystals: m.p. 137–140 °C (dec.); NMR data see the Table. Anal. Calcd for $C_{22}H_{22}N_2O_8Ni$: C, 52.73; H, 4.42; N, 5.59. Found: C, 52.75; H, 4.36; N, 5.63.

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