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Dipodal ligands from chiral spiro[2.4]hepta-4,6-dienes: solid state conformational effects by tether substitution in dipodal η^5,η^1-CpP–ruthenium(II) complexes

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Abstract—New chiral spiro[2.4]hepta-4,6-dienes were prepared and used in an efficient synthesis of cyclopentadienyl ruthenium complexes with pendant phosphine donors. Solid state structures reveal a conformation trend among three structurally homologous complexes that involves subtle twisting about the tether with increasing substitution at the alpha carbon. These results suggest architectural requirements for future ligand designs.

The considerable progress realized in the coordination chemistry of Cp complexes is due in part to the ease with which steric and electronic properties of the ligand can be tuned through substitution on the Cp.[1–4] The tethering of a pendant donor atom to the Cp is a powerful strategy for modifying the chemistry of Cp transition metal complexes.[5] In addition to changing the steric and electronic environment around the Cp scaffold, a tether restricts the spatial and conformational freedom of the donor atom. A metal bound to a dipodal or tripodal Cp complex experiences a different environment compared to that presented by the analogous intermolecular counterpart. Comprehensive reviews on Cp ligands with pendant donors have appeared that focused on nitrogen,[6] oxygen,[7] phosphorus,[8] arsenic[8] and sulfur[8] donors.[9]

Herein, we report two new structurally homologous η^5,η^1-CpP–Ru(II) complexes (**1a** and **2a**, Fig. 1).[10] These complexes are tethered through either a tertiary or quaternary substituted carbon, and coordination differences between these two structures and select literature examples are discussed. This work provides insight into the effects that non-bonded interactions between the α-substituents on the tether and the C(2) and C(5) positions on the Cp ring have on the overall conformation of the complex. These particular complexes have potential as well defined chiral Lewis acid catalysts.[11]

Pioneering investigations into serial Cp tripodal bisphosphine complexes by Wolterman, Kauffmann, et al. showed that lithium diphenylphosphide and related species are efficient nucleophiles for the ring opening of spiro[2.4]hepta-4,6-diene.[12,13] Despite the sustained interest in dipodal and tripodal Cp metal complexes, the potential of chiral spiroheptadienes for ligand synthesis has remained virtually untapped.[14,15] The nucleophilic phosphide ring opening of hydroxymethyl substituted spiroheptadienes such as **3** or **4** had not been reported, and a pronounced counter ion effect was observed in these reactions (Scheme 1). For example,

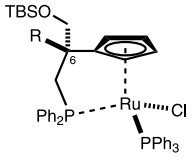
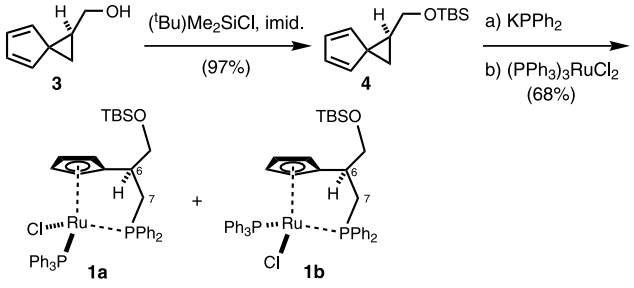


Figure 1. Subject compounds **1a** (R = H) and **2a** (R = Bn).



Scheme 1.

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lithium diphenyl phosphide required 2 h in refluxing THF for complete reaction, whereas the potassium phosphide reacted completely within 5 min at room temperature. The sodium salts gave fickle results. The rate of nucleophilic phosphide addition to the *anion* of **3** was faster than reaction with the *neutral* silyl (e.g. **4**), methyl or benzyl ethers, which indicates the importance of the inductive electron withdrawing ability of substituents on the cyclopropane. The substituted spiroheptadiene **3** is available in optically active form by alkylation of glycidol derivatives with Cp anion.[16,17]

Addition of $(PPh_3)_3RuCl_2$[18] to a solution of the Cp anion generated in situ from the cyclopropane ring opening reaction of **4** by $KPPh_2$ afforded the dipodal ruthenium complexes **1a** and **1b** as a 1:1 mixture of diastereomers in 68% yield after chromatography on silica gel.[19] Single crystals of diastereomer **1a** were grown by slow evaporation of a chloroform solution (Fig. 2).

To explore the effects of tether substitution, a complex analogous to **1a** was prepared wherein the tether methine hydrogen at C(6) was replaced with a benzyl group (i.e. **2**, Scheme 2). The allylic alcohol **6** was made in good yield from dihydrocinnamaldehyde using standard procedures.[20] After Sharpless asymmetric epoxidation the epoxide **7** was converted to the tosylate, and alkylation with 2 equiv. of LiCp gave the substituted spiroheptadiene **9** in 82% yield.[21] Addition of $KPPh_2$ to **10** and trapping of the resultant Cp anion in situ with $(PPh_3)_3RuCl_2$ gave a 54% isolated yield of complex **2** as a 2:1 mixture of diastereomers. Diastereomer **2a** crystallized preferentially from an ether–hexane solution, and its structure was determined by X-ray crystallography (Fig. 3).

A wide variety of optically active ligands with a quaternary tether are available by this methodology. The

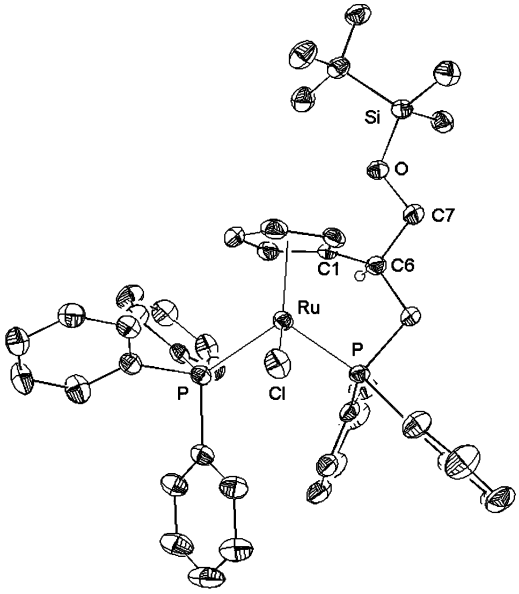
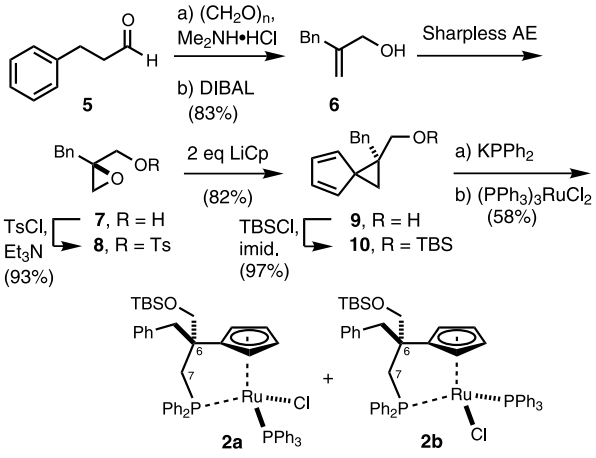


Figure 2. ORTEP diagrams of **1a**. Displacement ellipsoids are scaled to the 50% probability level.



Scheme 2.

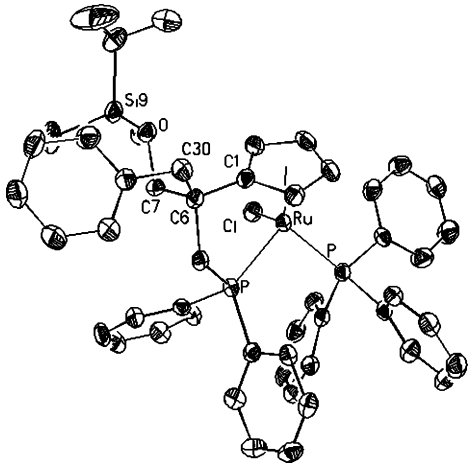
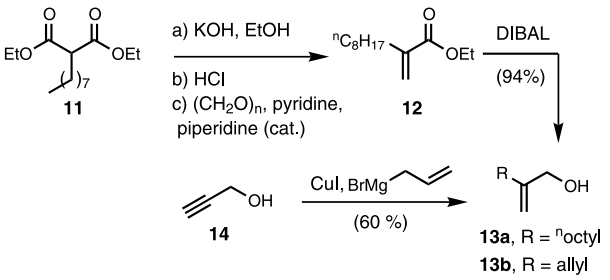


Figure 3. ORTEP diagrams of **2a**. Displacement ellipsoids are scaled to the 50% probability level.

substituted allylic alcohols for the ligand syntheses were prepared from diethyl malonate,[22,23] or more conveniently, by copper-mediated Grignard addition to propargyl alcohol.[24] Representative preparations are shown in Scheme 3. While additional ruthenium complexes were made from these alcohols, none of them provided crystals suitable for X-ray analysis.

Several ruthenium–cyclopentadienyl complexes with pendant phosphine donors connected via a two- or three-carbon tether have been characterized by X-ray crystallography.[25,26] The crystal structure of **15** (Fig. 4), the unsubstituted 'parent' of **1a** and **2a** had been reported,[27] and the relevant bond angles for the three complexes are summarized in Table 1. Some interesting conformational trends emerged from a comparison of these structures.

Substitution at C(6) causes tether twisting, and like winding a spring, results in contraction of the P(1)–Ru–Cp bond angle (entry 1, where 'Cp' is the calculated plane of the Cp and P(1) is the tethered phosphine). In the dipodal complexes, the tethered phosphine is positioned closer to the Cp and the



Scheme 3.

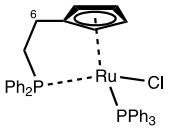


Figure 4. The parent complex **15**.[27]

Cp–Ru–P bond angle contracts in comparison to $CpRuCl(PPh_3)_2$[28] (121.6 and 121.4°) or $Cp^*RuCl(PPh_3)_2$[29] (125.2 and 126.8°). The 'twisting' can clearly be seen in Figure 5, where the perspective is looking down the C(6)–C(1) bond. The dihedral angle, defined by the Ru, the Cp centroid, C(6) and C(7), highlighted in black for emphasis, increases from 15.83° for the unsubstituted **15**, to 34.14° for mono-substituted **1a** to 42.16° for **2a**.

One explanation that explains the relationship of substitution with twisting is the minimization of quasi-1,3-allylic strain between the hydrogens on C(2) and C(5) of the Cp and the α-substituents on C(6) of the tether.[30] In **1a** the hydrogen on C(6) resides in an eclipsed position (3.6°), which allows the larger CH_2OTBS group to be orthogonal to the Cp (115.4°). In **2a**, the additional twisting allows the large CH_2OTBS group to deviate (−11.9°) from a fully eclipsed position.

If the silyloxymethyl group in **1a** were replaced with a second donor atom, such as another phosphine, the conformational preference for the second side chain in

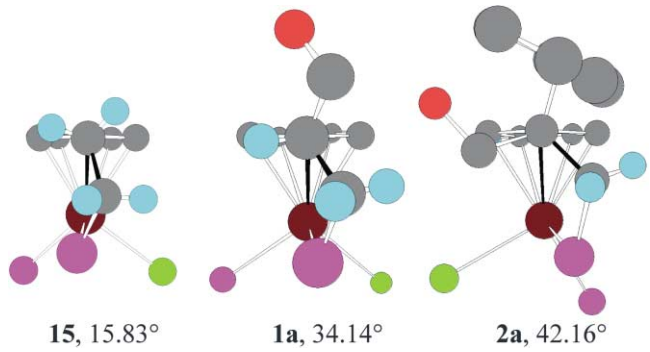


Figure 5.

a pre-tripodal complex to occupy a position remote from the metal (e.g. **16**, R = H; Fig. 6) is likely to disfavor tripodal complexation (e.g. **17**). However, tethering through a quaternary center as in **2a**, (e.g. **16**, R = Bn) renders the two pre-tripodal conformations **16** and **16′** essentially energetically degenerate. To date, the only well-characterized [η5,η1,η1-CpPP]–Ru(II) parallel-architecture tripodal complexes have invariably utilized a quaternary substituted tether, but in those complexes the branching occurs on C(7) (the β-carbon of the tether).[31]

A systematic investigation underway in our laboratory will test whether tethering through a quaternary tether is better at promoting tripodal complexation than a tertiary tether. Initial studies have focused on ligands employing a tertiary substituted tether connecting two phosphine donors.[32] However, none of the complexes shown in Figure 7 could be thermally coaxed into

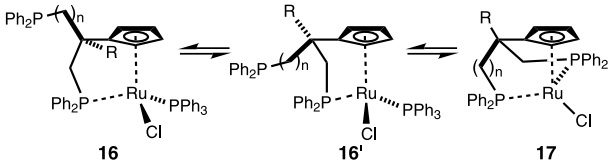


Figure 6. Relevant solution state structures.

Table 1. Bond measurements for **1a**, **2a** and comparative structures (° or Å)

Entry	Measurement	**15**	**1a**	**2a**	**Cp**[d]	**Cp***[e]
1[a,b]	P(1)–Ru–Cp	115.0	114.9	114.2	121.6	125.2
2	P(2)–Ru–Cp	125.3	122.7	131.4	121.4	126.8
3	Cl–Ru–Cp	121.9	120.7	119.1	122.5	117.3
4	P–Ru–P	99.9	102.7	99.1	104.0	96.4
5	P(1)–Ru	2.311	2.327	2.313	2.335	2.345
6	P(2)–Ru	2.306	2.320	2.330	2.337	2.336
7	Cl–Ru	2.456	2.466	2.450	2.453	2.458
8	P(1)–Ru–C(1)–C(6)	5.3	7.2	17.6	–	–
9	C(2)–C(1)–C(6)–$R_{C(6)}$	138.1(H)	115.4	110.0 (Bn)	–	–
10[c]	C(2)–C(1)–C(6)–$R'_{C(6)}$	19.5(H)	−3.6(H)	−11.9	–	–

[a] Cp = the least squares centroid defined by C(1), C(2), C(3), C(4) and C(5).
[b] P(1) = tethered phosphine, where applicable.
[c] Negative values are below the plane of the Cp.
[d] **Cp** = $CpRuCl(PPh_3)_2$.[28]
[e] **Cp*** = $(C_5Me_5)RuCl(PPh_3)_2$.[29]

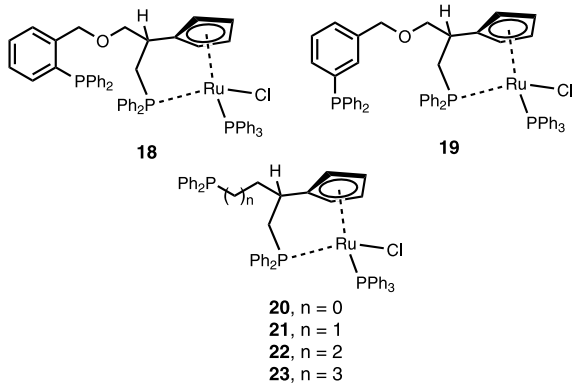


Figure 7. Additional Ru–Cp Complexes.

tripodal complexation, nor was exchange of one tethered phosphine for the other at the metal center observed. Complex **1a** did react with external phosphines, and the PPh_3 exchanged with $(tol)_3P$ and was completely displaced by PBu_3. These results together suggest that a two carbon tether between the phosphine and the Cp makes for a particularly stable complex.

In summary, hydroxymethyl substituted spiro[2.4]-hepta-4,6-dienes were shown to be efficient precursors for the synthesis of chiral cyclopentadienyl ruthenium complexes with pendant phosphine donors. This method was used to prepare several new dipodal [η^5,η^1-CpP]–Ru(II) complexes. A comparison of the X-ray structures for three related complexes revealed a conformational trend that suggests architectural requirements for future ligand designs.

Acknowledgements

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References

1. Petasis, N. A.; Hu, H.-H. *Curr. Org. Chem.* **1997**, *1*, 249–286.
2. Duthaler, R. O.; Hafner, A.; Alsters, P. L. *Pure Appl. Chem.* **1992**, *64*, 1897–1910.
3. Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1144.
4. Coville, N. J.; du Plooy, K. E.; Pickl, W. *Coord. Chem. Rev.* **1992**, *116*, 1–267.
5. Okuda, J. *Comments Inorg. Chem.* **1994**, *16*, 185–205.
6. (a) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175–185; (b) Jutzi, P.; Redeker, R. *Eur. J. Inorg. Chem.* **1998**, 663–674.
7. Siemeling, U. *Chem. Rev.* **2000**, *100*, 1495–1526.
8. Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527–1564.
9. Hogerheide, M. P.; Boersma, J.; van Koten, G. *Coord. Chem. Rev.* **1996**, *155*, 87–126.
10. Crystallographic data for structures **1a** and **2a** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 208711 and 208712, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or email: deposit@ccdc.cam.ac.uk].
11. (a) Kundig, E. P.; Saudan, C. M.; Viton, F. *Adv. Synth. Catal.* **2001**, *343*, 51–56; (b) Kundig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1220–1223; (c) Viton, F.; Bernardinelli, G.; Kundig, E. P. *J. Am. Chem. Soc.* **2002**, *124*, 4968–4969.
12. Kauffmann, R.; Ennen, J.; Lhotak, H.; Rensing, A.; Steinseifer, F.; Woltermann, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 328–329.
13. Kauffmann, T.; Bisling, M.; Konig, R.; Rensing, A.; Steinseifer, F. *Chem. Ber.* **1985**, *118*, 4517–4530.
14. Recently the phosphide ring opening of a phenyl substituted spiroheptadiene was reported: Ciruelos, S.; Englert, U.; Salzer, A.; Bolm, C.; Maischak, A. *Organometallics* **2000**, *19*, 2240–2242.
15. With a chiral indene: (a) Brookings, D. C.; Harrison, S. A.; Whitby, R. J.; Crombie, B.; Jones, R. V. H. *Organometallics* **2001**, *20*, 4574–4583; (b) Rieger, B.; Jany, G.; Steimann, M.; Fawzi, R. Z. *Naturforsch B.* **1994**, *49*, 451–458; (c) Rieger, B.; Jany, G.; Fawzi, R.; Steimann, M. *Organometallics* **1994**, *13*, 647–653.
16. (a) Corey, E. J.; Shiner, C. S.; Volante, R. P.; Cyr, C. R. *Tetrahedron Lett.* **1975**, *16*, 1161–1164; (b) Ledford, B. E.; Carreira, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 11811–11812; (c) Antczak, K.; Kingston, J. F.; Fallis, A. G.; Hanson, A. W. *Can. J. Chem.* **1987**, *65*, 114–123; (d) Okada, K.; Sakai, H.; Oda, M.; Yoshimura, A.; Ohno, T. *Tetrahedron Lett.* **1989**, *30*, 1091–1094.
17. Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936–938.
18. Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237–240. $(Ph_3P)_3RuCl_2$ is also available from Strem.
19. Kettenbach, R. T.; Bonrath, W.; Butenschön, H. *Chem. Ber.* **1993**, *I*, 1657–1669.
20. Nakatsuji, Y.; Nakamura, T.; Yonetani, M.; Yuya, H.; Okahara, M. *J. Am. Chem. Soc.* **1988**, *110*, 531–538.
21. Katsuki, T. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer: Heidelberg, 1999; Vol. 2, Chapter 18.1, pp. 621–648.
22. Hewlins, S. A.; Murphy, J. A.; Lin, J.; Hibbs, D. E.; Hursthouse, M. B. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1559–1570.
23. Grieco, P. A. *Synthesis* **1975**, 67–82.
24. DuBoudin, J. G.; Jousseaume, B. *J. Organomet. Chem.* **1979**, *168*, 1–11.
25. Moreland, J. A.; Doedens, R. *J. Inorg. Chem.* **1976**, *15*, 2486–2490.
26. Van der Zeijden, A. A. H.; Jimenez, J.; Mattheis, C.; Wagner, C.; Merzweiler, K. *J. Inorg. Chem.* **1999**, 1919–1930.
27. Slawin, A. M.; Williams, D. J.; Crosby, J.; Ramsden, J. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1988**, 2491–2494.
28. Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398–1405.

29. Guzei, I. A.; Paz-Sandoval, M. A.; Torres-Lubian, R.; Juarez-Saavedra, P. *Acta Crystallogr., Sect. C.* **1999**, 1090–1092.
30. Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841–1860.
31. (a) Antelmann, B.; Huttner, G.; Vogelgesang, J.; Walter, O.; Winterhalter, U. *J. Organomet. Chem.* **1997**, *549*, 139–148; (b) Huttner, G.; Buechner, M.; Bakos, J. *J. Organomet. Chem.* **1996**, *520*, 45–58; (c) Scherer, J.; Huttner, G.; Heidel, H. *J. Organomet. Chem.* **1997**, *539*, 67–76.
32. Ligands for complexes **20**–**23** were prepared by tosylation of the corresponding spiroheptadienyl alcohol (e.g. **3**, *n*-BuLi; TsCl) followed by displacement with $LiPPh_2$. Full details will be disclosed elsewhere.