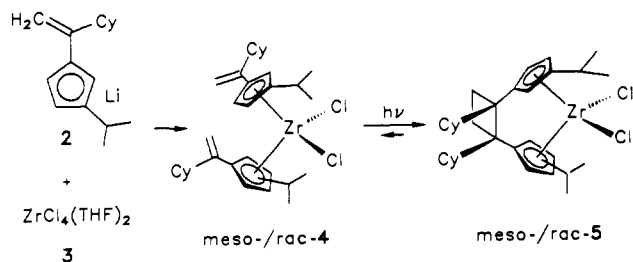


photostationary equilibrium of *meso*-5 and *meso*-4. The [2 + 2] cycloaddition product was crystallized from pentane and analyzed by X-ray diffraction.

The X-ray crystal structure analysis of *meso*-5 revealed that stereoselective head-to-head addition had occurred exclusively at the bent metallocene unit giving only one of two possible *Z*-substituted cyclobutane products, namely the one having the cyclohexyl substituents at the four-membered ring and the isopropyl groups at the Cp rings in a syn arrangement. The newly formed cyclobutane moiety is slightly puckered. The carbon-carbon bond between the tetrasubstituted ring carbons C(6)–C(7) is rather long at 1.624 (2) Å; in contrast the C(8)–C(9) distance is as expected for a "normal" C(sp³)–C(sp³) single bond at 1.524 (3) Å.⁷ The Cp(centroid)–Zr–Cp(centroid) angle of the *ansa*-metallocene *meso*-5 is 123.9°. The Cl(1)–Zr–Cl(2) angle is 97.2 (1)°. These values place complex *meso*-5 in a typical range of characteristic structural features of C₂-bridged group 4 *ansa*-metallocenes.⁸



The chiral bis(alkenyl-Cp)metal dihalide complex *rac*-4 produces a slightly different photostationary equilibrium at *rac*-5/*rac*-4 = 75:25⁶ when irradiated under analogous conditions (room temperature, 90 min, toluene solution, Philips HPK-125 lamp, Pyrex-filter). Extraction of the mixture with pentane gave pure *rac*-5 (mp 180–182 °C, 60% isolated). The spectroscopic data again revealed that stereoselective head-to-head [2 + 2] cycloaddition had taken place giving the *Z*-configured cyclobutane-bridged *ansa*-metallocene. Thus, complex *rac*-5 exhibits two sets of cyclopentadienyl NMR resonances (C₁ symmetry), whereas the respective Cp signals of the *meso*-5 isomer (C_s) are symmetry equivalent.⁹

In orientating experiments both 1,2-cyclohexylcyclobutene-bridged *ansa*-metallocenes were used for generating homogeneous propene polymerization catalysts. Activation of *meso*-5 with methylalumoxane in toluene (Al/Zr ratio = 1600) gave a catalyst system which produced atactic polypropylene (–8 °C, activity *a* ≈ 2000 g polymer/g[Zr]·h). The *rac*-5/(MeAlO)_x catalyst (Al/Zr = 400) gave partially isotactic polypropylene at –22 °C

(7) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* 1987, S1.

(8) Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1979, 173, 175. Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1985, 288, 63. Wochner, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1985, 288, 69. Schäfer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1987, 328, 87. Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* 1988, 342, 21. Gutmann, S.; Burger, P.; Hund, H.-U.; Hofmann, J.; Brintzinger, H. H. *J. Organomet. Chem.* 1989, 369, 343. Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem.* 1989, 101, 1536. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1511. Gómez, R.; Cuenca, T.; Royo, P.; Herrmann, W. A.; Herdtweck, E. *J. Organomet. Chem.* 1990, 382, 103. Gómez, R.; Cuenca, T.; Royo, P.; Hovestreydt, E. *Organometallics* 1991, 10, 2516 and references cited therein.

(9) *meso*-5: X-ray crystal structure analysis, space group P2₁/n, *a* = 13.779 (1) Å, *b* = 13.245 (1) Å, *c* = 16.423 (1) Å, β = 95.55 (1)°, 11 101 reflections measured, 7936 observed, *V* = 2983.4 Å³, *d*_{calc} = 1.32 g cm⁻³, *Z* = 4, 500 parameters refined, *R* = 0.035, *R*_w = 0.039. Selected ¹H/¹³C NMR data (benzene-*d*₆) δ 6.12, 6.07, 5.87 (CH, Cp-hydrogens), 3.28 (2 H), 1.18 and 1.08 (6 H each, CH₃, isopropyl)/δ 148.7, 138.4, 115.7, 112.0, 104.9 (Cp carbon atoms), 31.1, 23.4, 22.8 (isopropyl). *rac*-5: Anal. Calcd for C₃₇H₄₆Cl₂Zr: C, 64.83; H, 7.82. Found: C, 64.17; H, 7.97. Selected ¹H/¹³C NMR data (benzene-*d*₆) δ 6.63, 6.15, 6.01, 5.89 (double intensity), 5.85 (6 H, Cp hydrogens), 3.40, 3.26 (2 H), 1.42, 1.21, 1.18, 1.08 (3 H each, CH₃, isopropyl)/δ 149.0 (double intensity), 141.4, 138.7, 115.0, 112.9, 111.6, 108.7, 106.2, 104.7 (Cp carbon atoms), 33.7, 33.7, 23.6, 22.6, 22.1, 21.4 (isopropyl).

(*M*_n = 3500, *a* = 126). Stereochemical analysis of this polymer (¹³C NMR methyl pentades with statistical treatment as previously described¹⁰) revealed a typical situation of double stereodifferentiation [formally 60% enantiomeric site control (α = 0.73) and 40% chain end control (σ = 0.81)].^{10,11}

In contrast to the metallocenes of the late transition metals only very few reactions at the Cp rings of the much more sensitive early d- and f-element metallocenes have been found so far. Using photochemical reactions such as the one described here provides attractive alternatives for synthesizing useful metallocene derivatives of these electropositive and very oxophilic elements.

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Supplementary Material Available: Tables of X-ray crystal structure analysis data for complex *meso*-5 including lists of bond lengths and angles and atomic coordinates (11 pages); listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

(10) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* 1975, 8, 1565. Farina, M. *Top. Stereochem.* 1987, 17, 1. Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* 1960, 44, 173. Sheldon, R. A.; Fueno, T.; Tsuntsuga, T.; Kurukawa, J. *J. Polym. Sci. B* 1965, 3, 23. Inoue, J.; Itabashi, Y.; Chujo, R.; Doi, Y. *Polymer* 1984, 25, 1640. For details concerning the procedures used for the polymer analysis, see: Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Krüger, C.; Noe, R. *J. Am. Chem. Soc.* 1991, 113, 7594 and references cited therein.

(11) Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* 1989, 101, 642. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 628.

A Double Addition Product of C₆₀: C₆₀[Ir(CO)Cl(PMe₂Ph)₂]₂. Individual Crystallization of Two Conformational Isomers

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Multiple addition reactions, which are frequently reversible, have emerged as a major feature of the chemistry of C₆₀.¹ Often the occurrence of these multiple additions has given rise to mixtures of products that are difficult to separate and fully characterize. The most thoroughly characterized multiple addition products include the brominated derivatives (C₆₀Br₂₄,² C₆₀Br₃₃,³ and C₆₀Br₆₃)³ and organometallic derivatives (C₆₀[Pt(PEt₃)₂]₂,⁴ C₆₀[Pd(PEt₃)₂]₂,⁵

(1) Holloway, J. H.; Hope, E. G.; Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* 1991, 966. Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem.* 1991, 103, 1339. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1309. Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* 1991, 314, 363. Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* 1991, 254, 1183. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* 1991, 254, 1186. Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* 1991, 113, 9387. Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* 1991, 113, 9385. Tebbe, F. N.; Becker, J. Y.; Chase, D. B.; Firment, L. E.; Holler, E. R.; Malone, B. S.; Krusic, P. J.; Wasserman, E. *J. Am. Chem. Soc.* 1991, 113, 9900. Wudl, F. *Acc. Chem. Res.* 1992, 25, 157. Hawkins, J. M. *Acc. Chem. Res.* 1992, 25, 150.

(2) Tebbe, F. N.; Harlow, R. L.; Chase, D. B.; Thorn, D. L.; Campbell, G. C., Jr.; Calabrese, J. C.; Herron, N.; Young, R. J., Jr.; Wasserman, E. *Science* 1992, 256, 822.

(3) Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* 1992, 357, 479.

(4) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* 1991, 113, 9408.

(5) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* 1992, 25, 134.

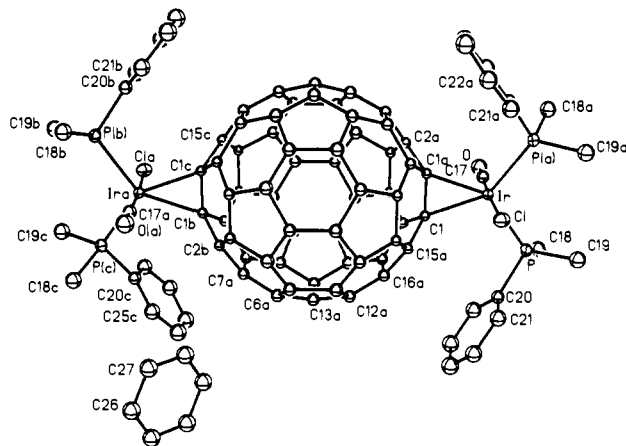


Figure 1. A perspective view of **1**, $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2 \cdot C_6H_6$, with 50% thermal contours. Selected bond distances (Å): Ir–C(1), 2.170 (7); Ir–P, 2.331 (2); Ir–C(17), 1.828 (9); Ir–Cl, 2.411 (3); C(1)–C(1a), 1.477 (15). Angles (deg): C(1)–Ir–C(1a), 39.8 (4); P–Ir–P(a), 109.8 (1).

and $C_{60}[O_2OsO_2(t-Bu)_2]_2$.⁶ Previously we have shown that $Ir(CO)Cl(PPh_3)_2$ adds to C_{60} and C_{70} ,⁸ and that the more reactive $Ir(CO)Cl(PMe_2Ph)_2$ ⁹ forms a double addition product with C_{70} , $C_{70}[Ir(CO)Cl(PMe_2Ph)_2]_2$.¹⁰ Here we report the first crystallographic characterization of a double addition product of C_{60} and the unexpected occurrence of conformational isomers which crystallize separately from the reaction mixture.

The reaction between solutions of C_{60} and $Ir(CO)Cl(PMe_2Ph)_2$ in dioxxygen-free benzene yields rapid precipitation of deep violet material. Microscopic examination of material grown with C_{60} :Ir ratios of 1:1, 1:2, and 1:3 shows the formation of similar material consisting of well-formed purple-black obelisks, **1**, small purple plates, **2**, clumps of needles, and an apparently amorphous material. The mixture is highly air sensitive and has negligible solubility in benzene and dichloromethane, which normally are good solvents for complexes of this sort. Infrared spectra of crystals that had been carefully separated manually under a microscope (in Paratone oil) show similar values of $\nu(CO)$ for **1** (2009 cm^{-1}) and **2** (2007 cm^{-1}), which suggests that they contain related structures, while the clumps of needles have $\nu(CO)$ at 2027 cm^{-1} . Both the obelisks **1** and the plates **2** have been subjected to X-ray diffraction study. The clumps of needles, which may be the single addition product, are still under study.

The structure of the molecule in the obelisks **1**, $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2 \cdot C_6H_6$,¹¹ is shown in Figure 1. The complex has crystallographic C_{2h} symmetry. Two iridium atoms are bound to 6:6 ring fusions at opposite ends of the C_{60} moiety and are 11.366 (1) Å apart. The coordination geometry at iridium is similar to that seen in other iridium complexes of C_{60} , C_{70} , and electron deficient olefins.^{7,8,10} The phenyl rings of the dimethylphenylphosphine ligands lie over the C_{60} moiety in a π - π stacking arrangement.^{10,12}

The geometry of the molecule in the plates **2**, $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2 \cdot 2C_6H_6$,¹³ is shown in Figure 2. The centrosymmetric

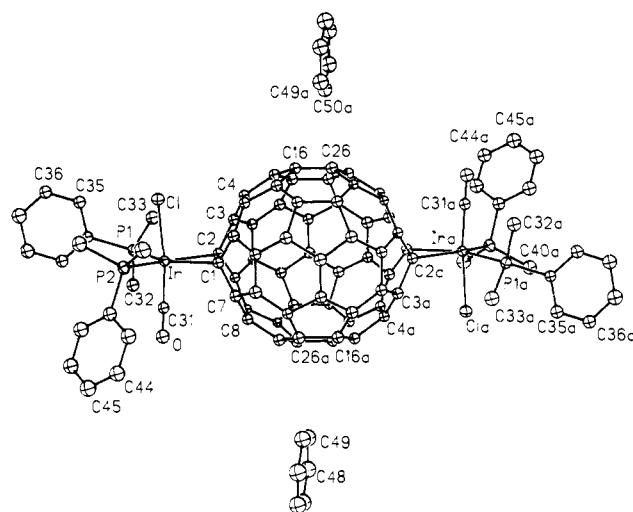


Figure 2. A perspective view of **2**, $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2 \cdot 2C_6H_6$, with 50% thermal contours. Selected bond distances (Å): Ir–C(1), 2.179 (7); Ir–C(2), 2.155 (8); Ir–P(1), 2.336 (2); Ir–P(2), 2.340 (2); Ir–C(31), 1.843 (10); Ir–Cl, 2.405 (3); C(1)–C(2), 1.499 (12). Angles (deg): C(1)–Ir–C(2), 40.5 (3); P(1)–Ir–P(2), 109.0 (1).

complex is a conformational isomer of the one seen in the obelisks **1**. Again the two iridium atoms are bound to 6:6 ring fusions at opposite ends of the C_{60} portion. In this case, however, the phosphine ligands are rotated about the Ir–P bonds so that the phenyl groups do not interact with the surface of the C_{60} portion. Moreover, in this less compact form, there are no intermolecular face-to-face contacts between C_{60} and the phenyl rings. There are, however, edge-to-surface interactions. The most prominent of these involves the benzenes of solvation. As seen in Figure 2, this ring is oriented so that H(49) lies 3.09 Å from the 6:6 ring fusion that involves C(16) and C(26). Edge-to-surface interactions are well recognized as a major attractive contribution in the crystal energetics of solid arenes.¹⁴ In **2**, this edge-on orientation of the benzene places the positively charged hydrogen substituent directly above the electron rich C–C bond at a 6:6 ring junction.

1 and **2** form a novel pair of conformational isomers. Both, however, have the same relative arrangement of the $C_{60}Ir_2$ unit. Electronic structure calculations on $\eta^2-C_{60}Pt(PH_3)_2$ have shown that the electronic structure of the hemisphere of the C_{60} portion that is furthest from the platinum is barely perturbed by binding of that metal.¹⁵ Thus binding of two metal complexes to opposite portions of C_{60} is favored on both electronic and steric grounds. The lack of solubility of **1** and **2** also plays a key role in their formation. The compact shape and high symmetry of these "para" isomers may contribute to their low solubility. It is significant to note that the related "para" isomer of $C_{60}[O_2OsO_2(t-Bu)_2]_2$ also has very low solubility.⁶ The ready formation of **1** and **2** suggests that it should be possible to form linear polymers of C_{60} in the solid state through the use of suitably designed organometallic reagents.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen positions and drawings showing the atomic numbering schemes for **1** and **2** (18 pages); listing of observed and calculated structure factors for **1** and **2** (24 pages). Ordering information is given on any current masthead page.

(14) Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. S. *Proc. R. Soc. London, A* **1958**, *247*, 1. Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23. Gavezzotti, A.; Desiraju, G. R. *Acta Crystallogr.* **1988**, *B44*, 427. Linse, P. *J. Am. Chem. Soc.* **1992**, *114*, 4366.

(15) Lichtenberger, D. L.; Wright, L. L.; Gruhn, N. E.; Rempe, M. E. *Synth. Met.*, in press.

(6) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Bunz, U.; Nunlist, R.; Ball, G. E.; Ebbesen, T. W.; Tanigaki, K. *J. Am. Chem. Soc.* **1992**, *114*, 7954.

(7) Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980.

(8) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953.

(9) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 1802.

(10) Balch, A. L.; Lee, J. W.; Olmstead, M. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1356.

(11) Purple obelisks of $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2 \cdot C_6H_6$ form in the orthorhombic space group $Ibam$ with $a = 26.170$ (3) Å, $b = 12.198$ (2) Å, $c = 21.026$ (4) Å at 120 K with $Z = 4$, $d(\text{calcd}) = 1.843$ g/cm³. Refinement of 1823 reflections with $F > 6.0\sigma(F)$ and 128 parameters yielded $R = 0.042$, $R_w = 0.045$.

(12) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 5455.

(13) Purple plates of $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2 \cdot 2C_6H_6$ form in the triclinic space group $P\bar{1}$ with $a = 9.935$ (2) Å, $b = 13.158$ (2) Å, $c = 14.864$ (2) Å, $\alpha = 71.65$ (1)°, $\beta = 78.46$ (1)°, $\gamma = 85.04$ (1)° at 123 K with $Z = 1$, $d(\text{calcd}) = 1.784$ g/cm³. Refinement of 3379 reflections with $F > 6.0\sigma(F)$ and 253 parameters yielded $R = 0.036$, $R_w = 0.034$.