tion of 2 under an atmosphere of carbon monoxide at 150 °C for 2.5 h. The decomposition products have been isolated and identified by ^1H NMR, IR, GC, and GC–MS analyses.

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Stereoselective Preparation of a Rigid Trimethylenemethane Complex by Reaction of Allene with an Iridium Methylidene Derivative. X-ray Crystal Structure of *fac*-Ir[η^4-$C(CH_2)_3$][$N(SiMe_2CH_2PPh_2)_2$]

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Summary: The trimethylenemethane complex *fac*-Ir[η^4-$C(CH_2)_3$][$N(SiMe_2CH_2PPh_2)_2$] was prepared from the reaction of the methylidene derivative Ir=CH_2[$N(SiMe_2CH_2PPh_2)_2$] with allene.

Trimethylenemethane, a structural isomer of butadiene, exists only fleetingly at ambient conditions.[1] However, this reactive organic fragment can be stabilized by coordination to a metal complex. Indeed, such complexes have been known since 1966,[2] and interest has continued culminating with the use of certain palladium allyl complexes as synthetic precursors to trimethylenemethane units in cyclopentanoid natural product synthesis.[3] Preparation of the parent trimethylenemethane ligand has for the most part used preformed C_4 fragments[4] relying on halide displacement,[5] trimethylsilyl acetate/chloride elimination,[6] ring opening of methylenecyclopropane[7] or C–H activation/elimination[8] to generate the η^4-$C(CH_2)_3$ unit. In this paper, we report the synthesis and X-ray crystal structure of a trimethylenemethane–iridium complex which involves carbon–carbon bond formation[9] between an iridium–methylidene derivative and allene. A surprising and unique aspect of this reaction is that the trimethylenemethane unit forms in a completely stereoselective fashion.

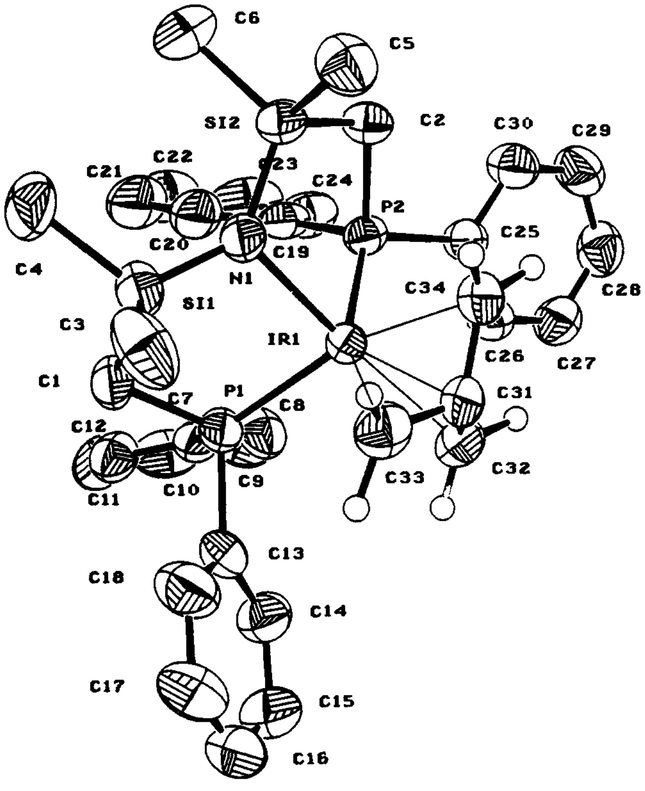

Figure 1. Molecular structure and numbering scheme for *fac*-Ir[η^4-$C(CH_2)_3$][$N(SiMe_2CH_2PPh_2)_2$] (2). Selected bond distances (Å) and bond angles (deg) are as follows: Ir–P(1), 2.296 (1); Ir–P(2), 2.295 (1); Ir–N(1), 2.198 (4); Ir–C(31), 2.055 (5); Ir–C(32), 2.189 (5); Ir–C(33), 2.222 (5); Ir–C(34), 2.202 (5); C(31)–C(32), 1.426 (7); C(31)–C(33), 1.437 (7), C(31)–C(34), 1.441 (7); P(1)–Ir–P(2), 106.49 (5); P(1)–Ir–N(1), 87.0 (1); P(1)–Ir–C(31), 123.1 (1); P(2)–Ir–N(1), 83.0 (1); P(2)–Ir–C(31), 120.7 (1); N(1)–Ir–C(31), 126.2 (2); Ir–C(31)–C(32), 75.5 (3); Ir–C(31)–C(33), 76.8 (3); Ir–C(31)–C(34), 75.8 (3); C(32)–C(31)–C(33), 115.2 (5); C(32)–C(31)–C(34), 114.7 (5); C(33)–C(31)–C(34), 113.3 (5).

Results and Discussion

Previously, we reported[10] the structure and preparation of the iridium–methylidene complex Ir=CH_2[$N(SiMe_2CH_2PPh_2)_2$] (1). Upon exposure to allene (ca. 5

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(1) Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726.

(2) Emerson, G. F.; Ehrlich, K. Giering, W. P.; Lauterber, P. C. *J. Am. Chem. Soc.* **1966**, *88*, 3172.

(3) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

(4) Marr, G.; Rockett, B. W. In *Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Ed.; Wiley: New York, 1982; Vol. 1, p 388.

(5) Ward, J. S.; Pettit, R. *J. Chem. Soc., Chem. Commun.* **1970**, 1419.

(6) Jones, M. D.; Kemmitt, D. W.; Platt, A. W. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1411.

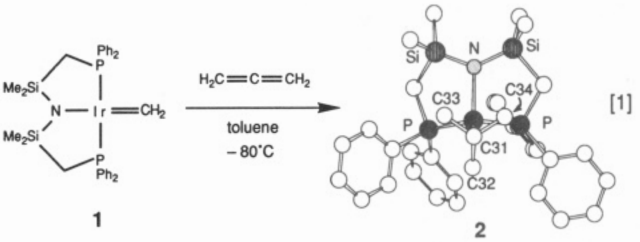
(7) (a) Pinhas, A. R.; Samuelson, A. G.; Risember, R.; Arnold, E. V.; Clardy, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 1668, and references therein. (b) Barnes, S. G.; Green, M. *J. Chem. Soc., Chem. Commun.* **1980**, 267.

(8) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651.

(9) Fischer carbenes are also reported to generate trimethylenemethane type complexes by reaction with substituted allenes, see: (a) Aumann, R.; Trentmann, B. *Chem. Ber.* **1989**, *122*, 1977. (b) Aumann, R.; Jurgen, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 357. Binuclear complexes also can induce C–C bond formation between allene and a bridging methylene: Fildes, M. J.; Knox, S. A. R.; Orpen, A. G.; Turner, M. L.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 1680.

(10) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708.

equiv) in toluene at −80 °C, the purple color of the starting material fades to light yellow over a period of 1 h. Monitoring this reaction by ^1H and ^{31}P NMR spectroscopy even at these low temperatures shows that only a single product is produced with no evidence of any intermediates; yellow crystals of $Ir[\eta^4\text{-}C(CH_2)_3][N(SiMe_2CH_2PPh_2)_2]$ (**2**) were obtained in 80% yield (eq 1). That the methylidene unit



1 **2** [1]

and allene have coupled to generate a trimethylenemethane moiety was apparent from the ^1H NMR spectrum of **2** which showed three resonances (see Experimental Section) typical for this type of ligand.[6] It was also apparent from the ^1H NMR spectrum that the tridentate amido–phosphine ancillary ligand was bound in a facial manner since both the methylene (PCH_2Si) and the phenyl (PC_6H_5) proton resonance patterns were characteristic for this type of coordination mode found in other complexes[11] with the phosphine donors cis disposed. The trimethylenemethane formulation was also confirmed by a single-crystal X-ray determination; the result is shown in Figure 1 along with some pertinent bond lengths and angles.

The meridional arrangement of the ancillary tridentate ligand in **1** changes to facial in the trimethylenemethane complex **2** as indicated by the P(1)–Ir–P(2) bond angle of 106.49°. The electron density is delocalized over the trimethylenemethane ligand as evidenced by the similar C–C bond lengths (cf. C(31)–C(32), 1.426 (7) Å; C(31)–C(33), 1.437 (7) Å; C(31)–C(34), 1.441 (7) Å). The central carbon C(31), of the trimethylenemethane ligand is closest to the iridium center (Ir–C(31), 2.055 (5) Å), and the three terminal methylene carbons are all at similar distances (range from 2.19 to 2.22 Å). This results in the trimethylenemethane unit adopting the characteristic "umbrella" shape. In analogy to other iridium–trimethylenemethane systems,[6] the complex can be considered to possess an octahedral geometry with the $\eta^4\text{-}C(CH_2)_3$ unit and the $Ir[N(SiMe_2CH_2PPh_2)_2]$ moiety in a staggered conformation (phenyl groups omitted for clarity):

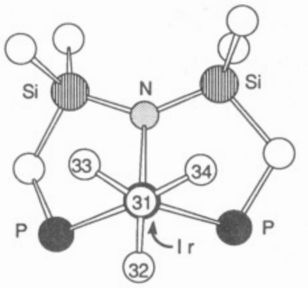
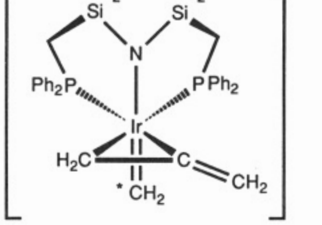


Table I. Crystallographic Data[a]

compd	$Ir[\eta^4\text{-}C(CH_2)_3][N(SiMe_2CH_2PPh_2)_2]$
formula	$C_{34}H_{42}IrNP_2Si_2$
fw	775.05
habit	prism
cryst size, mm	0.12 × 0.25 × 0.35
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	11.202 (2)
b, Å	13.829 (2)
c, Å	10.972 (2)
α, deg	90.43 (2)
β, deg	90.80 (2)
γ, deg	96.67 (2)
V, Å^3	1687.9 (6)
Z	2
T, °C	21
D_c, g/cm^3	1.525
$F(000)$	776
radiation	Mo
wavelength, Å	0.71069
μ, cm^{-1}	41.27
transmissn factors	0.54–1.00
scan type	$\omega - 2\theta$
scan range, deg in ω	$1.10 + 0.35 \tan\theta$
scan speed, deg/min	32
data collected	$+h, \pm k, \pm l$
$2\theta_{max}$, deg	60
cryst decay	negligible
total no. of rflns	10289
no. of unique rflns	9822
R_{int}	0.030
no. of rflns with $I \geq 3\sigma(I)$	6397
no. of variables	385
R	0.034
R_w	0.036
gof	1.27
max Δ/σ (final cycle)	0.08
residual density e/Å^3	−1.35, +1.29 (both near Ir)

[a] Temperature 294 K, Rigaku AFC6S diffractometer, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B) + (0.03F^2)^2]Lp^2$ (S = scan speed, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

The solution ^1H NMR spectral parameters of $Ir[\eta^4\text{-}C(CH_2)_3][N(SiMe_2CH_2PPh_2)_2]$ remain unchanged between −85 °C and +80 °C, thus indicating that rotation of the trimethylenemethane unit about the Ir–centroid bond (Ir–C(31)) is slow on the NMR time scale. In fact, we were able to show that there is no rotation even on the chemical time scale by the following labeling experiment: Reaction of the ^{13}C-labeled complex $Ir{=}^{13}CH_2[N(SiMe_2CH_2PPh_2)_2]$ with allene generates a material having only the unique CH_2 unit, C(32), labeled; consistent with this experiment is the reaction of the deuterated methylidene starting material, $Ir{=}CD_2[N(SiMe_2CH_2PPh_2)_2]$, with allene which also produces the trimethylenemethane complex with deuterium only at the C(32) methylene unit. These results taken together suggest that the transition state for this stereoselective carbon–carbon coupling process is "product-like", similar to



The trimethylenemethane complex **2** is thermally robust as no change is observed (by ^1H NMR spectroscopy) after heating to 80 °C for 48 h in benzene solution. Exposure of a solution of **2** to CO gas (1 atm) for weeks or to methyl iodide for 24 h also results in no reaction.

Table II. Final Atomic Coordinates (Fractional) and B(eq)

atom	x	y	z	B(eq), Å^2
Ir(1)	0.123 81 (2)	0.219 81 (1)	0.185 61 (2)	3.049 (7)
P(1)	0.268 8 (1)	0.136 78 (9)	0.272 4 (1)	3.61 (5)
P(2)	0.064 4 (1)	0.320 45 (8)	0.334 7 (1)	3.33 (5)
Si(1)	0.400 0 (1)	0.302 2 (1)	0.128 7 (1)	4.50 (6)
Si(2)	0.219 2 (1)	0.453 0 (1)	0.166 5 (1)	3.87 (6)
N(1)	0.266 1 (3)	0.341 0 (3)	0.159 5 (4)	3.8 (2)
C(1)	0.416 5 (4)	0.202 8 (4)	0.243 8 (5)	4.3 (2)
C(2)	0.082 6 (5)	0.441 3 (3)	0.267 9 (4)	3.9 (2)
C(3)	0.416 7 (6)	0.257 0 (6)	−0.029 6 (6)	6.9 (3)
C(4)	0.533 2 (5)	0.394 6 (5)	0.155 9 (7)	7.1 (3)
C(5)	0.172 9 (5)	0.502 3 (4)	0.016 8 (5)	5.3 (3)
C(6)	0.332 3 (6)	0.550 9 (4)	0.235 0 (6)	6.3 (3)
C(7)	0.272 0 (5)	0.108 6 (3)	0.436 0 (5)	3.9 (2)
C(8)	0.166 5 (5)	0.100 9 (4)	0.501 8 (5)	5.1 (3)
C(9)	0.168 9 (7)	0.080 1 (5)	0.624 5 (6)	6.5 (3)
C(10)	0.272 7 (8)	0.069 1 (4)	0.683 4 (5)	6.5 (3)
C(11)	0.379 5 (7)	0.076 5 (5)	0.619 5 (6)	6.2 (3)
C(12)	0.377 0 (5)	0.095 4 (4)	0.496 6 (5)	4.9 (2)
C(13)	0.273 9 (5)	0.015 6 (4)	0.206 7 (5)	4.4 (2)
C(14)	0.208 2 (5)	−0.065 4 (4)	0.257 1 (5)	5.1 (3)
C(15)	0.207 6 (6)	−0.157 5 (4)	0.204 6 (7)	6.7 (3)
C(16)	0.272 1 (7)	−0.170 1 (5)	0.102 4 (8)	7.1 (4)
C(17)	0.338 1 (7)	−0.091 0 (6)	0.050 6 (7)	7.6 (4)
C(18)	0.338 4 (6)	0.001 4 (4)	0.102 4 (6)	6.3 (3)
C(19)	0.146 1 (5)	0.339 2 (3)	0.480 6 (4)	4.1 (2)
C(20)	0.271 6 (6)	0.356 6 (4)	0.477 5 (5)	5.4 (3)
C(21)	0.338 4 (7)	0.372 7 (5)	0.582 4 (7)	7.4 (4)
C(22)	0.281 (1)	0.372 4 (5)	0.693 8 (7)	8.5 (5)
C(23)	0.159 (1)	0.353 9 (5)	0.698 8 (5)	7.9 (4)
C(24)	0.088 7 (6)	0.338 1 (4)	0.592 8 (5)	5.7 (3)
C(25)	−0.090 9 (4)	0.300 4 (3)	0.384 8 (4)	3.7 (2)
C(26)	−0.141 4 (5)	0.207 0 (4)	0.417 6 (5)	4.4 (2)
C(27)	−0.256 4 (5)	0.191 6 (4)	0.464 1 (5)	5.0 (3)
C(28)	−0.322 7 (5)	0.267 3 (5)	0.479 0 (6)	5.4 (3)
C(29)	−0.275 3 (5)	0.360 9 (4)	0.447 5 (6)	5.6 (3)
C(30)	−0.160 4 (5)	0.376 6 (4)	0.398 8 (5)	4.8 (2)
C(31)	0.003 7 (4)	0.159 8 (4)	0.055 0 (5)	4.1 (2)
C(32)	−0.026 2 (5)	0.104 6 (4)	0.161 8 (5)	4.5 (2)
C(33)	0.118 3 (5)	0.147 3 (4)	0.003 9 (5)	4.8 (2)
C(34)	−0.018 7 (5)	0.260 2 (4)	0.062 4 (5)	4.4 (2)

Experimental Section

All synthetic reactions were performed under prepurified nitrogen in a Vacuum Atmosphere HE-533-2 glove box or in standard Schlenk-type glassware. Solvents were purified as previously described.[11b] The NMR spectra were recorded in C_6D_6 on the Varian XL-300 spectrometer. The ^{1}H NMR spectra were referenced to the residual solvent proton at 7.15 ppm, and the $^{31}P\{^1H\}$ NMR spectra were referenced to external $P(OMe)_3$ set at +141.00 ppm. The $^{13}C\{^1H\}$ NMR spectra were referenced to the solvent carbons at 128.00 ppm (triplet for C_6D_6).

Synthesis of *fac*-Ir[η^4-C(CH$_2$)$_3$][N(SiMe$_2$CH$_2$PPh$_2$)$_2$]. An excess of allene (~5×) was condensed into a toluene solution (5 mL) of Ir=CH$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$][10] (100 mg, 0.14 mmol) at −78 °C. At this temperature, the purple color of the methylidene complex faded to light yellow over 1 h. The solution was warmed to room temperature, and toluene and excess allene were removed in vacuo. The off-white residue was recrystallized from hexanes/toluene at room temperature which afforded light yellow crystals of the analytically pure product. Yield: 80%. ^{1}H NMR (300 MHz, C_6D_6): SiMe$_2$, 0.43 (s), 0.68 (s); PCH$_2$Si, 1.76 (m), 2.03 (m); C(CH$_2$)$_3$, 1.54 (H^1 pseudotriplet, $^4J_{HH} = {}^4J_P = 3.0$ Hz), 1.45 (H^2 1:2:6:2:1 quintet, AA′XX′ where A = H^2 and X = P and $J_{AA'} = 4.6$, $J_{AX} = 9.2$ Hz), 2.37 (H^3 dd, $^4J_P = 9.3$ Hz); PPh$_2$, 6.81, 7.01, 7.15 (m, para/meta protons), 7.50 (m, ortho protons). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): PPh$_2$, 0.45 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): SiMe$_2$, 5.35 (s), 6.18 (s); PCH$_2$Si, 24.13 (m); η^4-C(CH$_2$)$_3$ (CH$_2$) 31.89 (d, $^2J_{C,P} = 4.2$ Hz), 47.64 (d, $^2J_{C,P} = 44.3$ Hz); (C) 101.00 (s); PPh$_2$, 126–134 (m). Anal. Calcd for $C_{34}H_{42}NP_2Si_2Ir$: C, 52.7; H, 5.46; N, 1.81. Found: C, 52.9; H, 5.67; N, 1.71.

X-ray Crystallographic Analysis of Ir[η^4-C(CH$_2$)$_3$][N(SiMe$_2$CH$_2$PPh$_2$)$_2$]. Crystallographic data appear in Table I. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 25.3$–$30.0°$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, remained essentially constant. The data were processed[12] and corrected for Lorentz and polarization effects, and absorption (empirical, based on azimuthal scans for three reflections). A total of 10 289 reflections with $2\theta \leq 60°$ was collected on a Rigaku AFC6S diffractometer, 9822 were unique ($R_{int} = 0.030$) and those 6397 having $I \geq 3\sigma(I)$ were employed in the solution and refinement of the structure.

The structure was solved by conventional heavy atom methods, the coordinates of the Ir, P, and Si atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the (η^4-C(CH$_2$)$_3$) ligand were refined with isotropic thermal parameters and all other hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from ref 13. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table II; bond lengths, bond angles, and measured and calculated structure factor amplitudes included as supplementary material.

Acknowledgment. Financial support was provided by NSERC of Canada. We also thank Johnson Matthey for the generous loan of IrCl$_3$.

Supplementary Material Available: Tables of intramolecular bond distances and bond angles (6 pages); a listing of calculated and observed structure factors (66 pages). Ordering information is given on any current masthead page.

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(11) (a) Fryzuk, M. D., Joshi, K.; Chadha, R. K. *J. Am. Chem. Soc.* **1989**, *111*, 4498. (b) Fryzuk, M. D.; Joshi, K.; Rettig, S. J. *Polyhedron* **1989**, *8*, 2291.

(12) TEXSAN/TEXRAY structure analysis package which includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(13) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor D. Reidel: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.