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Regiospecific C=C Protection and Cyclopropanation of Dienes Both Assisted by $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^+$

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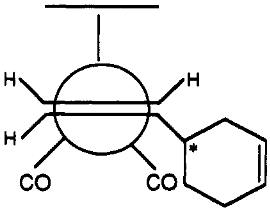
Summary: $[Fp'(\eta^2\text{-diene})][BF_4]$ $[Fp' = (\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ reacts with the in situ generated methylene complex $[Fp'(=CH_2)][OTf]$ to give $[Fp'(\eta^2\text{-alkenylcyclopropane})][BF_4]$ and $[Fp'(OTf)]$. Regiospecific cyclopropanation of the dienes 1,7-octadiene, 1,5-cyclooctadiene, isoprene, and 4-vinyl-1-cyclohexene has been achieved.

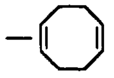
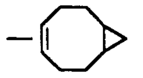
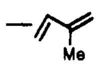
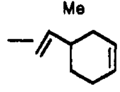
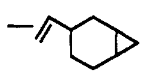
Electrophilic iron–carbene complexes have proven to be of synthetic interest as efficient cyclopropanation reagents of olefins, but similar reactions with dienes have not been developed.[1] It has been shown that the two double bonds of dienes are generally reactive toward cyclopropanation and the observed regioselectivities depend dramatically on the carbene transfer reagent used.[2-5] The reactivity of one C=C site can be inhibited by temporary η^2-coordination to a transition metal,[6,7] and therefore, prior η^2-complexation of unsymmetrical dienes should allow to direct the subsequent cyclopropanation reaction. We report here the *regiospecific methylenation* of dienes mediated by $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^+ = Fp'^+$, wherein the organometallic unit acts as a protecting group toward both the methylene fragment and the less substituted alkene function. We describe our results in representative cases, namely the preparation and characterization of new complexes containing cyclopropane and their precursors.

Complexation of the dienes is easily achieved from the aquo complex $[Fp'(H_2O)][BF_4]$[8] in refluxing CH_2Cl_2 in the presence of the appropriate substrates. The complexes $[Fp'(L)][BF_4]$ (1) [**a**, L = 1,7-octadiene; **b**, L = 1,5-cyclooctadiene;[8] **c**, L = 2-methyl-1,3-butadiene; **d**, L = 4-vinyl-1-cyclohexene] have thus been prepared in good yields (70–80%). In the case of unsymmetrical dienes, regiospecific η^2-coordination is observed: the only product isolated is that in which the less substituted alkene function is coordinated to the iron center (Table I). This is readily checked by NMR studies, the ^1H and ^{13}C olefinic resonances being shifted upfield upon iron complexation.[9] Moreover, these complexes (except **1b**) are chiral as evidenced by their ^{13}C NMR data for the diastereotopic CO ligands. This feature is illustrated by the Newman projection of **1d**



which clearly shows that the two CO groups are magnetically inequivalent whatever the position of the C=C bond. Consequently, compound **1d**, derived from 4-vinyl-1-cyclohexene (which possesses a stereocenter at C-4), is

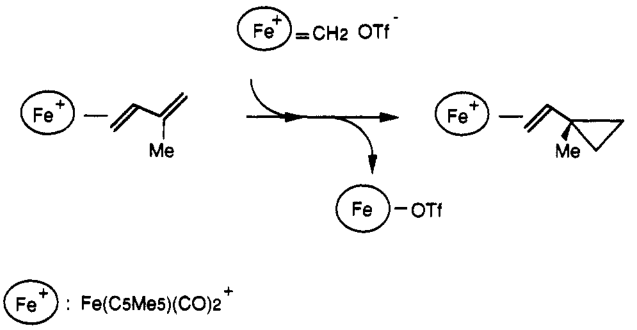
Table I. Methylenation of η^2-Dienes

$[Fp'(L)]^+$	L (1)	L′ (2)	conversion $(\%)^{a,b}$ of $[Fp'(\eta^2\text{-diene})]^+$
a			100
b			85
c			70
d			60

cis:*trans* 1:1

[a] The ratio of cyclopropane-containing complex:diene complex has been calculated on the basis of NMR spectra of the crude product (integration of the complexed olefinic resonances). [b] Reactions carried out with an excess of the methylene reagent did not give a better conversion.

Scheme I



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[1] Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411 and references therein.

[2] Kirmse, W. *Carbene Chemistry*; Academic Press: New York and London, 1971; p 296.

[3] Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

[4] For example, only the exocyclic double bond of free 4-vinylcyclohexene undergoes ethylidenation, whereas the methylenation reaction leads to a mixture of products due to reaction of both double bonds; see: Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862. Kremer, K. A. M.; Helquist, P. *J. Organomet. Chem.* **1985**, *285*, 231. O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739.

[5] Intermolecular monocyclopropanation of unactivated 1,3-dienes with Fischer carbene complexes has been recently reported; see: (a) Fischer, H.; Hofmann, J. *Chem. Ber.* **1991**, *124*, 981. (b) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 8916.

[6] Nicholas, K. M. *J. Am. Chem. Soc.* **1975**, *97*, 3254.

[7] Reger, D. L.; Gabrielli, A. *J. Am. Chem. Soc.* **1975**, *97*, 4421.

[8] Tahiri, A.; Guerchais, V.; Toupet, L.; Lapinte, C. *J. Organomet. Chem.* **1990**, *381*, C47.

[9] See, for example: Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

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formed as a 1:1 mixture of two diastereoisomers, all NMR (^{1}H, ^{13}C) signals being split.

We have used $[Fp'(=CH_2)]^+$ as a methylene transfer reagent (Scheme I) to achieve the intermolecular cyclopropanations.[10] Reactions are performed at −80 °C by treating a methylene chloride solution of the diene complex **1** with an equimolar quantity of $[Fp'(CH_2)][OTf]$, this latter species being in situ generated from $[Fp'(CH_2OMe)]$[10,11] with 1 equiv of Me_3SiOTf. The resulting alkenylcyclopropane complexes $[Fp'(L')][BF_4]$ (**2**) [**a**, L' = 5-hexenylcyclopropane; **b**, L' = bicyclo[6.1.0]non-4-ene; **c**, L' = 1-vinyl-1-methylcyclopropane; **d**, L' = *cis-trans*-4-vinylnorcarane] are isolated as yellow powders (60–70%) by precipitation with diethyl ether. The Et_2O-soluble $[Fp'(OTf)]$[10] is thus cleanly separated from the desired product.

The presence of the cyclopropyl group in **2a–d** is clearly demonstrated by the ^{1}H and ^{13}C NMR spectra, where its resonances are located at high field with a characteristic value $^1J_{C-H}$ of 160 Hz.[12] The rate of conversion is highly sensitive to the nature of the substrates, as already observed for monoalkenes.[1] Steric effects, i.e. the degree of substitution of the double bond, appear to be one of the limiting parameters as seen from the results in Table I.

It is noteworthy that although this process formally involves two cationic species, $[Fp'(=CH_2)]^+$ and $[Fp'(\eta^2\text{-diene})]^+$, our system is effective; the "free" doube bond—whether conjugated or not—is still reactive. Moreover, this procedure allows a facile isolation and characterization of the resulting carbene transfer products as metal complexes.

The alkene fragment in all these complexes is very labile: decoordination slowly occurs in solution at room temperature. Decomplexation has been cleanly accomplished by warming **2a** in $CDCl_3$ (40 °C), and 5-hexenylcyclopropane, readily separated from the organometallic product by a simple filtration through alumina, was identified by NMR (^{1}H and ^{13}C) as a pure compound (92% spectroscopic yield).

Experimental Section

General Data. All manipulations were carried out under an argon atmosphere with Schlenk or glovebox techniques. Solvents were dried and distilled under nitrogen before use by standard methods. NMR spectra (^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz) were recorded on a Bruker AC 3000 spectrometer by S.S. (CRMPO, Rennes, France). Infrared spectra were obtained with a Nicolet 205 FT-IR spectrometer. Microanalyses were performed by the "Centre de Microanalyse du CNRS" at Lyon, France. $[Fe(C_5Me_5)(CO)_2(H_2O)][BF_4]$[8] and $[Fe(C_5Me_5)(CO)_2(CH_2OMe)]$[10] were prepared by literature procedures.

General Procedure for Preparation of $[Fe(C_5Me_5)(CO)_2(\eta^2\text{-diene})][BF_4]$ (1). $[Fe(C_5Me_5)(CO)_2(H_2O)][BF_4]$ (352 mg, 1 mmol) in dichloromethane (10 mL) was treated with a 3-fold excess of the appropriate diene, and the solution was refluxed for 2 h. The solvent was evaporated to dryness, and the solid residue was washed with diethyl ether. Recrystallization from dichloromethane/diethyl ether gave yellow microcrystals.

$[Fe(C_5Me_5)(CO)_2(\eta^2\text{-1,7-octadiene})][BF_4]$ (1a). Yield: 70%. Anal. Calcd for $C_{20}H_{29}FeO_2BF_4$: C, 54.09; H, 6.58. Found: C, 53.78; H, 6.25. IR (CH_2Cl_2): 2054, 2014 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 5.77 (m, 1H, uncoordinated $=CH$), 4.99 (m, 2H, uncoordinated $=CH_2$), 3.95 (m, 1H, coordinated $=CH$), 3.14 (d, 1H, $^3J_{H-H(trans)}$ 14 Hz, coordinated $=CH_2$), 2.93 (d, 1H, $^3J_{H-H(cis)}$ 8 Hz, coordinated $=CH_2$), 2.33, 2.06, 1.65, 1.43, 1.24 (m, CH_2), 1.92 (s, 15H, C_5Me_5). ^{13}C[^{1}H] NMR ($CDCl_3$): δ 212.5 (CO), 212.0 (CO), 138.2 (uncoordinated $=CH$), 114.9 (uncoordinated $=CH_2$), 102.0 (C_5Me_5), 87.5 (coordinated $=CH$), 58.0 (coordinated $=CH_2$), 36.7, 33.3, 32.0, 28.4 (CH_2), 9.3 (C_5Me_5).

$[Fe(C_5Me_5)(CO)_2(\eta^2\text{-}CH_2{=}CHCMe{=}CH_2)][BF_4]$ (1c). Yield: 69%. Anal. Calcd for $C_{17}H_{23}FeO_2BF_4$: C, 50.79; H, 5.77. Found: C, 50.61; H, 5.82. IR (CH_2Cl_2): 2050, 2015 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 5.64 (s, 1H, uncoordinated $=CH_2$), 5.33 (q, 1H, $^4J_{H-H}$ 1 Hz, uncoordinated $=CH_2$), 4.62 (dd, 1H, $^3J_{H-H(trans)}$ 14.5 Hz, $^3J_{H-H(cis)}$ 8 Hz, coordinated $=CH$), 3.25 (dd, 1H, $^3J_{H-H(trans)}$ 14.5 Hz, $^2J_{H-H}$ 1.6 Hz, coordinated $=CH_2(H_Z)$), 2.85 (br d, 1H, $^3J_{H-H(cis)}$ 8 Hz, coordinated $=CH_2(H_E)$), 1.93 (s, 15H, C_5Me_5), 1.37 (s, 3H, Me). ^{13}C[^{1}H] NMR ($CDCl_3$): δ 212.6 (CO), 212.3 (CO), 141.1 (uncoordinated $=C$), 122.6 (uncoordinated $=CH_2$), 102.3 (C_5Me_5), 90.4 (coordinated $=CH$), 52.5 (coordinated $=CH_2$), 16.9 (Me), 9.1 (C_5Me_5).

$[Fe(C_5Me_5)(CO)_2(\eta^2\text{-}CH_2{=}CHC_6H_9)][BF_4]$ (1d). Two diastereoisomers exist. Yield: 72%. Anal. Calcd for $C_{20}H_{27}FeO_2BF_4$: C, 54.34; H, 6.16. Found: C, 54.44, H, 6.06. IR (CH_2Cl_2): 2053, 2013 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 5.70–5.58 (2 × m, uncoordinated cyclic $=CH$), 4.05–3.93 (2 × m, coordinated exocyclic $=CH$), 3.17–3.16 (2 × d, $^3J_{H-H(trans)}$ 15 Hz, coordinated $=CH_2$), 2.88–2.86 (2 × d, $^3J_{H-H(cis)}$ 8 Hz, coordinated $=CH_2$), 2.10 (m, $CHCH_2$), 1.94–1.93 (2 × s, C_5Me_5). ^{13}C[^{1}H] NMR ($CDCl_3$): δ 212.6 (CO), 212.59–212.55 (2 × s, CO), 127.2 (uncoordinated cyclic $=CH$), 125.2–124.9 (2 × s, uncoordinated cyclic $=CH$), 102.3 (C_5Me_5), 93.6–93.2 (2 × s, coordinated $=CH$), 54.6–54.5 (2 × s, coordinated $=CH_2$), 39.3–39.0 (CH), 33.9–32.2 (CH_2), 30.4–29.3 (CH_2), 24.9–24.5 (CH_2), 9.35–9.32 (2 × s, C_5Me_5).

General Procedure for Methylenation Reactions: Synthesis of $[Fe(C_5Me_5)(CO)_2(\eta^2\text{-alkenylcyclopropane})][BF_4]$ (2). In a typical experiment, stoichiometric amounts of $[Fe(C_5Me_5)(CO)_2(\eta^2\text{-diene})][BF_4]$ (0.5 mmol) and $[Fe(C_5Me_5)(CO)_2(CH_2OMe)]$ (146 mg, 0.5 mmol) in 10 mL of dichloromethane were treated at −80 °C with 1 equiv of $Me_3SiOSO_2CF_3$ (97 μL, 0.5 mmol). The mixture was warmed to room temperature. After evaporation of the solvent, the red compound $[Fe(C_5Me_5)(CO)_2(OSO_2CF_3)]$[10] was removed by extraction with diethyl ether (3 × 10 mL) and the residual yellow solid was analyzed by ^{1}H NMR. Recrystallization from dichloromethane/diethyl ether afforded yellow microcrystals.

$[Fe(C_5Me_5)(CO)_2(\eta^2\text{-5-hexenylcyclopropane})][BF_4]$ (2a). Yield: 70%. Anal. Calcd for $C_{21}H_{31}FeO_2BF_4$: C, 55.06; H, 6.82. Found: C, 54.81; H, 6.48. IR (CH_2Cl_2): 2055, 2016 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 3.96 (m, 1H, $=CH$), 3.15 (d, 1H, $^3J_{H-H(trans)}$ 14 Hz, $=CH_2$), 2.94 (d, 1H, $^3J_{H-H(cis)}$ 8 Hz, $=CH_2$), 2.33 (m, 1H, CH_2), 1.92 (s, 15H, C_5Me_5), 1.75, 1.66, 1.42, 1.20 (m, CH_2), 0.63 (m, 1H, cyclopropyl CH), 0.40 (m, 2H cyclopropyl *H*CH*H*CH), −0.01 (m, 2H, cyclopropyl HC*H*HC*H*). ^{13}C[^{1}H] NMR ($CDCl_3$): δ 212.5 (CO), 212.1 (CO), 102.1 (C_5Me_5), 87.8 ($=CH$), 58.0 ($=CH_2$), 37.0, 34.3, 32.5, 29.3 (CH_2), 10.6 (cyclopropyl CH), 9.4 (C_5Me_5), 4.4 (cyclopropyl CH_2).

$[Fe(C_5Me_5)(CO)_2(\eta^2\text{-bicyclo[6.1.0]non-4-ene})][BF_4]$ (2b). Yield: 58%. IR (CH_2Cl_2): 2051, 2012 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 3.79 (m, 2H, $=CH$), 2.57 (m, CH_2), 1.91 (s, 15H, C_5Me_5), 1.51 (m, CH_2), 1.02 (m, 2H, cyclopropyl C*H*C*H*), 0.83 (m, 1H, cyclopropyl *H*CH), 0.18 (m, 1H, cyclopropyl HC*H*). ^{13}C[^{1}H] NMR ($CDCl_3$): δ 212.8 (CO), 101.8 (C_5Me_5), 82.4 ($=CH$), 34.8, 31.3 (CH_2), 20.1 (cyclopropyl CH), 16.6 (cyclopropyl CH_2), 9.3 (C_5Me_5).

$[Fe(C_5Me_5)(CO)_2(\eta^2\text{-}CH_2{=}CH\text{-}c\text{-}C_3H_4Me)][BF_4]$ (2c). Yield: 52%. IR (CH_2Cl_2): 2053, 2014 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 4.09 (dd, 1H, $^3J_{H-H(trans)}$ 14.6 Hz, $^3J_{H-H(cis)}$ 8 Hz, $=CH$), 3.11 (dd, 1H, $^3J_{H-H(trans)}$ 14.6 Hz, $^2J_{H-H}$ 1.4 Hz, $=CH_2$), 2.67 (dd, 1H, $^3J_{H-H(cis)}$ 8 Hz, $^2J_{H-H}$ 1.4 Hz, $=CH_2$), 1.92 (s, 15H, C_5Me_5), 1.09–0.94 (2 × m, 4H, cyclopropyl CH_2CH_2), 0.89 (s, 3H, Me). ^{3}C[^{1}H] NMR ($CDCl_3$): δ 213.0 (CO), 212.5 (CO), 105.2 ($=CH$), 101.8 (C_5Me_5), 50.4 ($=CH_2$), 21.7, 20.5 (cyclopropyl CH_2), 19.7 (Me), 19.5 (cyclopropyl C), 9.5 (C_5Me_5).

$[Fe(C_5Me_5)(CO)_2(\eta^2$-*cis,trans*-4-vinylnorcarane$)][BF_4]$ (2d) exists as an equimolecular mixture of four diastereoisomers, due to additional *cis–trans* isomerism of the resulting cyclopropanated ligand. Yield: 74%. IR (CH_2Cl_2): 2054, 2017 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 3.89 (m, 1H, $=CH$), 3.11 (m, 1H, $=CH_2$), 2.79 (m, 1H, $=CH_2$), 1.93, 1.92, 1.91 (3 × s, 15H, C_5Me_5), 0.90 (m, 1H, cyclopropyl CH), 0.64 (m, 2H, cyclopropyl $CHCH_2$),

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[10] Guerchais, V.; Astruc, D.; Nunn, C. M.; Cowley, A. H. *Organometallics* **1990**, *9*, 1036.

[11] Guerchais, V.; Lapinte, C.; Thêpot, J.-Y.; Toupet, L. *Organometallics* **1988**, *7*, 604.

[12] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972; pp 258 and 286.

−0.10 (m, 1H, cyclopropyl CH_2).

Spectroscopic Characterization of 5-Hexenylcyclopropane. A $CDCl_3$ solution of **2a** (115 mg, 0.25 mmol) was heated for 2 h at 40 °C, and filtration of the resulting red solution through alumina afforded a colorless solution of 5-hexenylcyclopropane (92% yield based on ferrocene; 47 mg, 0.25 mmol). ^1H NMR ($CDCl_3$, ferrocene as internal standard): δ 5.83 (m, 1H, =CH), 4.97 (m, 2H, $=CH_2$), 0.65 (m, 1H, cyclopropyl CH), 0.39 (m, 2H cyclopropyl *H*CH*H*CH), −0.02 (m, 2H, cyclopropyl HC*H*HC*H*). $^{13}C[^1H]$ NMR ($CDCl_3$): δ 139.3 (=CH), 114.2 ($=CH_2$), 10.9 (cyclopropyl CH), 4.4 (cyclopropyl CH_2).

Acknowledgment. Dr. J.-R. Hamon is gratefully acknowledged for helpful discussions.

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Additions and Corrections

Keith H. Pannell,* Toshiaki Kobayashi, and Ramesh N. Kapoor: Thermal and Photochemical Properties of [(1-Heptamethyltrisilyl)methyl]iron and [(2-Heptamethyltrisilyl)methyl]iron Complexes $(\eta^5\text{-L})Fe(CO)_2CH_2Si_3Me_7$ (L = C_5H_5, C_5Me_5, C_9H_7). **1992**, *11*, 2229–2235.

On page 2229, eq 2 should read

$$FpCH_2SiMe_2SiMe_3 \xrightarrow{1.\ LDA} \xrightarrow{2.\ MeI} (\eta^5\text{-}Me_3SiCH_2SiMe_2C_5H_4)Fe(CO)_2CH_3 \quad (2)$$

Linda L. Lopez, P. Bernatis, J. Birnbaum, R. C. Haltiwanger, and M. Rakowski DuBois*: Mechanistic Study of Hydrogen Activation by Cationic Dinuclear (μ-Sulfido)molybdenum Complexes. **1992**, *11*, 2424–2435.

In the Experimental Section the part entitled "Dependence of Reaction Rates on Temperature" on p 2434 should include the following corrections and additions.

In line 10 of the first paragraph in this part, the formula should read ($k_2 = (1/2)k_{obs}/[H_2]$). The factor of 1/2 is explained in ref 14. In line 12, the correlation coefficient should read 0.999. The last sentence in the first paragraph should read as follows: From the slope and intercept of this line the ΔH and ΔS values of activation were calculated to be 81 kJ/mol and −23 J/(mol K), respectively.

Paragraph 2 in this part should read as follows: The solubility of H_2 (1 atm) in CD_2Cl_2 at 19 °C was found to be 2.69×10^{-3} M by comparing the NMR integration of the hydrogen resonance to that of the internal standard, *t*-BuCl. An average value from multiple NMR experiments was used. Integrations were compared for data collected with a 20-s pulse delay. A similar procedure was used to determine the solubilities of H_2 at 19 °C (3 atm), 40 °C (1 atm), and 60 °C (1 atm). Solubility values for 3 atm of H_2 at the higher temperatures were estimated from the relative solubilities at 19 °C, which generally showed good agreement with Henry's Law. Rate constants were corrected for the differences in hydrogen solubilities determined over this temperature range.

The activation parameters in the abstract, line 13, and on p 2430, lines 3–4 in the first column, should read as follows: $\Delta H^* = 81$ kJ/mol; $\Delta S^* = -23$ J/(mol K).

Christopher J. Tokar, Peter B. Kettler, and William B. Tolman*: Enantiomerically Pure Copper(I) and Zinc(II) Complexes of a Novel C_3-Symmetric Polypyrazole Ligand. **1992**, *11*, 2737–2739.

The incorrect enantiomer was chosen for refinement in the X-ray crystal structure of **6**·$2CH_2Cl_2$ (Figure 1) due to an error made during placement of the rigid group for camphor (ref 10). Refinement of the data using the mirror image of the structure shown in Figure 1 gave improved discrepancy indices of $R = 0.061$ and $R_w = 0.076$. A revised ORTEP drawing (with camphor rings now in agreement with those drawn in Scheme I) and new tables of X-ray data have been deposited as supplementary material.

Supplementary Material Available: An ORTEP drawing and tables of positional and thermal parameters and bond distances and angles for 6·$2CH_2Cl_2$ (33 pages). Ordering information is given on any current masthead page.