

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

George R. Newkome* and David W. Evans#

*Departments of Polymer Science and Chemistry, The University of Akron, Akron, Ohio 44325

#Chemistry Department, Presbyterian College, Clinton, SC 29325

E-mail: newkome@uakron.edu

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, Pd(II)-complex, Pt(II)-complex, Ni(II)-complex

Introduction

We have been interested in the synthesis of stable organo-Pd(II) complexes¹⁻³ 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

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 CH₂ 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 CH₂ 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).

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

Cpd.	<i>H</i> -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	<i>C</i> /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	----	----	----	----	----
3a	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

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.

Acknowledgments

We wish to thank the National Science Foundation and the Louisiana State University Center for Energy Studies.

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- α,α' -bis(methoxycarbonyl)(2,2'-dipyridine)-6,6'-di(propionate)]nickel(II) (2a). A solution of the bipyridinyl ligand ⁵ **1** in anhydrous CH₂Cl₂ was slurried with anhydrous NiBr₂ (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 CH₂Cl₂, 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 C₂₂H₂₄N₂O₈NiBr₂·0.5 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 C₂₂H₂₂N₂O₈Ni: C, 52.73; H, 4.42; N, 5.59. Found: C, 52.75; H, 4.36; N, 5.63.

References

1. Newkome, G. R.; Evans, D. W.; Fronczek, F. R. *Inorg. Chem.* **1987**, *26*, 3500.
2. Newkome, G. R.; Evans, D. W. *Organometallics* **1987**, *6*, 2592.
3. Yoneda, A.; Newkome, G. R.; Theriot, K. J. *J. Organomet. Chem.* **1991**, *401*, 217.

4. Newkome, G. R.; Puckett, W. E.; Kiefer, G. E.; Gupta, V. K.; Fronczek, F. R.; Pantaleo, D. C.; McClure, G. L.; Simpson, J. B.; Deutsch, W. A. *Inorg. Chem.* **1985**, *24*, 8116.
5. Newkome, G. R.; Evans, D. W.; Kiefer, G. E.; Theriot, K. J. *Organometallics* **1988**, *7*, 2537.
6. Yoneda, A.; Newkome, G. R.; Morimoto, Y.; Higuchi, Y.; Yasuoka, N. *Acta Cryst. C* **1993**, *49*, 476.
7. Yoneda, A.; Ouchi, M.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Chem. Lett.* **1993**, 709.
8. Billodeaux, D. R.; Fronczek, F. R.; Yoneda, A.; Newkome, G. R. *Acta Cryst. C* **1998**, *54*, 1439.
9. Yoneda, A.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Organometallics* **1994**, *13*, 4912.
10. Ohfuchi, S.; Kitamura, C.; Maekawa, Y.; Newkome, G. R.; Yoneda, A. *Nippon Kagaku Kaishi* **1999**, 151.
11. Newkome, G. R. U.S. Pat. 4,598,073. 1986. Baton Rouge, LA.
12. Newkome, G. R.; Gupta, V. K. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 609.
13. Newkome, G. R.; Gupta, V. K.; Fronczek, F. R. *Acta Cryst. C* **1986**, *42*, 1643.
14. Evans, D. W.; Baker, G. R.; Newkome, G. R. *Coord. Chem. Rev.* **1989**, *93*, 155.
15. Newkome, G. R.; Theriot, K. J.; Fronczek, F. R.; Villar, B. *Organometallics* **1989**, *8*, 2513.
16. Yoneda, A.; Newkome, G. R.; Morimoto, Y.; Ohfuchi, S.; Yasioka, N. *Anal. Sci.* **1997**, *13*, 877.
17. Ohfuchi, S.; Kitamura, C.; Newkome, G. R.; Yoneda, A. *Nippon Kagaku Kaishi* **2002**, in press.
18. Longoni, G.; Fantucci, P.; Canziani, F. *J. Organomet. Chem.* **1972**, *39*, 413.
19. Longoni, G.; Chini, P.; Canziani, F.; Fantucci, P. *Gazz. Chim. Ital.* **1974**, *104*, 249.
20. Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285.
21. Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, M. W.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 1379.
22. Hipler, B.; Uhlig, E.; Vogel, J. *J. Organomet. Chem.* **1981**, *218*, C1.
23. Rimmi, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C9.
24. Jacob, V. K.; Pietzner, E.; Vastag, S.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1977**, *432*, 187.
25. Jolly, P. W.; Wilke, G. In *Organometallic Chemistry Series: The Organic Chemistry of Nickel, Vol. I: Organonickel Complexes*; Academic Press: New York, 1974.
26. Hayashi, T.; Konishi, M.; Yokota, K.-I.; Kumada, M. *J. Organomet. Chem.* **1985**, *285*, 359.
27. Chiusoli, G. P. *J. Organomet. Chem.* **1986**, *300*, 57.
28. Yamamoto, A. *J. Organomet. Chem.* **1986**, *300*, 347.
29. Evans, D. W.; Newkome, G. R.; Fronczek, F. R. *Acta Cryst. C* **1990**, *46*, 490.
30. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*; 4th Edn; Wiley-Interscience: New York, 1980.
31. La Mar, G. N.; Horrocks, W. D.; Holm, R. H. *NMR of Paramagnetic Molecules: Principles and Applications*; Academic Press: New York, 1973.

32. Butcher, R. J.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 2334.
33. Dinjus, E.; Goerls, H.; Uhlig, E.; Walther, D. *J. Organomet. Chem.* **1984**, 276, 257.