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## Communications

# Synthesis of a Zirconocene Tropyne Complex and Comparison with Its Platinum Analogue

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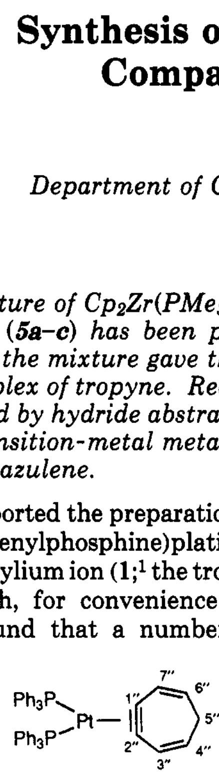
*Summary: A mixture of $Cp_2Zr(PMe_3)$ complexes of cycloheptadienyne (**5a–c**) has been prepared. Hydride abstraction from the mixture gave the first example of a zirconium complex of tropyne. Reaction of **5a–c** with 2-butyne followed by hydride abstraction gave the first example of a transition-metal metallacycle with the $\pi$ framework of an azulene.*

We recently reported the preparation and characterization of a bis-(triphenylphosphine)platinum complex of the cycloheptadienynylium ion (**1**;[1] the tropylium analogue of benzyne,[2,6a] which, for convenience, is referred to as tropyne) and found that a number of its properties suggested delocalization of electrons from the platinum fragment into the LUMO of the tropylium ion. For comparison, we thought it would be interesting to prepare a tropyne complex in which the complexing metal is devoid of nonbonding d electrons. At this time we report the preparation and some properties of the highly unstable (decomposes above −50 °C) $Cp_2Zr(PMe_3)$ complex of tropyne (**6**) and preliminary evidence for formation of the equally unstable formal alkyne reductive coupling product **7**, the first recorded example of a metallacycle with the $\pi$ framework of an azulene.



**1**

Preparation of **6** is outlined in Scheme 1. A mixture of $\sigma$ complexes (**4**; six possibilities) was prepared from a mixture of three isomeric cycloheptatrienyllithiums (**3a–c**)[3–5] by standard procedures.[6] Warming **4** from −78 °C to room temperature in the presence of $PMe_3$ led to elimination of cycloheptatriene (identified by $^1H$ NMR) and formation of an inseparable mixture of the three possible cycloheptadienyne complexes **5a–c** (1:0.5:0.5 based on $^1H$ NMR; 67%). Structure assignments are based on analytical data for the mixture and NMR spectra. As with analogous zirconium alkyne complexes, the dienynes appear to lie in planes that eclipse the $PMe_3$ and bisect the Cp rings.[6a,7] Geometry assignments rest on the nonequivalence of ring hydrogens in **5a**, NOE enhancements in the $CH_2$ group in **5b** and H3′ in **5c** when the hydrogens of the $PMe_3$ are saturated, and similar enhancement of the $CH_2$ group in **5c** and H7° in **5b** when

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(1) Lu, Z.; Abboud, K.; Jones, W. M. *J. Am. Chem. Soc.* **1992,** *114,* 10991.

(2) For transition-metal complexes of benzynes, see: (a) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1296. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991,** *113,* 3404.

(3) The cycloheptatrienyllithiums were prepared from butyllithium and a mixture of bromocycloheptatrienes.[4,5] To our surprise, it was found that the resulting mixture must be kept below −40 °C to prevent reversal to *n*-BuLi.

(4) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *Inorg. Chem.* **1982,** *21,* 1321.

(5) Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988.

(6) (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988,** *88,* 1047 and references therein. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989,** *111,* 3336.

(7) (a) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989,** *111,* 397. (b) Buchwald, S. L.; Lum, R. T.; Fisher, R. A. *J. Am. Chem. Soc.* **1989,** *111,* 9113. (c) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987,** 623.

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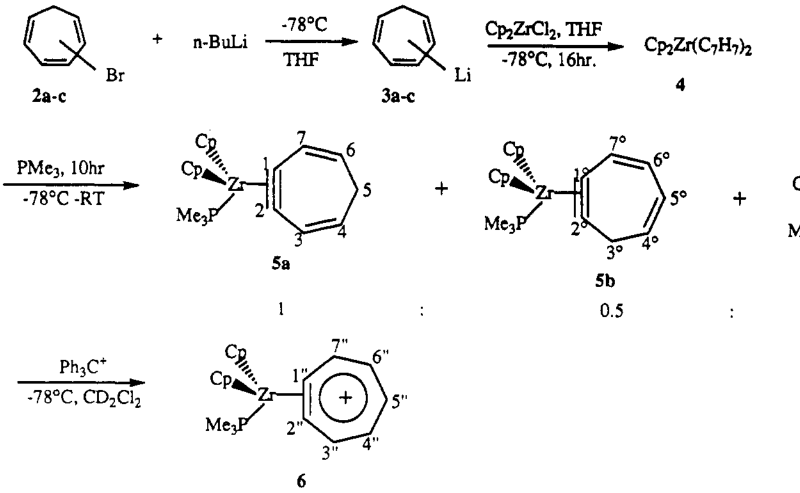
Scheme 1



the Cp hydrogens are saturated.[8] All three dienyne complexes are air-sensitive solids; **5b**,**c** are also thermally unstable.[9]

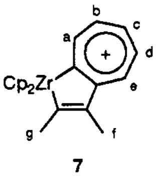
Treatment of a $CD_2Cl_2$ solution of a mixture of the cycloheptadienyne complexes with $Ph_3C^+BF_4^-$ at −78 °C cleanly produces the zirconocene tropyne complex **6** (with $BF_4^-$ counterion).[10] Unlike the robust platinum complex **1**,[1] **6** is extremely thermally unstable, decomposing to a complex mixture of products above −50 °C. Replacing the counterion with either $BPh_4^-$ or $B(C_6F_5)_4^-$ did not increase its stability. Its structure is therefore based on its spectra[10] and chemistry. In the $^1H$ NMR, the ring resonances appear between 7.8 and 9.1 ppm. For hydrogen assignments, a doublet with a chemical shift at 8.85 ppm is assigned to H3″ on the basis of a 1.0% NOE enhancement upon irradiation of the $PMe_3$ methyl resonances and the remaining hydrogen resonances were then assigned from a COSY experiment. Carbon resonances were assigned by a CH 2D NMR experiment. From the appearance of $^1H$ resonances from five different kinds of hydrogens, it is clear that, as with its dienyne precursors, the plane of the tropyne ring eclipses the phosphine, bisects the Cp rings, and shows no evidence of rotation about the carbon–metal bond on an NMR time scale.

With chemical reagents such as alkenes, alkynes, nitriles, and ketones, the zirconocene tropyne complex showed only complex mixtures of products, which presumably result from thermal decomposition before loss of phosphine and reductive coupling can occur. However, as with **1**,[1] the zirconocene tropyne complex is readily reduced back to its dienyne precursors a reaction that we take as strong evidence for its structure. For example, treatment of **6** with 1 equiv of $KB(Et)_3H$ in THF led cleanly to a mixture of **5a**–**c**. However, to our surprise, the reduction gave almost exclusively **5b** and **5c** (**5a**:**5b**:**5c** = 0.06:1.0:1.0), products that require hydride delivery to the sterically less accessible positions (confirmed as sterically less accessible by MM2 calculations on reasonable transition states). This was found to be even more pronounced when **6** was reduced with the bulkier $LiAl(O\text{-}t\text{-}Bu)_3H$ (**5a**:**5b**:**5c** = 0.01:1.0:1.0). A similar but less dramatic preference was also found for reduction of **1** with $KBEt_3H$ (para: ortho = 0.13:1.0). In an attempt to understand these interesting results, EHMO calculations were carried out on **1** and **6** to compute the net atomic charges on the carbons of the tropyne ring. Results are given in Table 1. In each case the ortho carbons (C3 and C7) are significantly more positive than the more remote para carbon (C5), which is consistent with frontier orbital control in the reduction of both **1** and **6**. It is interesting that the ortho carbons in **1** are more positive than in **6** while the reduction is noticeably less regioselective. However, MM2 calculations indicate a more crowded environment near the metal in the former which apparently somewhat offsets the electronic effect.

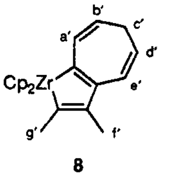
**Table 1. Net Atomic Charges of the Carbons on the Tropyne Ring (au)**

| | C1″ | C2″ | C3″ | C4″ | C5″ | C6″ | C7″ |
|---|---|---|---|---|---|---|---|
| **1** | −0.0042 | −0.0417 | 0.1675 | 0.0989 | 0.0367 | 0.1026 | 0.1608 |
| **6** | 0.0462 | −0.0381 | 0.1291 | 0.0785 | 0.0661 | 0.0801 | 0.1229 |

In **6**, zirconium is formally $d^0$ and should therefore not be able to participate in aromaticity if incorporated into a cyclic conjugated ring that contains (4*n*) π electrons. However, from EHMO calculations, Hoffmann[11] has concluded that $Cp_2Ti$ does, in fact, contribute d electrons to the π system of a five-membered ring from a $Cp_2Ti$ molecular orbital with 19% $d_{xz}$ contribution. Although this contribution is not great, it may be sufficient to lend some aromatic character to an appropriately designed metallacycle containing the requisite number of π electrons.[12] We therefore undertook to prepare **7**, in which the $Cp_2Zr$ group is incorporated into the five-membered



**7**



**8**

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(8) All proton resonances of the seven-membered rings in **5a**–**c** were unequivocally assigned by a 2D COSY experiment, and all carbons except those of the triple bond (due to lack of protons) and C6 and C6′ (due to overlap) were assigned by C–H 2D NMR (see the supplementary material).

(9) Decomposition of **5b**,**c** led to cycloheptatriene. Its origin is unknown.

(10) Spectral data for **6** (see supplementary material for complete experimental data): $^1H$ NMR (300 MHz, $CD_2Cl_2$, −78 °C, δ) 8.95 (d, H7″, $^3J_{H-H}$ = 6.5 Hz), 8.85 (d, H3″, $^3J_{H-H}$ = 6.6 Hz), 8.00 (t, H5″, $^3J_{H-H}$ = 10.5 Hz), 7.85 (m, H4″ and H6″), 5.35 (s, Cp), 1.41 (d, $PMe_3$, $^2J_{P-H}$ = 6.0 Hz); $^{13}C$ NMR (75 MHz, $CD_2Cl_2$, −78 °C, δ) 235.5 (d, $^2J_{P-C}$ = 11.1 Hz) and 214.1 (d, $^2J_{P-C}$ = 22.1 Hz) (either C1″ or C2″), 156.0 (C3″), 152.4 (C7″), 143.2 (C5″), 141.7 and 140.3 (either C4″ or C6″), 104.0 (Cp), 16.4 (d, $PMe_3$, $^1J_{P-C}$ = 20.6 Hz); $^{31}P$ NMR (121 MHz, $CD_2Cl_2$, −78 °C, δ, 85% $H_3PO_4$ at room temperature as the reference) −4.6.

(11) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

portion of a bicyclic ring system containing eight $\pi$electrons. Incorporation into the five-membered ring was desirable to retard carbene migratory insertion, a reaction that may be the cause of the instability of some transition metallacycles that might otherwise show aromaticity.[12]

The most straightforward synthesis of **7** by reductive coupling of an alkyne with **6** failed, giving, as mentioned above, only decomposition products. To circumvent this, the mixture of zirconocene dienyne complexes **5a–c** was allowed to react with an excess of 2-butyne in benzene at room temperature to give decomposition products typical of **5b,c** and **8** (based on its $^1$H and $^{13}$C NMR spectra, NOE, COSY, and H–C 2D HECTCOR; see supplementary material for details). Treatment of a methylene chloride solution of **8** with $Ph_3C^+$ at low temperature gave a product to which structure **7** has been assigned. The stability of **7** varied with its counterion; both the $BF_4^-$ and $BPh_4^-$ salts decomposed above −40 °C, while the $B(C_6F_5)_4^-$ species was stable at room temperature. Despite its relative thermal stability, **7** could only be isolated as an impure brown solid, although $^1$H and most of the $^{13}$C NMR resonances could be assigned with confidence.[13] Unfortunately, these were not particularly revealing *vis à vis* the question of aromaticity (or, possible antiaromaticity) in **7**; all of the $^1$H vinyl resonances appeared between 7.15 and 8.13 ppm, a bit upfield from the chemical shifts of both the tropylium ion (9.55 ppm)[14] and the tropyne complex **6**, while the remote carbons showed resonances upfield from the tropylium ion ($\delta$ 160.6)[15] but were similar to the tropyne complex. These are about where intuition would expect the vinyl tropylium ion resonances to appear and suggest that the zirconium does not play a significant role in the electronic structure of **7**. Syntheses of metallaazulenes in which the transition metal should be a better electron donor are currently underway.

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**Supplementary Material Available:** Text giving experimental details for the preparation and properties of **5a–c** and **6–8** and Figures 1–6, giving NMR spectra for **5a–c**, and **6**, and **7** (14 pages). Ordering information is given on any current masthead page.

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[12] For examples of metallabenzenes and derivatives, see: (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (b) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *4*, 614. (c) Mike, C. A.; Ferede, R.; Allison, N. T. *Organometallics* **1988**, *7*, 1457. (d) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. (e) Bleeke, J. R.; Xie, Y. F.; Peng, W. J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118. (f) Bleeke, J. R.; Peng, W. J.; Xie, Y. F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113. (g) Bleeke, J. R.; Xie, Y. F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4703. (h) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271. (i) Bleeke, J. R.; Bass, L. A.; Xie, Y. F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213.

[13] **7** (see supplementary material for complete experimental data): $^1$H NMR (300 MHz, $CD_2Cl_2$, $\delta$) 7.15 ($H_a$), 7.45 (t, $H_b$, $^3J_{H-H}$ = 9.0 Hz), 7.79 (t, $H_c$, $^3J_{H-H}$ = 9.0 Hz), 8.13 (t, $H_d$, $^3J_{H-H}$ = 10.0 Hz), 7.88 (d, $H_e$, $^3J_{H-H}$ = 10.0 Hz), 2.04 (s, $H_f$), 1.67 (s, $H_g$), 6.42 (s, Cp) ($H_e$ shows 6.5% NOE enhancement when $H_f$ is saturated); $^{13}$C NMR (75 MHz, $CD_2Cl_2$, $\delta$) 148.0 ($C_a$), 136.8 ($C_b$), 140.5 ($C_c$), 147.8 ($C_d$), 134.6 ($C_e$), 15.8 ($C_f$), 21.4 ($C_g$), 113.5 (Cp).

[14] Gansow, O. A.; Schenxnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406.

[15] Stewart, R. P., Jr.; Isbrandt, L. R.; Benedict, J. J.; Palmer, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 3215.