

with this transformation, which causes the reaction to proceed exclusively through the alternative pathway leading to the allyl 3. Work directed toward a better understanding of this and other aspects of these interesting transformations is presently under way.

Acknowledgment. We thank Dr. Brevard (Bruker Spectrospin, France) for the 2D NMR experiments carried out with complex 4. M.C.N. and P.J.P. thank the Spanish Ministry of Education (MEC) for research grants. O.B. and E.C. thank the EEC for the award of a research grant (Contract No. SC1* 481). We also gratefully acknowledge generous support from the Dirección General de Investigación Científica y Técnica (Proyecto PB87-0201-C03-01) and the Junta de Andalucía.

Note Added in Proof. We have recently learned that some Russian workers have observed the formation in very low yields of oxycarbene ligands derived from tetrahydrofuran in a photochemically induced radical process. See: Ustynyuk, N. A.; Vinogradova, V. N.; Kravtsov, D. N.; Oprunenko, Y. F.; Batsanov, A. S.; Struchkov, Y. T. *Organometallic Chem. USSR* 1991, 4, 155. We thank Dr. M. J. Winter (University of Sheffield) for bringing this work to our attention.

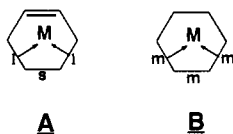
Supplementary Material Available: Tables of crystal and intensity collection data, bond distances and angles, atomic coordinates, and thermal parameters for $\text{Tp}^*\text{Ir}(\text{H})(\eta^4\text{-C}_6\text{H}_9)(=\text{C}(\text{CH}_2)_3\text{O})$ (4 pages); listing of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

Stepwise Metal-Assisted Reduction of η^4 -Coordinated Benzene to Cyclohexene

Claudio Bianchini,*[†] Kenneth G. Caulton,*[†]
Kirsten Folting,[†] Andrea Meli,[‡] Maurizio Peruzzini,[‡]
Alfonso Polo,[‡] and Francesco Vizza[‡]

Department of Chemistry and
Molecular Structure Center, Indiana University
Bloomington, Indiana 47405
Istituto per la Studio della Stereochimica ed.
Energetica dei Composti di Coordinazione
CNR, via J. Nardi 39, 50132 Florence, Italy
Received March 9, 1992

The chemical reactivity of benzene coordinated in an η^4 fashion¹ is unexplored, but it is anticipated to be unusual (e.g., different from that of cyclohexadiene) since it is established that the pattern of C/C bond lengths of this ligand (A; s = short, m = medium, l = long) differs markedly from that of cyclohexadiene (and all conjugated dienes) coordinated to the late transition metals (B).² We report here the regiochemistry of reduction of η^4 -benzene coordinated to $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]\text{Ir}^+$ ((triphos)Ir⁺).



Treatment³ (Scheme I) of (triphos)Ir(η^4 -benzene)⁺ with a 5-fold excess of LiHBEt₃ in THF at 25 °C gives (1 h) yellow (triphos)Ir(η^3 -cyclohexadienyl) (2).^{4,5} The ¹H NMR spectrum of 2

[†] Indiana University.

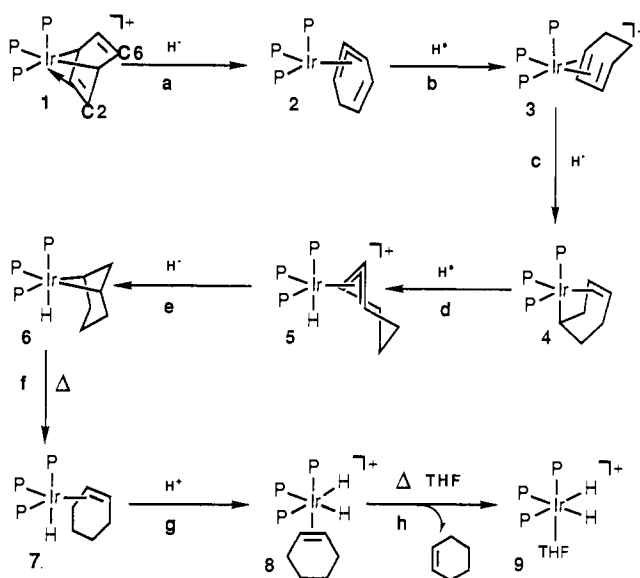
[‡] Istituto per la Studio della Stereochimica ed. Energetica dei Composti di Coordinazione.

(1) Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* 1991, 113, 5127.

(2) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* 1988, 24, 1.

(3) All cations were employed as BPh₄⁻ salts.

Scheme I



at 20 °C shows seven resonances for the cyclohexadienyl ring, which indicates that migration of Ir to the uncomplexed vinyl carbons, if it occurs at all, is slow.

Compound 2 is protonated immediately (by HBF₄·OEt₂, HSO₃CF₃, or even EtOH) in THF to give (triphos)Ir(η^4 -cyclohexadiene)⁺ (3).^{6,7} This molecule shows phosphorus site exchange which is rapid at 20 °C but slowed (³¹P{¹H} NMR pattern) at -50 °C; the variable temperature ¹³C{¹H} NMR spectrum shows mirror symmetry, with P-C coupling consistent with the phosphorus site exchange.

Treatment of 3 with 5 equiv of LiHBEt₃ in THF gives immediate and complete transformation to 4, a cyclohex-1-en-4-yl complex, by delivery of hydride to the internal carbon of the diene.^{8,9} The lack of mirror symmetry in the ¹³C NMR spectrum shows that the C₆H₉ ring is *not* bound by three contiguous carbons to Ir (i.e., η^3 -allyl), and the one large *J*(PC) value to an sp³-hybridized carbon (10.0 ppm) suggests a structure with that carbon trans to P in a trigonal bipyramid.

Protonation (stoichiometric HBF₄·OEt₂ in THF at 25 °C) of 4 yields a monohydride cation, 5, in which the cyclohex-1-en-4-yl ligand has been isomerized to an η^3 -allyl bonding mode.^{10,11} The hydride signal shows large (129 Hz) coupling to one phosphorus, suggesting a location trans to one phosphorus and cis (15 Hz) to the other two.

Hydride transfer (5 equiv of LiHBEt₃ in THF) to the cation 5 occurs to the central carbon of the allyl group to yield 6,¹² whose

(4) Selected spectral data: ³¹P{¹H} NMR (-70 °C, THF-*d*₆) δ_A = -17.64 (dd), δ_M = -19.46 (dd), δ_Q = -24.11 (dd), *J*_{AM} = 28, *J*_{AQ} = 15, *J*_{MQ} = 22 Hz; ¹H NMR (20 °C, THF-*d*₆) 6.78 (br, 1 H), 4.89 (br d, *J* = 8 Hz, 1 H), 4.65 (br, 1 H), 3.68 (br, 1 H), 3.43 (br, 1 H), as well as lines at 2.0 and 1.6 ppm (masked by triphos CH₂ and CH₃) detected by ¹H-¹H-COSY experiments.

(5) In THF, compound 2 transforms (slowly at 20 °C or within 2 h at 50 °C) into (triphos)Ir(H)₂(C₆H₅) by apparent oxidative addition of two C-H bonds (Ir^I → Ir^{III}). This product was made independently by thermal (60 °C) oxidative addition of benzene following elimination of ethane from (triphos)Ir(H)₂Et.

(6) Selected spectral data: ³¹P{¹H} NMR (-50 °C, CD₂Cl₂) δ_A = -19.45, δ_M = -24.11, *J*_{AM} = 8 Hz; ¹³C{¹H} NMR (20 °C, CD₂Cl₂) vinylic carbons at 85.24 (s), 53.74 (q, *J*_{CP} = 10 Hz), and 25.59 (q, CH₂, *J*_{CP} = 3 Hz).

(7) This compound can be independently synthesized in 80% yield by reflux (3 h in THF) of 1 in the presence of 30 equiv of 1,3-cyclohexadiene.

(8) Selected spectral data: ³¹P{¹H} NMR (20 °C, CD₂Cl₂) δ_A = -20.07, δ_M = -22.52, δ_Q = -32.61, *J*_{AM} = 18, *J*_{AQ} = 48, *J*_{MQ} = 17 Hz; ¹³C{¹H} NMR (CD₂Cl₂, 20 °C) 47.2 (ddd, *J*_{CP} = 35, 8, 3, vinyl), 22.96 (dd, *J*_{CP} = 31, 7, vinyl), 10.00 (dd, *J*_{CP} = 68, 5, Ir-C alkyl).

(9) In contrast to 2, 4 is stable to ethanol.

(10) Selected spectra data (20 °C, CD₂Cl₂): ³¹P{¹H} NMR AM₂ with δ_A = -16.59, δ_M = -26.74, *J*_{AM} = 25 Hz; ¹³C{¹H} NMR 84.85 (s, 1 C, allylic), 59.11 (d, *J*_{CP} = 26 Hz, 2 allylic C), 26.49 (s, 2 C), 23.78 (d, *J*_{CP} = 4 Hz, 1 C); ¹H NMR -11.16 (dt, *J*_{PH} = 129, 15, Ir-H); IR (Nujol) 2200 cm⁻¹ (Ir-H).

(11) Cation 5 was independently synthesized in 70% yield by reflux of 1 (7 h in THF) with 20 equiv of cyclohexene.

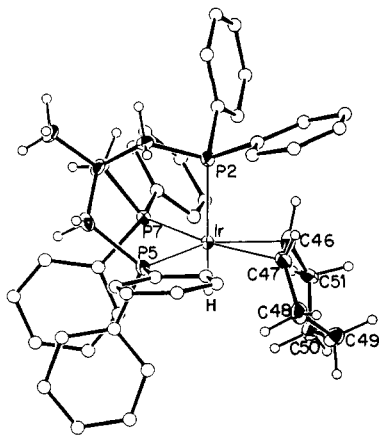


Figure 1. ORTEP drawing of $[\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3]\text{IrH}(\text{C}_6\text{H}_{10})$, showing selected atom labeling. For clarity, phenyl hydrogens have been omitted and their carbons are shown as spheres. The coplanarity of five of the six cyclohexene hydrogens is evident. Selected structural parameters: Ir–C46, 2.168 (7) Å; Ir–C47, 2.171 (7); Ir–P2, 2.301 (2); Ir–P5, 2.278 (2); Ir–P7, 2.291 (2); C46–C47, 1.463 (10).

critical spectral features include a static $^{31}\text{P}\{^1\text{H}\}$ AM₂ pattern and a hydride trans ($J(\text{HP}) = 149$ Hz) to one phosphorus and cis ($J(\text{HP}) = 13$ Hz) to two others. This compound is acid sensitive, regenerating **5** (with elimination of H₂) on treatment with HBF₄·OEt₂. The 1,3-diyl product **6** is the kinetic product, and it isomerizes in THF solution (2 days, 20 °C) to the cyclohexene isomer, **7**.¹³ Since this isomerization also occurs in the solid state (80% conversion in 10 days), we suggest that the isomerization is intramolecular. The ^{31}P , ^1H , and ^{13}C NMR spectra of **7** are consistent with a static (^{31}P NMR) molecule based on a trigonal bipyramid. This was confirmed by X-ray diffraction¹⁴ (Figure 1).

Protonation (i.e., oxidation) of **7** with equimolar HBF₄·OEt₂ in THF yields (triphos)Ir(H₂)(THF)⁺ (**9**)¹⁵ as the only metal-containing product and completes the stepwise conversion of three molecules of acetylene to cyclohexene (GC and ^1H NMR evidence). A detectable intermediate in this process is the Ir^{III} dihydrido cyclohexene complex **8**.¹⁶

Certain of these results deserve comment: (1) The hydride nucleophiles in steps c and e (Scheme I) are delivered to the internal carbon of the coordinated olefin, consistent with certain previous literature reports.¹⁷ It is noteworthy that the hydride in step e does not deprotonate this cationic hydride, but instead acts as a nucleophile at carbon. (2) The “central carbon attack” product **6** in reaction e is not thermodynamically stable, consistent with literature reports.¹⁸ (3) Deuterium labeling studies will be

(12) Selected spectral data (20 °C, CD₂Cl₂): $^{31}\text{P}\{^1\text{H}\}$ NMR AM₂ with $\delta_{\text{A}} = -28.06$, $\delta_{\text{M}} = -23.42$, $J_{\text{AM}} = 12$; ^1H NMR $\delta_{\text{IrH}} = -8.85$ (dt, $J = 149$ and 13); IR (Nujol) 2052 cm⁻¹ (Ir–H).

(13) Selected spectroscopic data (all at 20 °C in CD₂Cl₂): $^{31}\text{P}\{^1\text{H}\}$ NMR YX₂ spin system $\delta_{\text{Y}} = -18.55$, $\delta_{\text{X}} = -18.03$, $J_{\text{XY}} = 20$ Hz; $^{13}\text{C}\{^1\text{H}\}$ NMR 30.89 (vinyl, AXX'Y spin system), 35.6 (CH₂, d, $J_{\text{CP}} = 5$), 24.81 (CH₂, s); ^1H NMR of hydride nucleus $\delta_{\text{M}} = -11.52$ (MXX'Y) spin system with $J_{\text{MX}} = 14$, $J_{\text{MY}} = -141$; IR (Nujol) 2063 cm⁻¹ (Ir–H).

(14) Crystallographic data for (triphos)IrH(C₆H₁₀) at -170 °C: $a = 10.102$ (1) Å, $b = 14.994$ (2), $c = 25.674$ (3), $\beta = 90.56$ (0)° with $Z = 4$ in space group P2₁/c. Using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on all hydrogen atoms, $R(F) = 0.0351$ and $R_w(F) = 0.0317$ for 4310 reflections with $F > 3\sigma(F)$.

(15) Selected spectral data: $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₆, 20 °C) AM₂, $\delta_{\text{A}} = -1.53$, $\delta_{\text{M}} = -6.26$ ($J = 12$ Hz); ^1H NMR (THF-*d*₆, 20 °C) AA'XX'Y, $\delta(\text{H}) = -6.68$ ($J_{\text{AX}} + J_{\text{AX}'} = 127$ Hz, $J_{\text{AY}} = 15$ Hz); IR (Nujol) 2050 cm⁻¹ (Ir–H).

(16) Selected spectral data: $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-*d*₆, 20 °C) AM₂, $\delta_{\text{A}} = -3.04$, $\delta_{\text{M}} = -21.20$ ($J = 20$ Hz); ^1H NMR (THF-*d*₆, 20 °C) AA'XX'Y, $\delta_{\text{M}} = -10.86$ ($J_{\text{AX}} + J_{\text{AX}'} = 111$ Hz, $J_{\text{AY}} = 12$ Hz).

(17) (a) Sautet, P.; Eisenstein, O.; Nicholas, K. M. *Organometallics* **1987**, *6*, 1845. (b) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497.

(18) (a) Wakefield, J. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7057 and references therein. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (c) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388. (d) Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16.

required to establish whether all reactions occur by direct attack on carbon or whether, in certain cases, the kinetic site of attack is at the metal.

Acknowledgment. We thank the Indiana University Institute for Advanced Study for supporting C.B. in Bloomington and the U.S. NSF (Grant No. CHE-9103915) and Progetti Finalizzati “Chimica Fine II”, CNR, Rome, Italy, for operating expenses.

Supplementary Material Available: Listings of full synthetic, spectroscopic, and analytical details, (for **7**) atomic positional parameters, and bond lengths and angles (12 pages). Ordering information is given on any current masthead page.

A Protecting Group Strategy for Desymmetrization

Thomas R. Hoye* and Nancy E. Witowski

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received February 14, 1992

Desymmetrization issues in synthesis are important.^{1–3} Through our interest in epoxide cascade reactions,⁴ the need arose to regioselectively convert the symmetrical diepoxide diol **1** into

(1) Examples from the last decade involving enzymatic approaches include the following: (a) Ohno, M. In *Organic Syntheses, An Interdisciplinary Challenge*, Proceedings of the 5th IUPAC Symposium Organic Synthesis; Streith, J., Prinzbach, H., Schill, H., Eds.; Blackwells: Oxford, 1984; pp 189–204. (b) Wang, Y.; Chen, C.; Girdaukas, G.; Sih, C. J. *Ciba Found. Symp. Enzymes Org. Synth.* **1985**, *111*, 128. (c) Ohno, M. *Ciba Found. Symp. Enzymes Org. Synth.* **1985**, *111*, 175. (d) Jones, J. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 9. (e) Schneider, M.; Engel, N.; Hönicke, P.; Heinemann, G.; Görisch, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 67. (f) Jones, J. B.; Francis, C. J. *Can. J. Chem.* **1984**, *34*, 4087 (and earlier refs). (g) Gais, H.-J.; Lukas, K. L.; Ball, W. A.; Braun, S.; Lindner, H. J. *Liebigs Ann. Chem.* **1986**, *687* (and earlier refs). (h) Guo, Z.; Wu, S.; Chen, C.; Girdaukas, G.; Sih, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 4942 (and earlier refs). (i) Kurihara, M.; Kamiyama, K.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1985**, *26*, 5831. (j) Deardorff, D. R.; Matthews, A. J.; McMeekin, D. S.; Craney, C. L. *Tetrahedron Lett.* **1986**, *27*, 1255. (k) Kazlauskas, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4953. (l) Estermann, H.; Prasad, K.; Shapiro, M. J.; Repic, O.; Hardtmann, M. J.; Bolsterli, J. J.; Walkinshaw, M. D. *Tetrahedron Lett.* **1990**, *31*, 445. (m) Gutman, A. L.; Zuobi, K.; Bravdo, T. J. *Org. Chem.* **1990**, *55*, 3546. (n) Guanti, G.; Banfi, L.; Narisano, E. *Tetrahedron Lett.* **1990**, *31*, 6421. (o) Johnson, C. R.; Golebiowski, A.; McGill, T. K.; Steensma, D. H. *Tetrahedron Lett.* **1991**, *32*, 2597 (and earlier refs).

(2) Examples involving various chemical approaches: (a) Schreiber, S. L. *Chem. Scr.* **1987**, *27*, 563 (and earlier refs). (b) Hajos, Z. G.; Parrish, D. R. *Organic Syntheses*; Saucy, G., Ed.; Wiley: New York, 1985; Vol. 63, p 26 (and earlier refs). (c) Hoye, T. R.; Peck, D. P.; Trumper, P. K. *J. Am. Chem. Soc.* **1981**, *103*, 5618. (d) Bartlett, P. A.; Johnson, W. S.; Elliot, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 2088. (e) Bertz, S. H. *Tetrahedron Lett.* **1983**, *24*, 5576. (f) Whitesell, J. K.; Allen, D. E. *J. Org. Chem.* **1985**, *50*, 3025. (g) Hatakeyama, S.; Sakurai, K.; Takano, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1759. (h) Häfle, B.; Schröter, D.; Jäger, V. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 87. (i) Dokuzovic, Z.; Roberts, N. K.; Sawyer, J. F.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1986**, *108*, 2034. (j) Oshima, M.; Mukaiyama, T. *Chem. Lett.* **1987**, 377 (and earlier refs). (k) Aubé, J.; Burgett, P. M.; Wang, Y. *Tetrahedron Lett.* **1988**, *29*, 150. (l) Naruse, Y.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *44*, 6021 (and earlier refs). (m) Smith, D. B.; Wang, Z.; Schreiber, S. L. *Tetrahedron* **1990**, *46*, 4793 (and earlier refs). (n) Tamao, K.; Topma, T.; Inui, N.; Nakayama, O.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 7333. (o) Harada, T.; Wada, I.; Uchimura, J.; Inoue, A.; Tanaka, S.; Oku, A. *Tetrahedron Lett.* **1991**, *32*, 1219. (p) Wang, Z.; Deschenes, D. *J. Am. Chem. Soc.* **1992**, *114*, 1090.

(3) Examples involving lactonization reactions: (a) Nagao, Y.; Ikeda, T.; Yagi, M.; Fujita, E.; Shiro, M. *J. Am. Chem. Soc.* **1982**, *104*, 2079. (b) Hoye, T. R.; Peck, D. P.; Swanson, T. A. *J. Am. Chem. Soc.* **1984**, *106*, 2738. (c) Fujii, K.; Node, M.; Terada, S.; Murata, M.; Nagasawa, H.; Taga, T.; Machida, K. *J. Am. Chem. Soc.* **1985**, *107*, 6404. (d) Kurth, M. J.; Brown, E. G. *J. Am. Chem. Soc.* **1987**, *109*, 6844. (e) Sakamoto, A.; Yamamoto, Y.; Oda, J. *J. Am. Chem. Soc.* **1987**, *109*, 7188 (and earlier refs). (f) Askin, D.; Volante, R. P.; Reamer, R. A.; Ryan, K. M.; Shinkai, I. *Tetrahedron Lett.* **1988**, *29*, 277. (g) Villalobos, A.; Danishefsky, S. J. *J. Org. Chem.* **1989**, *54*, 12. (h) Schreiber, S. L.; Sammakia, T.; Uehling, D. E. *J. Org. Chem.* **1989**, *54*, 16. (i) Fujii, K.; Node, M.; Naniwa, Y.; Kawabata, T. *Tetrahedron Lett.* **1990**, *31*, 3175.

(4) (a) Hoye, T. R.; Suhadolnik, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5312. (b) Hoye, T. R.; Suhadolnik, J. C. *Tetrahedron* **1986**, *42*, 2855. (c) Hoye, T. R.; Jenkins, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 6196. (d) Hoye, T. R.; Hanson, P. A.; Kovelesky, A. C.; Ocain, T. D.; Zhuang, Z. *J. Am. Chem. Soc.* **1991**, *113*, 9369.