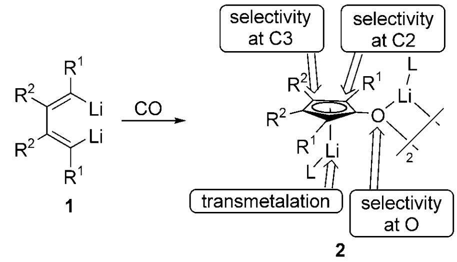
Dianion Chemistry

DOI: 10.1002/anie.200904298

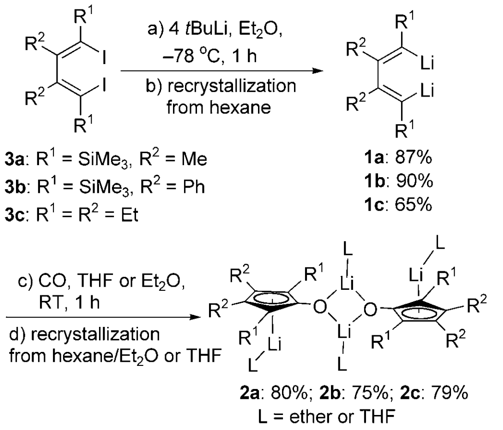
Isolation, Structural Characterization, and Synthetic Application of Oxycyclopentadienyl Dianions**

*Lantao Liu, Wen-Xiong Zhang, Chao Wang, Congyang Wang, and Zhenfeng Xi**

Cyclic dianions are considered to be useful synthons for the construction of a wide variety of cyclic organic compounds and organometallic complexes.[1–3] However, reported patterns of substituted cyclic dianions are very much limited owing to the lack of synthetic methods. Furthermore, information on the structure of dianion species is very rare, which also to some extent blocks the development of dianion synthesis and applications. The isolation of important dianion species and the investigation of their reactivity are of general interest for both organometallic chemists and synthetic organic chemists. This would not only contribute to the in-depth understanding of reaction mechanisms but could also lead to the discovery of new synthetically useful reactions. In this context, we report here the first isolation and the X-ray structure determination of a novel type of cyclic dianion, the fully substituted oxycyclopentadienyllithium compounds **2**, which were prepared by the reaction of the linear dianion **1**[1e–g] and CO (Scheme 1).[4] Because of the concomitance of the CpLi moiety, the exocyclic oxy anion, and the multiple reactive sites, these OCp dianions **2** are structurally unique and display novel reaction chemistry towards organic substrates and organometallic compounds.



Scheme 1. Generation and possible reactivity of cyclic dianions **2**.



Scheme 2. Preparation of **1** and reactions with CO leading to lithio oxycyclopentadienyl dianions **2**.

Pure crystalline compounds **1a–c** were isolated in high yield from the lithiation of the corresponding diiodides **3a–c** after filtration of LiI and recrystallization from hexane (Scheme 2). The structure of **1a** was determined by X-ray single-crystal structure analysis (see the Supporting Information).[5] Then, treatment of the isolated pure compounds **1** with CO in THF or Et_2O under mild conditions resulted quantitatively in the formation of OCp dianions **2** (Scheme 2). Recrystallization from *n*-hexane/THF or *n*-hexane/Et_2O afforded **2** in high yields as colorless (**2a**, **2c**) or yellow (**2b**) crystalline compounds.

X-ray structure analyses of single crystals of **2a** and **2b** shows that they both display centrosymmetric dimers (see Figure 1 for **2a**; see the Supporting Information for **2b**). Two Cp rings are connected through a four-membered "Li_2O_2" ring. In crystals of **2a**, for both Cp rings the distance between the lithium and the carbon atoms (Li1–(C1–C5): 2.141–2.213 Å; Li4–(C18–C22): 2.166–2.226 Å) are in quite narrow ranges, indicating that interactions between the lithium and every Cp carbon atom are nearly identical.[6] Accordingly each Cp ring is coordinated to a lithium atom in an η^5 mode. This is the first example of OCp dianions, formed conveniently from 1,4-dilithio-1,3-dienes and CO.

The concomitance of the CpLi moiety, the exocyclic oxy anion, and the multiple reactive sites (Scheme 1) makes this dianion species structurally unique, and novel reaction

---

[*] Dr. L. Liu, Prof. Dr. W.-X. Zhang, Dr. C. Wang, Dr. C. Y. Wang, Prof. Dr. Z. Xi
Beijing National Laboratory for Molecular Sciences (BNLMS)
Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education
College of Chemistry, Peking University
Beijing 100871 (China)
Fax: (+86) 10-6275-9728
E-mail: zfxi@pku.edu.cn
Dr. L. Liu
Institute of Chemistry, Chinese Academy of Sciences (China)
Prof. Dr. Z. Xi
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry, CAS (China)

[**] This work was supported by the Natural Science Foundation of China and the Major State Basic Research Development Program (2006CB806105). Qiu Shi Science & Technologies Foundation, BASF, Dow Corning Corporation, and Eli Lilly China are gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200904298.

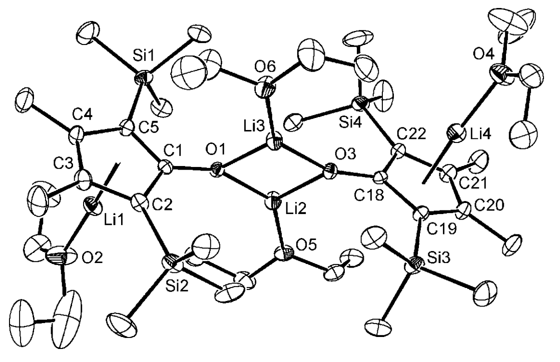
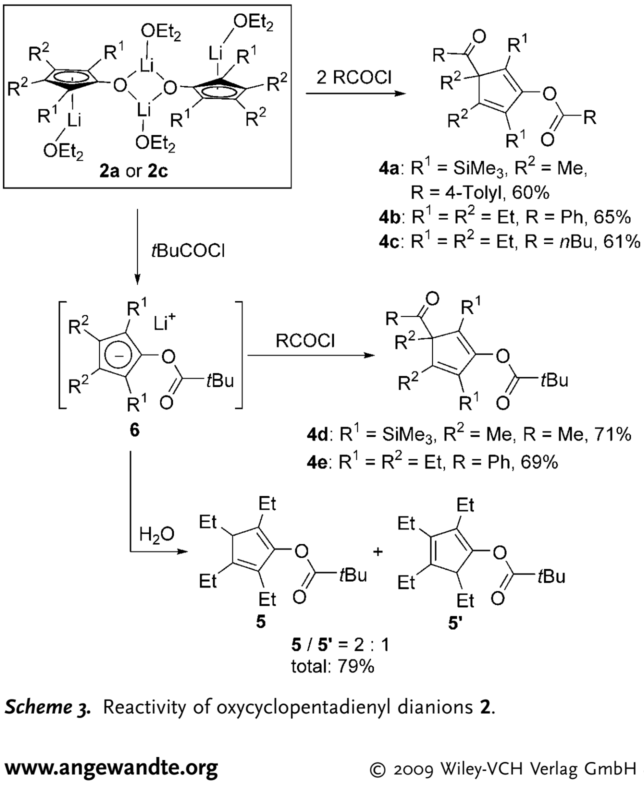


Figure 1. ORTEP drawing of **2a** (ellipsoids at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C2 1.434(3), C1–C5 1.440(3), C2–C3 1.460(4), C3–C4 1.390(4), C4–C5 1.459(3), C1–Li1 2.213(5), C2–Li1 2.174(5), C3–Li1 2.149(6), C4–Li1 2.141(6), C5–Li1 2.162(5), C18–Li4 2.226(5), C19–Li4 2.183(5), C20–Li4 2.167(6), C21–Li4 2.166(5), C22–Li4 2.190(5), C1–O1 1.347(3), O1–Li2 1.827(5), C18–O3 1.352(3), O3–Li2 1.881(5).

chemistry can be expected. Thus, after we had determined the structures of these reactive intermediates, we studied their applications for organic synthesis and transition-metal complexes.

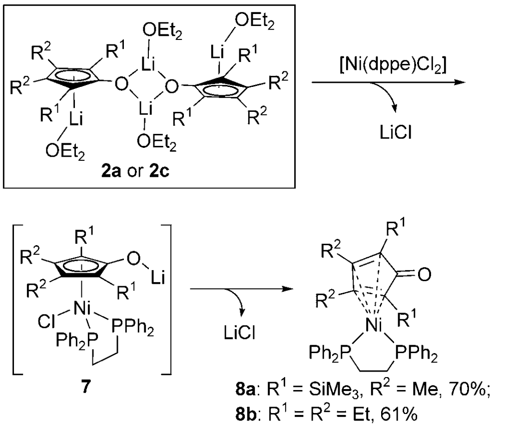
First, we investigated the reactivity of the OCp dianions **2** with acid chlorides. Obviously, there are (at least) two reactive sites in **2**, the CpLi moiety and the exocyclic OLi group. In addition, the issue of site-selectivity may arise for the CpLi moiety, specifically selectivity at C2 or C3. Chemo- and regioselectivity might thus be a crucial issue for the reaction of **2** with acid chlorides: both the Cp ring and the oxy anion may be acylated. Indeed, when **2a** or **2c** was treated with two equivalents of acid chloride, doubly acylated cyclopentadienes **4a–c** were obtained in good yields (Scheme 3).



Scheme 3. Reactivity of oxycyclopentadienyl dianions **2**.

The X-ray crystal structure of **4a** revealed that one acyl group is bonded to the oxygen atom and one is bonded to C3 of the cyclopentadiene ring (see the Supporting Information). Interestingly, when **2c** was treated with one equivalent of *t*BuCOCl and the reaction mixture was hydrolyzed, only a mixture of O-acylated products **5** and **5′** were obtained in 79% combined yield (Scheme 3); this can be explained by the steric effect of the *t*Bu group. This result indicated that, before quenching, the CpLi moiety in **6** might remain active. To test this hypothesis, we thereupon added another acid chloride to trap the proposed intermediate **6**. In fact, the mixed doubly acylated products **4d–e** were obtained as the only products in good yields (Scheme 3). These results demonstrated that the dianions **2** could be potentially applied as practical building blocks to synthesize functionalized five-membered rings. Further synthetic application of the monoacylated intermediate **6** can also be expected. It should be mentioned that when the reaction mixture of **1** with CO was treated with alkyl halides, only C2-alkylated products were obtained.[4a] The reason for this unexpected selectivity is not clear yet.

Expecting these OCp dianions **2** to serve as novel precursors and/or ligands for transition-metal complexes,[3] we next investigated their reactions with transition-metal compounds. Treatment of **2a** or **2c** with $[Ni(dppe)Cl_2]$ (dppe = 1,2-bis(diphenylphosphanylethane)) afforded the cyclopentadienone–nickel complexes **8a**,**b** in high yields (Scheme 4).



Scheme 4. Synthesis of η^4-cyclopentadieneone–nickel(0) complexes **8** from **2** and $[NiCl_2(dppe)]$.

The structures of **8a**,**b** have been identified by X-ray single-crystal structure analysis (see Figure 2 for **8a**; see the Supporting Information for **8b**). In **8a**, the cyclopentadienone ring displays alternating single and double and bonds. Meanwhile, the distance between the nickel and the carbonyl carbon atom (2.330 Å) is remarkably longer than that between the nickel and the four alkenyl carbon atoms (2.071–2.221 Å), which are all comparable with analogous data in the literature.[7] Furthermore, the ^{13}C NMR signals of the carbonyl group of **8** appear at a higher field (below 180 ppm) than those of free cyclopentadienones (over 200 ppm),[8] undoubtedly as a result of the back-donation of

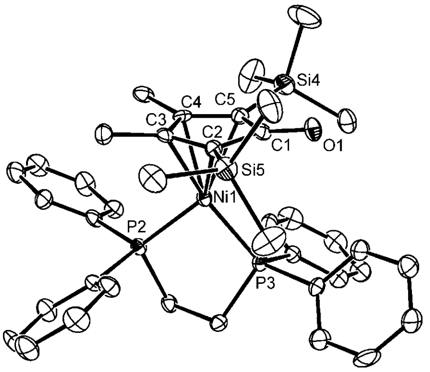


Figure 2. ORTEP drawing of **8a** (ellipsoids at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–O1 1.256(5), C1–C2 1.495(7), C1–C5 1.473(6), C2–C3 1.427(6), C3–C4 1.461(6), C4–C5 1.414(6), C1–Ni1 2.330(5), C2–Ni1 2.221(5), C3–Ni1 2.074(5), C4–Ni1 2.071(5), C5–Ni1 2.199(5), Ni1–P2 2.1515(15), Ni1–P3 2.1522(16).

electrons from Ni to the cyclopentadienone.[7a] All these results reveal that **8** is a Ni^0 complex, in which the cyclopentadienone unit acts as a neutral η^4-diene ligand.[7,9] The formation of **8** can be explained by an oxidation–reduction process of intermediate **7** with the elimination of two equivalents of LiCl. This method represents a novel reaction route of OCp dianions, which is also a promising synthetic method for cyclopentadienone–metal complexes. Moreover, the proposed intermediacy of **7** suggests that OCp dianions **2** can be utilized for the synthesis of new metallocene complexes.

In summary, the first oxycyclopentadienyl lithium compounds **2** have been isolated and structurally characterized. The application of these cyclic dianions for organic synthesis and for the preparation of organometallic complexes demonstrates their rich reaction chemistry and usefulness. Further experimental investigation and rationalization of the exclusive generation of cyclic OCp dianions from linear dilithio reagents **1** and CO, the excellent and interesting site-selectivity, and the transmetalation to afford other metal complexes are in progress.

Experimental Section

Isolation of **2**: CO was bubbled into a solution of 1,4-dilithio-1,3-butadiene **1** (1.0 mmol) in Et_2O or THF (5 mL) at −50 °C for approximately 10 min. The reaction mixture was allowed to warm to room temperature and stirred for 1 h under CO atmosphere. Solvent was removed under vacuum in a glovebox to give **2** as a powder (pure by NMR analysis). Recrystallization of **2a** from hexane/Et_2O at −30 °C affording crystals suitable for X-ray analysis. **2a**: Colorless solid, yield 80% (213 mg); ^1H NMR (300 MHz, C_6D_6): $\delta = 0.46$ (s, 18H, CH_3), 2.30 ppm (s, 6H, CH_3); ^{13}C NMR (75 MHz, C_6D_6, Me_4Si): $\delta = 3.27$ (6 CH_3), 14.07 (2 CH_3), 93.11 (br, 2 quart C), 114.12 (br, 2 quart C), 168.06 ppm (br, 1 CO).

Isolation of **8**: [Ni(dppe)Cl_2] (0.2 mmol, 105 mg) was added to a solution of the OCp dianion **2** (0.2 mmol) in THF (3 mL) at room temperature. The reaction mixture was stirred overnight. LiCl was then filtrated off and the filtrate was evaporated under vacuum to remove solvent. The resulting powder **8** was recrystallized from hexane at −30 °C to afford crystals suitable for X-ray analysis. **8a**: Dark green crystals, yield 70% (94 mg); ^1H NMR (300 MHz, C_6D_6, Me_4Si): $\delta = 0.36$ (s, 18H, CH_3), 0.38 (s, 6H, CH_3), 1.76 (m, 4H, CH_2), 7.13–7.19 (m, 12H, CH), 7.55 (t, $J = 7.8$ Hz, 4H, CH), 7.74 ppm (t, $J = 7.8$ Hz, 4H, CH); ^{13}C NMR (75 MHz, C_6D_6, Me_4Si): $\delta = 1.36$ (6 CH_3), 13.54 (2 CH_3), 29.17 (dd, $J^1 = 31.8$, 17.9 Hz, $J^2 = 29.6$, 15.0 Hz, 2 CH_2), 88.99 (2 quart C), 109.94 (2 quart C), 128.40 (d, $J_{C\text{-}P} = 9.3$ Hz, 4 CH), 128.56 (d, $J_{C\text{-}P} = 9.3$ Hz, 4 CH), 129.91 (4 CH), 133.10 (d, $J_{C\text{-}P} = 11.8$ Hz, 4 CH), 133.37 (d, $J_{C\text{-}P} = 11.8$ Hz, 4 CH), 134.69 (d, $J_{C\text{-}P} = 29.7$ Hz, 2 quart. C), 136.11 (d, $J_{C\text{-}P} = 34.0$ Hz, 2 quart. C), 179.61 ppm (br, 1 C=O).

Crystallographic data for **2a**: $C_{42}H_{88}Li_4O_6Si_4$, $M_w = 829.24\ g\,mol^{-1}$, $T = 123(2)$ K, triclinic, space group $P\bar{1}$, $a = 9.997(2)$, $b = 13.540(3)$, $c = 20.960(4)$ Å, $\alpha = 100.49(3)$, $\beta = 93.51(3)$, $\gamma = 105.27(3)°$, $V = 2673.3(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.030\ Mg\,m^{-3}$, $\mu = 0.148\ mm^{-1}$, GOF = 1.050, reflections collected: 24698, independent reflections: 11982 ($R_{int} = 0.0521$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0640$, $wR_2 = 0.1423$, R indices (all data): $R_1 = 0.1323$, $wR_2 = 0.1577$.

Crystallographic data for **8a**: $C_{39}H_{48}NiOP_2Si_2$, $M_w = 709.60\ g\,mol^{-1}$, $T = 163(2)$ K, monoclinic, space group $P2(1)/n$, $a = 9.861(2)$, $b = 20.275(4)$, $c = 20.010(4)$ Å, $\alpha = 90$, $\beta = 93.91(3)$, $\gamma = 90°$, $V = 3991.1(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.181\ Mg\,m^{-3}$, $\mu = 0.654\ mm^{-1}$, GOF = 1.024, reflections collected: 26772, independent reflections: 8892 ($R_{int} = 0.0909$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0641$, $wR_2 = 0.1298$, R indices (all data): $R_1 = 0.1523$, $wR_2 = 0.1434$.

Supporting information for this article (experimental details, X-ray data, and scanned NMR spectra of all new products) is available on the WWW under http://www.angewandte.org or from the author. CCDC 736194 (**1a**), 736195 (**2a**), 736196 (**2b**), 736197 (**4a**), 736198 (**8a**), and 736309 (**8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: August 1, 2009

Keywords: carbonylation · cyclic dianions · cyclopentadienyl ligands · Grignard reagents

---

[1] For representative reviews on dianion chemistry: a) C. M. Thompson, *Dianion Chemistry in Organic Synthesis*, CRC, Boca Raton, **1994**; b) P. Langer, W. Freiberg, *Chem. Rev.* **2004**, *104*, 4125; c) *Polylithiumorganic Compounds: Syntheses and Selected Molecular Structures*, C. Strohmann and D. Schildbach in *The Chemistry of Organolithium Compounds* (Ed.: Z. Rappoport, I. Marek), Wiley, Chichester, **2004**, pp. 941–996; d) F. Foubelo, M. Yus, *Curr. Org. Chem.* **2005**, *9*, 459; e) Z. Xi, *Eur. J. Org. Chem.* **2004**, 2773; f) Z. Xi, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1021; g) Z. Xi, W. X. Zhang, *Synlett* **2008**, 2557; h) W. X. Zhang, Z. Xi, *Pure Appl. Chem.* **2009**, *81*, 235.

[2] a) J. B. Lambert, S. M. Wharry, *J. Am. Chem. Soc.* **1982**, *104*, 5857; b) M. Koreeda, S. G. Mislankar, *J. Am. Chem. Soc.* **1983**, *105*, 7203; c) P. Baierweck, D. Hoell, K. Müllen. *Angew. Chem.* **1985**, *97, 959; Angew. Chem. Int. Ed. Engl.* **1985**, 24, 972; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 972; d) P. Baierweck, U. Simmross, K. Mullen, *Chem. Ber.* **1988**, *121*, 2195; e) R. Knorr, J. Mehlstaubl, P. Bohrer, *Chem. Ber.* **1989**, *122*, 1791; f) P. Langer, M. Döring, P. R. Schreiner, H. Görls, *Chem. Eur. J.* **2001**, *7*, 2617.

[3] a) Y. Blum, D. Czarkie, Y. Rahamim, Y. Shvo, *Organometallics* **1985**, *4*, 1459; b) J. S. M. Samec, A. H. Éll, J. B. Åberg, T. Privalov, L. Eriksson, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2006**, *128*, 14293; c) C. P. Casey, T. B. Clark, I. A. Guzei, *J. Am. Chem. Soc.* **2007**, *129*, 11821; d) C. P. Casey, S. E. Beetner, J. B. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 2285; e) C. P. Casey, H. Guan, *J. Am. Chem. Soc.* **2009**, *131*, 2499; f) A. Comas-Vives, G. Ujaque, A. Lledós, *Organometallics* **2008**, *27*, 4854; g) Y. Do, S.-B. Ko, I. C. Hwang,

K.-E. Lee, S. W. Lee, J. Park, *Organometallics* **2009**, *28*, 4624; see also: h) U. Siemeling, *Chem. Rev.* **2000**, *100*, 1495; i) H. Butenschön, *Chem. Rev.* **2000**, *100*, 1527.

[4] a) Q. Song, J. Chen, X. Jin, Z. Xi, *J. Am. Chem. Soc.* **2001**, *123*, 10419; for representative cases of carbonylation of organolithium reagents with CO, also see: b) D. Seyferth, R. M. Weinstein, *J. Am. Chem. Soc.* **1982**, *104*, 5534; c) H. Kai, K. Iwamoto, N. Chatani, S. Murai, *J. Am. Chem. Soc.* **1996**, *118*, 7634; d) T. Takahashi, S. Huo, R. Hara, Y. Noguchi, K. Nakajima, W. Sun, *J. Am. Chem. Soc.* **1999**, *121*, 1094.

[5] a) A. J. Kos, P. von R. Schleyer, *J. Am. Chem. Soc.* **1980**, *102*, 7928; b) A. J. Ashe, J. W. Kampf, P. M. Savla, *Organometallics* **1993**, *12*, 3350; c) M. Saito, M. Nakamura, T. Tajima, M. Yoshioka, *Angew. Chem.* **2007**, *119*, 1526; *Angew. Chem. Int. Ed.* **2007**, *46*, 1504; *Angew. Chem.* **2007**, *119*, 1526.

[6] a) S. D. Stults, R. A. Andersen, A. Zalkin, *J. Am. Chem. Soc.* **1989**, *111*, 4507; b) G. Fraenkel, X. Chen, A. Chow, J. C. Gallucci, H. Liu, *J. Org. Chem.* **2005**, *70*, 9131; c) J. Paradies, G. Erker, F. Fröhlich, *Angew. Chem.* **2006**, *118*, 3150; *Angew. Chem. Int. Ed.* **2006**, *45*, 3079.

[7] a) P. Jutzi, U. Siemeling, A. Müller, H. Bögge, *Organometallics* **1989**, *8*, 1744; for a review on metal–cyclopentadienone complexes, see: b) R. Gleiter, D. B. Werz, *Organometallics* **2005**, *24*, 4316.

[8] a) Z. Xi, Q. Song, *J. Org. Chem.* **2000**, *65*, 9157; b) Q. Luo, C. Wang, W.-X. Zhang, Z. Xi, *Chem. Commun.* **2008**, 1593.

[9] In situ NMR analysis showed that the complexes **8** could be easily decomplexed by air, changing into the corresponding free cyclopentadienone derivatives selectively. For similar results, see: H.-J. Knölker, H. Goesmann, R. Klauss, *Angew. Chem.* **1999**, *111*, 727; *Angew. Chem. Int. Ed.* **1999**, *38*, 702.