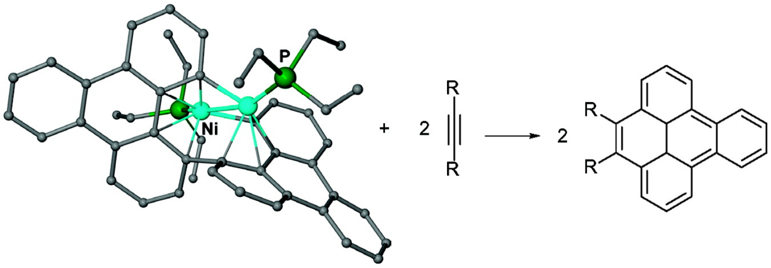
ORGANOMETALLICS

Communication

Carbon–Carbon Bond Formation and Cleavage in the Dimerization of a Nickelacycle

T. V. V. Ramakrishna, and Paul R. Sharp

Organometallics, **2004**, 23 (13), 3079-3081 • DOI: 10.1021/om0497590



Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

ORGANOMETALLICS

Volume 23, Number 13, June 21, 2004

Communications

Carbon−Carbon Bond Formation and Cleavage in the Dimerization of a Nickelacycle

T. V. V. Ramakrishna and Paul R. Sharp*

125 Chemistry, University of Missouri−Columbia, Columbia, Missouri 65211

Received April 2, 2004

Summary: Addition of 1,12-dilithiotriphenylenediyl to L_2NiCl_2 *(L =* PEt_3*) gives the nickelacycle* L_2Ni*(1,12-triphenylenediyl), which decomposes to a dimer (*$L_2Ni_2C_{36}H_{20}$*) containing two coupled triphenylene moieties with a new C−C bond. Thermolysis of the dimer completes the coupling, yielding a chiral tetraphenylene, while alkyne addition leads to cleavage of the newly formed C−C bond of the dimer and cycloaddition of the alkyne to the triphenylene fragment.*

Nickel has long been known to be an active metal in C−C bond-making and -breaking reactions.[1] Pioneering work by Eisch[2−6] and Hoberg[7−11] has shown that nickelacycles can be important species in these reactions, and nickelacycles have continued to attract attention in bond-making and -breaking processes.[12−17] Our group is interested in expanding nickelacycle and other metallacycle chemistry into polycyclic aromatic systems in order to develop new syntheses and derivatization procedures for polycyclic aromatic carbon compounds.[18−20] The ready availability of 1,12-dilithiotriphenylenediyl (**1**) by double deprotonation of triphenylene with *n*-butyllithium/tmeda[21] allows easy access to triphenylene metallacycle chemistry. We report here the nickelacycle chemistry of the triphenylene system involving C−C bond formation through nickelacycle dimerization and following dimer reaction chemistry that results in retention or cleavage of the newly formed carbon−carbon bond.

Treatment of L_2NiCl_2 (L = PEt_3) with 1 equiv of **1** at 0 °C followed by warming to room temperature gives a brown solution from which brown crystals are isolated (Scheme 1). Spectroscopic data (Supporting Information)

---

* To whom correspondence should be addressed. E-mail: sharpp@missouri.edu.

(1) Jolly, P. W. *The Organic Chemistry of Nickel*; Academic Press: New York, 1975.

(2) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1975**, *96*, C23−C26.

(3) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224−231.

(4) Eisch, J. J.; Piotrowski, A. M.; Aradi, A. A.; Krueger, C.; Romao, M. J. *Z. Naturforsch., B* **1985**, *40B*, 624−635.

(5) Eisch, J. J.; Galle, J. E.; Aradi, A. A.; Boleslawski, M. P. *J. Organomet. Chem.* **1986**, *312*, 399−416.

(6) Reference deleted on revision.

(7) Hoberg, H.; Herrera, A. *Angew. Chem.* **1980**, *92*, 951−952.

(8) Hoberg, H.; Richter, W. *J. Organomet. Chem.* **1980**, *195*, 355−362.

(9) Herrera, A.; Hoberg, H.; Mynott, R. *J. Organomet. Chem.* **1981**, *222*, 331−336.

(10) Hoberg, H.; Schaefer, D. *J. Organomet. Chem.* **1982**, *238*, 383−387.

(11) Hoberg, H.; Schaefer, D. *J. Organomet. Chem.* **1982**, *236*, C28−C30.

(12) Campora, J.; Palma, P.; Carmona, E. *Coord. Chem. Rev.* **1999**, *195*, 207−281.

(13) Bennett, M. A.; Kopp, M. R.; Wenger, E.; Willis, A. C. *J. Organomet. Chem.* **2003**, *667*, 8−15.

(14) Campora, J.; Lopez, J. A.; Maya, C.; Palma, P.; Carmona, E.; Valerga, P. *J. Organomet. Chem.* **2002**, *643−644*, 331−341.

(15) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Simhai, N.; Iverson, C. N.; Muller, C.; Satoh, T.; Jones, W. D. *J. Mol. Catal. A* **2002**, *189*, 157−168.

(16) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1975−1981.

(17) Koo, K.; Hillhouse, G. L. *Organometallics* **1998**, *17*, 2924−2925.

(18) Sharp, P. R. *J. Organomet. Chem.* **2003**, *683*, 288−294.

(19) Brown, J. S.; Sharp, P. R. *Organometallics* **2003**, *22*, 3604−3607.

(20) Begum, R. A.; Ramakrishna, T. V. V.; Sharp, P. R. Submitted for publication in *J. Am. Chem. Soc.*

10.1021/om0497590 CCC: $27.50 © 2004 American Chemical Society
Publication on Web 05/20/2004

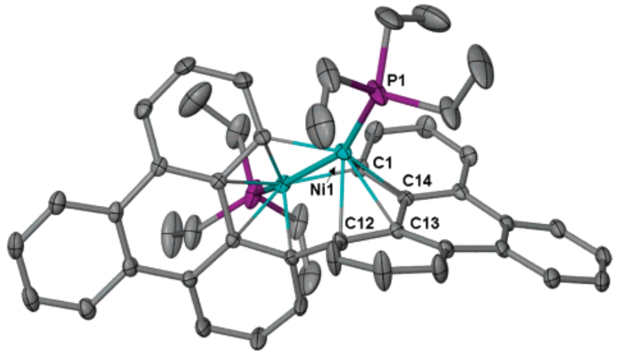
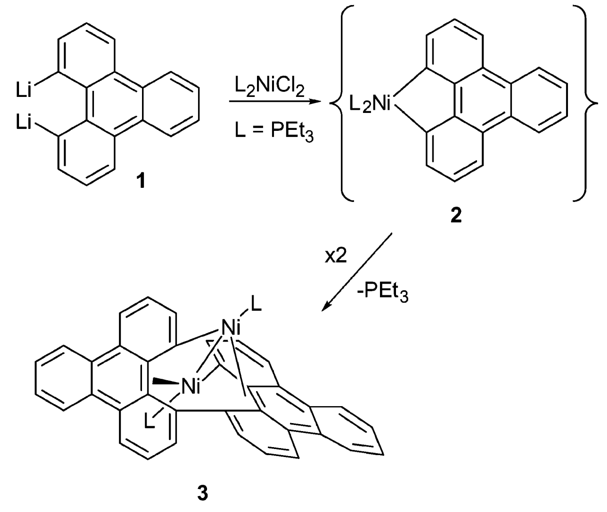
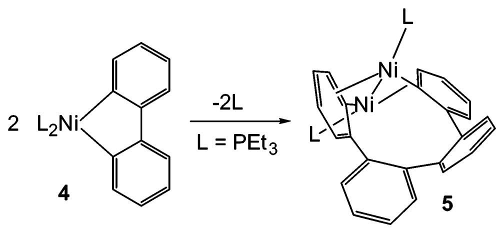


Figure 1. Drawing of **3** (30% probability ellipsoids). Primed and unprimed atoms are related by a 2-fold axis bisecting the Ni−Ni′ and C12−C12′ bonds. Selected distances (Å) and angles (deg): Ni1−Ni1′ = 2.3524(8), Ni1−C1 = 1.929(3), Ni1′−C1 = 2.055(3), Ni1−C12 = 2.118(3), Ni1−C13 = 2.234(3), Ni1−C14 = 2.300(3), C1−C14 = 1.452(5), C14−C13 = 1.461(4), C13−C12 = 1.441(4), C12−C12′ = 1.496(6), Ni1−P1 = 2.2034(11); C1−Ni1−C1′ = 102.88(13), Ni1−C1−Ni1′ = 72.31(11), Ni1−Ni1′−P1 = 157.84(4), C1−Ni1′−P1′ = 103.80(10), C1−Ni1−P1 = 137.35(10).

Scheme 1

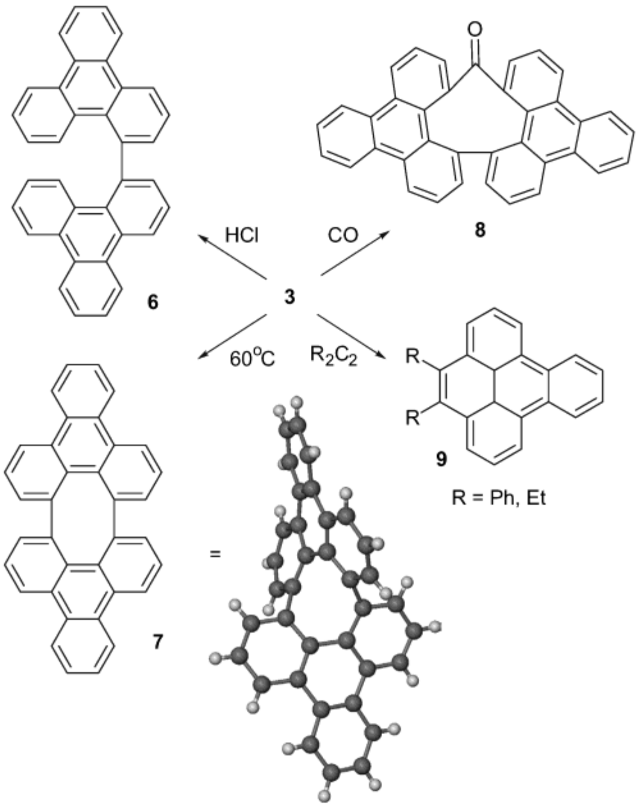


and single-crystal X-ray crystallography[22] reveal the brown complex to be the dimer **3** (Figure 1) and not the anticipated mononuclear nickelacycle L_2Ni(1,12-triphenylenediyl) (**2**). Although no significant color change is observed on warming the reaction mixture from 0 °C to room temperature, NMR spectroscopic monitoring of the brown reaction mixture reveals the initial formation of **2** as an intermediate that decomposes with PEt_3 loss to give brown **3** (Scheme 1). A similar dimerization of brown L_2Ni(2,2′-biphenyldiyl) (**4**) to the green dimer **5** was reported by Eisch (eq 1).[3] Dimer **5** displays some remarkable reaction chemistry, and we were interested in comparing this reaction chemistry with that of the triphenylene dimer **3**.



(1)

Scheme 2



The reaction chemistry for **3** is shown in Scheme 2 and is similar to that reported for the biphenylene dimer **5**, except for two important features. First, the tetraphenylene derivative **7**, produced in a second carbon−carbon bond-forming step on heating **3**, is chiral, as compared to the achiral tetraphenylene obtained from the biphenylene dimer **5**. Compound **7** has been characterized by single-crystal X-ray crystallography[22] and, though of poor quality, establishes the presence of the two enantiomers in the crystal. One of the enantiomers is depicted in Scheme 2. Chiral tetraphenylenes are of interest in chiral recognition and materials chemistry.[23−26] Tetraphenylene synthesis commonly utilizes ill-defined copper(II) coupling chemistry, multistep procedures, or metal-catalyzed biphenylene coupling.[24,27−30] The second feature is the reaction of **3** with alkynes. The biphenylene dimer **5** does not react with alkynes, whereas **3** readily gives the 4,5-disubstituted benzo[*e*]pyrenes **9** (R

---

(21) Ashe, A. J., III; Kampf, J. W.; Savla, P. M. *J. Org. Chem.* **1990**, *55*, 5558−5559.

(22) X-ray crystallography: Siemens SMART CCD diffractometer (173 K), refinement on F^2 (SHELXL). Crystal data for compound **3**, $C_{48}H_{50}P_2Ni_2\cdot 0.5Et_2O$: a = 23.3813(16) Å, b = 18.2753(12) Å, c = 10.3662(7) Å, β = 104.098(1)°, monoclinic, $C2/c$, Z = 4, R1 = 0.0564. Crystal data for compound **7**, $C_{36}H_{20}$: a = 22.512(5) Å, b = 7.7037(18) Å, c = 25.655(6) Å, β = 97.591(4)°, monoclinic, $P2_1/n$, Z = 8, R1 = 0.1805. Crystal data for compound **9**, $C_{32}H_{20}$: a = 15.0121(15) Å, b = 9.7971(10) Å, c = 13.7897(13) Å, β = 95.589(2)°, monoclinic, $P2_1/c$, Z = 4, R1 = 0.0451.

(23) Freedman, T. B.; Cao, X.; Rajca, A.; Wang, H.; Nafie, L. A. *J. Phys. Chem. A* **2003**, *107*, 7692−7696.

(24) Wen, J.-F.; Hong, W.; Yuan, K.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **2003**, *68*, 8918−8931.

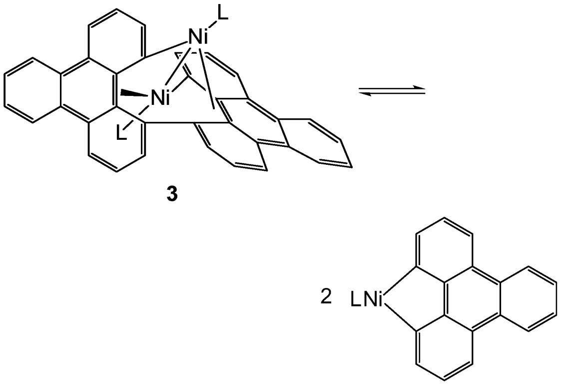
(25) Rajca, A.; Wang, H.; Bolshov, P.; Rajca, S. *Tetrahedron* **2001**, *57*, 3725−3735.

(26) Rajca, A.; Safronov, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **2000**, *122*, 3351−3357.

= Ph,[22] Et). Remarkably, these products result from carbon−carbon bond cleavage in **3** and cycloaddition of the alkyne to the triphenylene fragment.

A clue to this difference in alkyne reactivity and the C−C bond cleavage in **3** is seen in a comparison of the structures of the two dimers. The structural rigidity introduced by the added benzo groups in **3** forces a close distance of 2.118 Å between the nickel centers and the carbon atoms of the newly formed C−C bond (Ni1−C12 in Figure 1). The corresponding distance in the biphenyl dimer **5** is 3.376 Å, placing the C−C bond out of reach of the nickel centers. The close approach in **3** must activate the system to the C−C bond cleavage.

The alkyne reaction products **9** suggest the possibility of reversible carbon−carbon bond cleavage,[31] as depicted in eq 2. Nickelacycles related to **2** are known to give cycloaddition products with alkynes.[3,15,32,33] To investigate this possibility, a kinetic investigation of the PhCCPh reaction was undertaken. If the equilibrium in eq 2 is operative, than a half-order dependence on **3** should be observed. The reaction was found to be first order in alkyne and **3** (pseudo-first-order conditions of 10, 20, and 30 equiv of alkyne), eliminating the possibility of the equilibrium shown in eq 2 and indicating that the C−C bond cleavage in **3** is alkyne induced.



3

2-L

(2)

In conclusion, extension of the nickelacycle chemistry of 1,1′-biphenyldiyl to 1,12-triphenylenediyl has uncovered ligand-induced C−C bond formation reversibility in the dimerization of the nickelacycle. This new reactivity appears to result from increased rigidity in the triphenylene system, which forces nickel−carbon interactions absent in the biphenyl system. In addition, a chiral tetraphenylene is obtained from thermolysis of the triphenylene nickelacycle dimer, suggesting that this system could be useful in the enantiomeric synthesis of tetraphenylenes with potential applications in chiral recognition and materials chemistry.[23−26]

Acknowledgment. Grants from the National Science Foundation supported this work (Grant No. CHE-0101348) and provided a portion of the funds for the purchase of the NMR (Grant No. CHE 9221835) equipment.

Supporting Information Available: Text, figures, and tables giving synthetic procedures, NMR spectroscopic data, and kinetic data and crystallographic data for **3**, **7**, and **9** (R = Ph); crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0497590

---

(27) Kabir, S. M. H.; Hasegawa, M.; Kuwatani, Y.; Yoshida, M.; Matsuyama, H.; Iyoda, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 159−165.

(28) Mak, T. C. W.; Wong, H. N. C. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon Press: New York, 1996; Vol. 6, pp 351−369.

(29) Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, *382*, 191−200.

(30) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843−2853.

(31) For a recent example of reversible C−C bond cleavage at a Ni center see: Brunkan, N. M. B., Donna, M.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 3627−3641.

(32) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4660−4668.

(33) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4040−4049.