

5.25; found: C 48.42, H 5.35, N 5.32; $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 9.5$ ppm (s, $^1J_{\text{P(Te)}} = 1632$ Hz); ^{125}Te NMR: $\delta = -403.6$ ppm (d, $^1J_{\text{P(Te)}} = 1619$ Hz).

4: A mixture of $[\text{Li}(\text{thf})_2][\text{tBuNP}(\mu\text{-NbBu})_2\text{NbBu}]^{[21]}$ (0.200 g, 0.396 mmol), tellurium powder (0.101 g, 0.79 mmol), and TMEDA (0.368 g, 3.17 mmol) in toluene (5 mL) was heated at 80°C for 3 h. The mixture was centrifuged and the supernatant was decanted from unreacted tellurium. After removal of solvent under vacuum, the product was redissolved in *n*-hexane (ca. 1 mL). Yellow crystals of **4** (0.062 g, 19%) were deposited after one day at 23°C . Elemental analysis calcd for $\text{C}_{28}\text{H}_{68}\text{Li}_2\text{N}_8\text{P}_2\text{Te}_2$: C 39.66, H 8.08, N 13.22; found: C 38.06, H 8.23, N 12.25; ^1H NMR ($[\text{D}_8]\text{toluene}$, 235 K): $\delta = 1.62$ (s, 9H; NbBu), 1.97 (s, 9H; NbBu), 2.18 (s, 18H; $\mu\text{-NbBu}$), 2.20 (s, 12H; NMe_2), 2.30 ppm (s(br), 8H; NCH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = -113.7$ (s, $^1J_{\text{P(Te)}} = 1467$ Hz), -75.3 ppm (s, $^1J_{\text{P(Te)}} = 1309$ Hz); ^7Li NMR: $\delta = 0.70$ (s), 3.88 ppm (s); ^{125}Te NMR: $\delta = -289$ (d, $^1J_{\text{Te,P}} = 1352$ Hz), -87 ppm (d, $^1J_{\text{Te,P}} = 1486$ Hz). The values of $^1J_{\text{Te,P}}$ obtained from the ^{31}P NMR spectrum are more reliable than those obtained from the ^{125}Te NMR spectrum owing to the broad line widths ($\Delta\nu_{1/2} \sim 225$ Hz) in the latter spectrum.

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- [1] For recent reviews, see: a) S. Silvestru, J. E. Drake, *Coord. Chem. Rev.* **2001**, 223, 117–216; b) J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1996**, 2893–2901.
- [2] H. Rudler, B. Denise, J. R. Gregorio, J. Vaissermann, *Chem. Commun.* **1997**, 2299–2300.
- [3] W.-H. Leung, H. Zheng, J. L. C. Chim, J. Chan, W.-T. Wong, I. D. Williams, *J. Chem. Soc. Dalton Trans.* **2000**, 423–430.
- [4] S. W. Magennis, S. Parsons, A. Corval, J. D. Woollins, Z. Pikramenou, *Chem. Commun.* **1999**, 61–62.
- [5] J. G. H. du Preez, K. U. Knabl, L. Krüger, B. J. A. M. van Brecht, *Solvent Extr. Ion Exch.* **1992**, 10, 729.
- [6] a) T. Chivers, M. Krahn, M. Parvez, *Chem. Commun.* **2000**, 463–464; b) T. Chivers, M. Krahn, M. Parvez, G. Schatte, *Inorg. Chem.* **2001**, 40, 2547–2553; c) T. Chivers, C. Fedorchuk, M. Krahn, M. Parvez, G. Schatte, *Inorg. Chem.* **2001**, 40, 1936–1942.
- [7] G. R. Lief, C. J. Carrow, L. Stahl, *Organometallics* **2001**, 20, 1629–1635.
- [8] a) M. Bochmann, G. C. Bwembya, N. Whilton, X. Song, M. B. Hursthouse, S. J. Coles, A. Karanlov, *J. Chem. Soc. Dalton Trans.* **1995**, 1887–1892; b) M. Bochmann, G. C. Bwembya, M. B. Hursthouse, S. J. Coles, *J. Chem. Soc. Dalton Trans.* **1995**, 2813–2817.
- [9] a) O. J. Scherer, G. Schnabl, *Chem. Ber.* **1976**, 109, 2996–3004; b) O. J. Scherer, G. Schnabl, *Angew. Chem.* **1977**, 89, 500–501; *Angew. Chem. Int. Ed. Engl.* **1977**, 16, 486; c) S. Pohl, *Z. Naturforsch. Sect. B* **1978**, 33, 610–613; S. Pohl, *Z. Naturforsch. B* **1979**, 34, 256–261.
- [10] G. Briand, T. Chivers, M. Krahn, *Coord. Chem. Rev.* **2002**, in press.
- [11] G. Briand, T. Chivers, G. Schatte, M. Parvez, Abstract No. 475, 84th CSC Conference and Exhibition (Montreal), **2001**.
- [12] Crystal data for $3 \cdot 0.25 \text{C}_6\text{H}_{14} : \text{C}_{30}\text{H}_{36}\text{N}_3\text{NaP}_2\text{Te}_2 \cdot 0.25 \text{C}_6\text{H}_{14}$, $M_r = 800.29$, tetragonal, space group $I4_1/a$, $a = 35.7317(12)$, $c = 11.0884(3)$ Å, $V = 14,157.2(8)$ Å³, $Z = 16$, $\rho_{\text{calcd}} = 1.502 \text{ g cm}^{-3}$, $F(000) = 6312$, $T = 173(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer on a yellow needlelike crystal ($0.25 \times 0.08 \times 0.04 \text{ mm}^3$) coated with Paratone 8277 oil and mounted on a glass fiber using ω and ϕ scans. Of the 11 182 reflections collected, 6186 were unique ($R_{\text{int}} = 0.040$) and 4424 were observed [$I \geq 2.00\sigma(I)$] and used to refine 355 parameters. The structure was solved by direct methods (SIR92) expanded with Fourier techniques (DIRDIF94), and refined by SHELXL97. The non-hydrogen atoms were refined anisotropically. A disordered molecule of *n*-hexane was also located in the lattice with three carbon atoms (site occupancy 0.5 each) disordered over a wide area with large displacement parameters; these atoms were included with isotropic parameters. Hydrogen atoms were included at geometrically idealized positions and not refined; hydrogen atoms of the hexane solvate were ignored. Refinement by least-squares calculations converged at $R_1 = 0.038$ and $wR_2 = 0.083$.
- [13] J. Yang, J. E. Drake, S. Hernandez-Ortega, R. Rösler, C. Silvestru, *Polyhedron* **1997**, 16, 4061–4071.
- [14] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, **1960**, p. 514.

- [15] P. J. Bonasia, J. Arnold, *J. Chem. Soc. Chem. Commun.* **1990**, 1299–1301.
- [16] N. Kuhn, H. Schumann, G. Wolmershäuser, *Z. Naturforsch. B* **1987**, 42, 674–678.
- [17] C. Rømming, A. J. Iversen, J. Songstad, *Acta Chem. Scand. Ser. A* **1980**, 34, 333–342.
- [18] a) C. H. W. Jones, R. D. Sharma, *Organometallics* **1987**, 6, 1419–1423; b) N. Kuhn, G. Henkel, H. Schumann, R. Fröhlich, *Z. Naturforsch. B* **1990**, 45, 1010–1018.
- [19] Crystal data for **4**: $\text{C}_{28}\text{H}_{68}\text{Li}_2\text{N}_8\text{P}_2\text{Te}_2$, $M_r = 847.92$, monoclinic, space group $P2_1/c$, $a = 17.8810(3)$, $b = 9.7701(2)$, $c = 24.0003(5)$ Å, $\beta = 91.6451(6)^\circ$, $V = 4191.10(14)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.344 \text{ g cm}^{-3}$, $F(000) = 1728$, $T = 170(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer on a yellow plate ($0.20 \times 0.15 \times 0.08 \text{ mm}^3$) coated with Paratone 8277 oil and mounted on a glass fiber using ω and ϕ scans. Of the 16 883 reflections collected 9529 were unique ($R_{\text{int}} = 0.028$) and 7266 were observed [$I > 2.00\sigma(I)$] and used to refine 379 parameters. Structure solution and refinement followed the procedures described above for **3**. Refinement by least-squares calculations converged at $R_1 = 0.034$ and $wR_2 = 0.072$. CCDC-184064 and CCDC-184065 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [20] Prepared by a modification of the procedure reported by: J. Ellermann, M. Schütz, F. W. Heinemann, M. Moll, *Z. Anorg. Allg. Chem.* **1998**, 624, 257–262.
- [21] I. Schranz, L. Stahl, R. J. Staples, *Inorg. Chem.* **1998**, 37, 1493–1498.

Metallabenzenes and Valence Isomers. Synthesis and Characterization of a Platinabenzene**

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*Dedicated to Professor Gottfried Huttner
on the occasion of his 65th birthday*

In our group we have developed a convenient method for the preparation of iridabenzene starting from the C_5 synthetic equivalent *Z*-3-(2-iodovinyl)-1,2-diphenylcyclopropene (**1**).^[1] Using this precursor, iridabenzene synthesis can also be carried out in a stepwise manner via an iridabenzvalene intermediate, which could be characterized and converted into the corresponding iridabenzene by thermal treatment.^[2] In addition to varying the coordination pattern at the iridium center and the substituents on the vinylcyclopropene precursor,^[3] we are currently trying to show this concept to be generally applicable for the synthesis of metallabenzene and

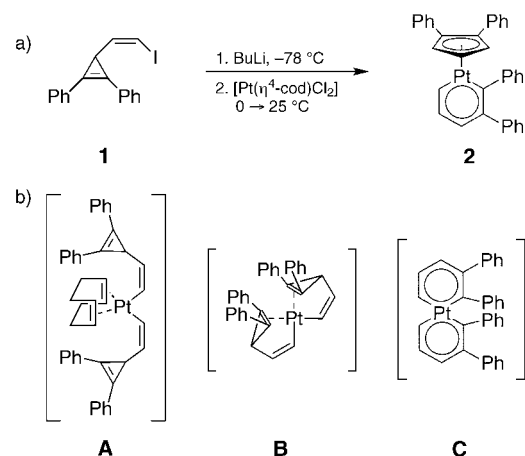
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their valence isomers containing metals other than iridium and osmium, which is the limiting factor of previous metal-labenzene syntheses. We report herein our initial studies using platinum complexes, which resulted in the formation and characterization of the first platinabenzene **2**.

Platinum chemistry is an attractive field of study, as a vast array of Pt compounds displaying a variety of metal-carbon bonding modes can be found in the literature.^[4] Complexes in which the coordination sphere around the Pt center is made up exclusively of hydrocarbon ligands are amply known for the three principal oxidation states of Pt^{0,II,IV}. The ligands therein are bonded to the Pt center in σ and/or π fashion. Especially for Pt^{II} complexes, ligand sets with almost every imaginable mixture of these donors are realized.^[5,6]

Exchange of chloride ligands in [Pt(η^4 -1,5-cod)Cl₂] (1,5-cod = 1,5-cyclooctadiene) by use of organolithium reagents is a well-known and commonly used method for the synthesis of Pt- σ -alkyl compounds.^[6] By treating [Pt(cod)Cl₂] with two equivalents of **1** (Scheme 1a), which was converted into a



Scheme 1. a) The formation of the first platinabenzene **2**; b) possible intermediates **A–C** in the formation of **2**.

nucleophilic agent by lithium-iodine exchange,^[1,2] we hoped to obtain a [Pt(η^4 -1,5-cod){-CH=CH-(cyclo-C₃HPh₂)₂}] complex (**A**; Scheme 1b) with two σ -bonded vinylcyclopropene ligands. Intramolecular displacement of the 1,5-cyclooctadiene ligand by the cyclopropene double bonds would give **B**. Subsequent ring-opening of the strained cyclopropenes would ideally lead to **C** or to other closely related platina-aromatics (i.e. **2**).

Upon addition of the vinyl lithiate, the colorless ethereal [Pt(cod)Cl₂] suspension immediately turned into a dark brown slurry containing an appreciable amount of light brown precipitate. Investigation of the crude reaction solution by ¹H NMR spectroscopy showed neither signals attributable to coordinated 1,5-cod as expected for **A**, nor for chelating vinylcyclopropene ligands coordinated in σ -alkenyl and π -fashions (i.e. **B**). The NMR spectrum was dominated by a broad shapeless absorption at $\delta \approx 6.7$ –7.3, which indicates degradation of the carbon skeleton of **1**. Pt-promoted decomposition^[7] of cyclopropene **1**, presumably through opening of the cyclopropene ring followed by oligomerization

or polymerization, appears to be the main process. In the downfield region of the spectrum, however, two signal groups at approximately $\delta = 12.8$ and 8.2 ppm were observed. The compound responsible for these resonances is (cyclopentadienyl)platinabenzene (**2**), which was isolated as a red solid after column chromatography.

¹H NMR spectra of orange-red C₆D₆ solutions of **2** show characteristically downfield-shifted signals. The multiplet at $\delta = 12.76$ ppm is clearly assignable to the metallaaromatic proton in the *ortho* position to Pt, because of its splitting pattern and the value for $^2J_{\text{PtH}} = 65$ Hz.^[8] The *para*-proton signal is well visible at $\delta = 8.20$ ppm, while the *meta*-proton gives rise to a pseudotriplet at $\delta = 7.42$ ppm ($^3J_{\text{PtH}} = 150$ Hz). Irida- and osmabenzenes exhibit signals with similar chemical shifts (*o*-H: $\delta = 9.0$ –14.0; *m*-H: $\delta = 6.6$ –8.0; *p*-H: $\delta = 7.0$ –8.6).^[9] The protons of the η^5 -coordinated^[5,10,11] 1,2-diphenylcyclopentadienyl ligand^[12] of **2** appear as a doublet and triplet at $\delta = 5.36$ and 5.09 ppm, respectively.

In the ¹³C NMR spectrum of **2**, the two signals at $\delta = 195$ and 204 ppm are attributable to the metallaaromatic carbon atoms directly bonded to the Pt; these δ values are again comparable to ¹³C NMR δ values in irida- and osmabenzenes.^[9] Pt–C couplings of $^1J_{\text{PtC}} \approx 1330$ and 1400 Hz are in the range of values reported for Pt^{II}-carbene and σ -alkenyl complexes.^[8,13,14] Signals for the carbon atoms of the 1,2-diphenylcyclopentadienyl ligand are found at $\delta = 96$, 98, and 115 ppm.

The structure of **2** was confirmed by X-ray crystallography (Figure 1).^[15] Selected bond lengths and angles are given in Table 1. Red blocks of **2**, which were obtained by cooling a saturated hexanes/EtOAc solution to 0 °C, crystallize in the triclinic space group $\bar{P}1$ without inclusion of solvent molecules. The Pt^{II} center is part of a six-ring metallacycle, formed by cyclopropene-vinylalkylidene rearrangement^[7,16] of the

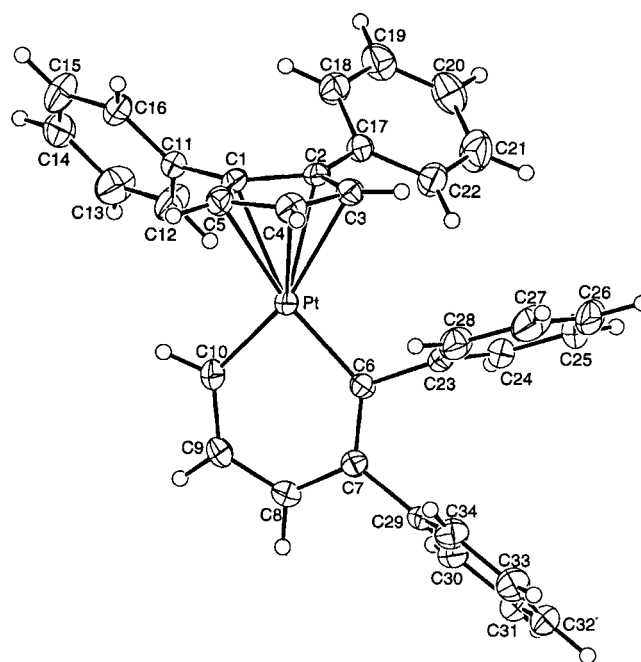


Figure 1. Molecular structure of platinabenzene **2**; ellipsoids drawn at the 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] in **2**.

Pt-C1	2.327(3)	C1-C2	1.439(5)
Pt-C2	2.342(3)	C2-C3	1.425(5)
Pt-C3	2.299(4)	C3-C4	1.399(6)
Pt-C4	2.270(4)	C4-C5	1.415(5)
Pt-C5	2.289(4)	C5-C1	1.414(5)
Pt-C6	1.959(3)	Pt-C10	1.929(4)
C6-C7	1.387(5)	C8-C9	1.381(6)
C7-C8	1.395(5)	C9-C10	1.364(6)
C6-Pt-C10	89.3(2)	C7-C8-C9	124.8(4)
Pt-C6-C7	129.2(3)	Pt-C10-C9	130.0(3)
C6-C7-C8	122.6(3)	C8-C9-C10	124.1(4)

strained precursor. Hughes and co-workers have reported the synthesis of a platinacyclohexadiene by a similar vinylcyclopropene rearrangement.^[14] In contrast to the puckered six-membered ring in that compound, the metallacycle in **2** is strictly planar (deviations from mean plane ≤ 0.02 Å, sum of angles = 720°). The two Pt–C bond distances in this ring are approximately equal (1.929, 1.959 Å), comparable to Pt–C bond lengths in Pt^{II}–carbene complexes.^[8] The C–C bonds in the aromatic ring are nonalternating and range between C–C single and double bonds (average 1.382 Å). The three C–C–C angles are about 124° , while C–Pt–C is close to 90° , and the Pt–C–C angles are around 130° . As with the NMR spectroscopic data, these structural observations are in good agreement with the values for reported metallabenzene structures^[9] and together corroborate the aromatic character of this ring. Pt–C_{ipso} distances around 2.30 ± 0.05 Å confirm η^5 -coordination of the 1,2-diphenylcyclopentadienyl ligand in the solid state.^[11,17] Interestingly, this ligand must also be derived from rearrangement of the vinylcyclopropene starting material, probably through a platinabenzene intermediate such as **C** (see Scheme 1b), which isomerizes into the η^5 -cyclopentadienyl ligand by extrusion of the metal fragment.^[9] Such a conversion involving an iridabenzene rearranging cleanly to an iridium(I) cyclopentadienyl complex has recently been observed.^[3]

Metallacycle **2** is the first example of a platinabenzene. The formation of **2**, which contains two different rearrangement products of the vinylcyclopropene precursor, as a stable compound in this complicated reaction can be rationalized by mutual stabilization of the η^5 -bonded cyclopentadienyl ligand and the platinabenzene moiety. The synthesis and characterization of this compound show that the existence of isolable metallabenzenes, which are not stabilized by η^6 -coordination to a second transition-metal fragment, is no longer confined to the classical cases of osmium and iridium.^[18] Experiments to extend our methodology to additional metals are underway.

Experimental Section

Cyclopropene **1** (688 mg, 2.0 mmol) was dissolved in dry Et₂O (20 mL) under Ar and cooled to -78°C . Butyllithium (0.8 mL, 2.5 M in hexanes, 2.0 mmol) was added dropwise and the resulting yellow solution was stirred at -78°C for 15 min. This solution was added dropwise to a stirred, ice-cooled suspension of [Pt(cod)Cl₂] (374 mg, 1.0 mmol) in Et₂O (5 mL). The resulting dark brown suspension was allowed to warm to room temperature and stirred for 12 h before filtration. The filtrate was evaporated to give a dark brown solid which was chromatographed twice on silica (25 × 1.5 cm) using hexanes/EtOAc (30:1) as the eluent. After evaporation, the red band afforded **2** (45 mg, 7%) as a red solid. M.p. 168°C (decomp.); ¹H NMR (500 MHz, C₆D₆, 25°C): δ = 5.09 (t, ³J(H,H) = 2.7 Hz, 1H; CpH), 5.36 (d,

³J(H,H) = 2.7 Hz, 2H; CpH), 6.74 (br t, ³J(H,H) = 7.5 Hz, 1H; C₆H₅), 6.85–6.94 (m, 3H; C₆H₅), 6.94–6.98 (m, 6H; C₆H₅), 6.99 (t, ³J(H,H) = 7.7 Hz, 2H; C₆H₅), 7.07 (d, ³J(H,H) = 7.3 Hz, 2H; C₆H₅), 7.13 (d, ³J(H,H) = 7.3 Hz, 2H; C₆H₅), 7.25–7.30 (m, 4H; C₆H₅), 7.42 (t, ³J(H,H) = 7.7 Hz, ³J(Pt,H) = 150 Hz, 1H; CH_{meta}), 8.20 (dd, ³J(H,H) = 8.1 Hz, ⁴J(H,H) = 1.7 Hz, 1H; CH_{para}), 12.76 ppm (dd, ³J(H,H) = 7.7 Hz, ⁴J(H,H) = 1.7 Hz, ²J(Pt,H) = 65 Hz, 1H; CH_{ortho}); ¹³C NMR (125 MHz, C₆D₆, 25°C): δ = 96.09 (s; CH_{Cp}), 97.83 (s; CH_{Cp}), 114.97 (s; CPh_{Cp}), 124.51, 125.00, 125.46, 125.72, 126.19, 128.51, 130.54, 130.92, 132.22 (all s; C₆H₅ and CH_{meta}), 135.73 (s; C_{ipso}), 140.99 (s, ³J(Pt,C) $\approx$ 150 Hz; CH_{para}), 144.17 (s; C_{ipso}), 161.74 (s; CPh_{meta}), 194.96 (s, ¹J(Pt,C) = 1330 Hz; CH_{ortho}), 204.01 ppm (s, ¹J(Pt,C) = 1400 Hz; CPh_{ortho}) (2 signals obscured by solvent peaks); ¹⁹⁵Pt{¹H} (107 MHz, C₆D₆, 25°C): δ = –5059 ppm (s);^[19] UV/Vis (CH₂Cl₂, λ_{max} , ϵ , M^{–1}cm^{–1}): 258 (120 000), 443 nm (43 000); elemental analysis calcd (%) for C₃₄H₂₆Pt: C 64.86, H 4.16; found: C 64.95, H 4.29.

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- a) R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 2597–2598; b) R. D. Gilbertson, T. L. Lau, S. Lanza, T. J. R. Weakley, M. M. Haley, unpublished results.
- R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2000**, *6*, 437–441.
- H.-P. Wu, S. Lanza, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 2824–2826.
- a) *Organometallic Compounds of Nickel, Palladium, Platinum, Copper, Silver and Gold* (Eds.: R. J. Cross, D. M. P. Mingos), Wiley, Chichester, **1985**, pp. 163–244; b) F. R. Hartley in *Comprehensive Organometallic Chemistry*, Vol. 6 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, New York, **1982**, pp. 471–762.
- a) R. Kumar, S. Roy, M. Rashidi, R. J. Puddephatt, *Polyhedron* **1989**, *8*, 551–553; b) D. O'Hare, *Organometallics* **1987**, *6*, 1766–1772; c) N. M. Boag, R. J. Goodfellow, M. Green, B. Hessner, J. A. K. Howard, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1983**, 2585–2591; d) H. C. Clark, A. Shaver, *Can. J. Chem.* **1976**, *54*, 2066–2076.
- H. C. Clark, L. E. Manzer, *J. Organomet. Chem.* **1973**, *59*, 411–428.
- a) Z. Goldschmidt in *The Chemistry of the Cyclopropyl Group*, Vol. 2 (Ed.: Z. Rappoport), Wiley, New York, **1995**, pp. 495–695; b) P. Binger, H. M. Büch, *Top. Curr. Chem.* **1987**, *135*, 77–155.
- a) M. E. Cucciolito, A. Panunzi, F. Ruffo, V. G. Albano, *Organometallics* **1999**, *18*, 3482–3489; b) G. W. V. Cave, A. J. Hallett, W. Errington, J. P. Rourke, *Angew. Chem.* **1998**, *110*, 3466–3468; *Angew. Chem. Int. Ed.* **1998**, *37*, 3270–3272; c) G. K. Anderson, R. J. Cross, *J. Chem. Soc. Dalton Trans.* **1979**, 690–694.
- J. R. Bleeker, *Chem. Rev.* **2001**, *101*, 1205–1227.
- a) G. Rosetto, P. Zanella, G. Carta, R. Bertani, G. M. Ingo, *Appl. Organomet. Chem.* **1999**, *13*, 509–513; b) G. E. Herberich, U. Englert, F. Marken, *J. Chem. Soc. Dalton Trans.* **1993**, 1979–1982; c) G. K. Anderson, *Organometallics* **1986**, *5*, 1903–1906; d) R. J. Cross, A. J. McLennan, *J. Chem. Soc. Dalton Trans.* **1983**, 359–362; e) N. M. Boag, M. Green, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1980**, 1220–1227.
- a) N. Oberbeckmann, K. Merz, R. A. Fischer, *Organometallics* **2001**, *20*, 3265–3273; b) O. V. Gusev, T. A. Peganova, M. A. Ievlev, A. G. Kropotova, K. A. Lyssenko, P. V. Petrovskii, Y. F. Oprunenko, N. A. Ustynyuk, *J. Organomet. Chem.* **2001**, *622*, 221–227; c) S. Fallis, L. Rodriguez, G. K. Anderson, N. P. Rath, *Organometallics* **1993**, *12*, 3851–3855; d) G. K. Anderson, R. J. Cross, K. W. Muir, L. Manojlovic-Muir, *J. Organomet. Chem.* **1989**, *362*, 225–235.
- a) G. Rio, M. Charifi, *Bull. Soc. Chim. Fr.* **1970**, 3585–3593; b) A. Pawda, T. J. Blacklock, D. Getman, N. Hatanaka, R. Loze, *J. Org. Chem.* **1978**, *43*, 1481–1492.
- G. Erker, B. Menjon, *Chem. Ber.* **1990**, *123*, 1327–1329.
- N. A. Grabowski, R. P. Hughes, B. S. Jaynes, A. L. Rheingold, *J. Chem. Soc. Chem. Commun.* **1986**, 1694–1695.
- Crystal data for **2**: C₃₄H₂₆Pt, M_r = 629.65, red block of dimensions 0.14 × 0.18 × 0.20 mm, triclinic, space group $P\bar{1}$, a = 9.2437(11), b = 10.2819(13), c = 14.1974(15) Å, α = 94.164(9), β = 102.027(9), γ = 106.022(9)°, V = 1256.3(3) Å³, ρ_{calc} = 1.664 g cm^{–3}, $2\theta_{\text{max}}$ = 52°, λ = 0.71073 Å, T = 296 K, 4925 independent reflections, 4505 reflections observed [$I \geq \sigma(I)$], structure refinement on F^2 (C atoms anisotropic,

phenyl H atoms riding) with teXsan (v. 1.7 for SGI workstations), 340 refined parameters, $R(F) = 0.022$ [$I \geq \sigma(I)$], $wR(F^2) = 0.051$, residual electron density: 1.29/−1.31 e Å^{−3}. Data was obtained on an Enraf-Nonius CAD-4 diffractometer. CCDC-185114 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

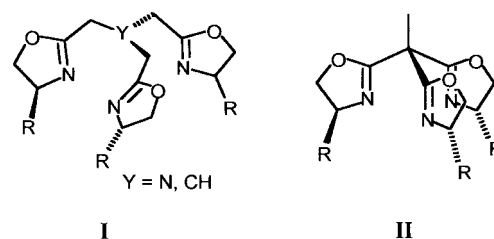
- [16] a) P. Binger, P. Müller, R. Benn, R. Mynott, *Angew. Chem.* **1989**, *101*, 647–648; *Angew. Chem. Int. Ed. Engl.* **1989**, *26*, 610–611; b) S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975; c) M. R. Gagne, R. H. Grubbs, J. Feldman, J. W. Ziller, *Organometallics* **1992**, *11*, 3933–3935.
- [17] a) F. Zheng, Y. Mu, L. Zhao, Y. Zhang, W. Bu, C. Chen, H. Zhai, H. Hong, *J. Organomet. Chem.* **2000**, *613*, 68–76; b) S.-G. Lee, H.-K. Lee, S. S. Lee, Y. K. Chung, *Organometallics* **1997**, *16*, 304–306.
- [18] Although 30–35 metallaaromatics are known, most include a second heteroatom (e.g. metallapyridine, metallapyrilium, etc.). Similarly, a majority of the remaining benzene-type structures are η^6 -coordinated to a second transition-metal fragment; therefore, only two prior classes, Roper's osmabenzenes and Bleck's iridabenzenes, are pure metallabenzenes.^[9] Compound **2** represents a new, third class.
- [19] Pt standard: 0.2M K₂PtCl₄/D₂O ($\delta = -1627$) against K₂PtCl₆; L. S. Hollis, S. J. Lippard, *J. Am. Chem. Soc.* **1983**, *105*, 3494–3503.

A Modular Approach to C₁ and C₃ Chiral N-Tripodal Ligands for Asymmetric Catalysis**

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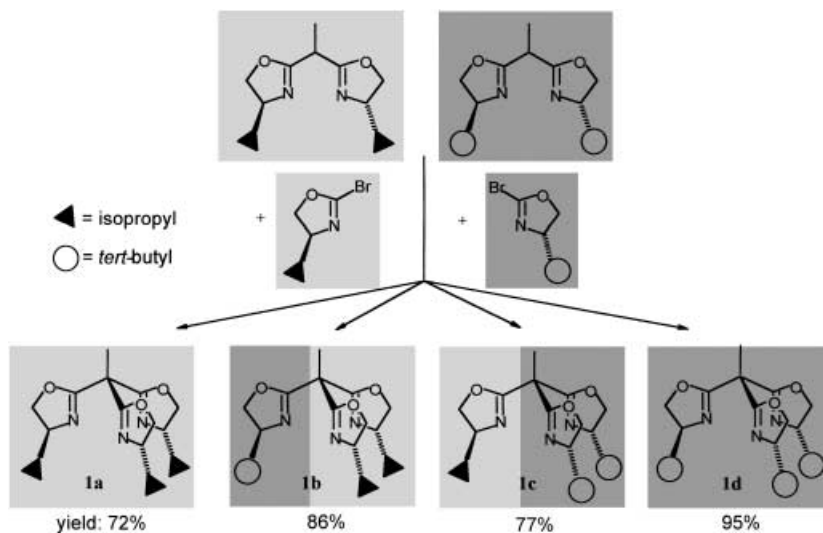
In memoriam John Osborn

In the development of nitrogen ligand based homogeneous catalysis,^[1] oxazoline derivatives have emerged as a paradigmatic class of ligands in asymmetric catalysis.^[2,3] Most attention has been centered on mono- or bisoxazoline ligands many of which proved to be highly efficient in a large variety of stereoselective transformations.^[4] In contrast, the combination of three oxazolines to form ligands of podand topology, possessing C₁ or C₃ symmetry, has received much less attention. There are several reports of trisoxazoline ligands,^[5,6] the most notable example being the N(CH₂-ox)₃ and CH(CH₂-ox)₃ (ox = 2-oxazolynyl) systems (**I**) developed by Katsuki's group, the copper complexes of which have been employed in asymmetric allylic oxidations.^[7] The way these conformationally very flexible trisoxazolines coordinate to the metal centers in the active catalysts remains an



open question. However, the access to 1,1,1-tris(oxazolynyl)-methane or -ethane ligands (**II**), which provide a geometry of the metal binding site that is most adapted to tripodal coordination of the metal center and would lead to a relatively rigid and well-defined coordination geometry, proved to be elusive for a long time.^[8]

Attempts to synthesize these tripodal ligands by sequential formation of the three oxazoline rings failed due to decarboxylation and related decomposition of the precursors during the formation of the third oxazoline ring. Very recently, we discovered that 1,1,1-tris(oxazolynyl)ethane derivatives may be synthesized by coupling lithiated bisoxazolines with 2-bromooxazolines and reported the achiral 1,1,1-tris[2-(4,4-dimethyl)oxazolynyl]ethane (“trisox-Me₂”, **II**).^[9] This strategy, which is formally based on a [1+2] condensation scheme of a metalated bisoxazoline^[10] with a 2-bromooxazoline^[11] has now been used for the synthesis of the first *chiral* tripods and it establishes 2-bromooxazolines as potentially powerful tools in ligand design (Scheme 1).



Scheme 1. Modular assembly of the trisoxazoline ligands **1a–1d** by reaction of the metalated bisoxazolines with 2-bromooxazoline derivatives.

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Our synthetic method allows the high-yield access to symmetrically substituted derivatives, such as 1,1,1-tris[2-((S)-4-isopropyl)oxazolynyl]ethane (**1a**) or 1,1,1-tris[2-((S)-4-tert-butyl)oxazolynyl]ethane (**1d**). Additionally, the synthesis of tripods with mixed substitution patterns, such as **1b** and **1c**, is achieved in excellent yields. This opens up the possibility to approach the synthesis of such polydentate oxazolines in a *modular* way, as displayed in Scheme 1 for the isopropyl/tert-butyl couple. From the point of view of ligand design these