

Complex **2** (1.08 g, 0.88 mmol, 0.09 M) reacts with  $\text{CH}_3\text{NH}_2$  (34.7 mmol) at 23 °C to give a nearly quantitative yield of the iridium hydride complex **3** (900 mg, 0.87 mmol),  $\text{CH}_3\text{NH}_3^+\text{BF}_4^-$  (101 mg, 0.85 mmol), and the novel carbene coupling product **4** in 92% yield (112 mg, 0.81 mmol).<sup>7,9</sup> Pyridine also reacts with **2** to give **4** and iridium hydride **5**;<sup>7</sup> however, the reaction is much slower (20 h, 55 °C) and the yield lower (46%) than for  $\text{CH}_3\text{NH}_2$ . It is noteworthy that **4** is formed as a single isomer; although we favor the *E* isomer, the spectroscopic data do not allow unambiguous determination of alkene stereochemistry. Exposure of a  $\text{CHCl}_3$  solution of **4** (21 mg, 0.15 mmol, 0.38 M) to air for 6.5 h at 23 °C results in conversion to furan **6** in 64% yield.<sup>7</sup>

When the reaction of **2** ( $7.9 \times 10^{-3}$  M) and  $\text{CH}_3\text{NH}_2$  (0.19 M) in  $\text{CDCl}_3$  is followed by low-temperature (-5 °C)  $^1\text{H}$  NMR spectroscopy, initial conversion of **2** to an intermediate identified as the vinyl ether complex,  $\text{Ir}(\text{CR}=\text{C}(\text{R})\text{CR}=\text{CR})(\text{PPh}_3)_2$  ( $=\text{C}(\text{CH}_2)_3\text{O}(\text{C}=\text{CHCH}_2\text{CH}_2\text{O})$ , **7**, is observed.<sup>10</sup> Complex **7** is then cleanly converted to **3** and **4** in a first-order process ( $k = 2.4 \times 10^{-4} \text{ s}^{-1}$ ), with no detection of additional intermediates.<sup>11</sup>

Reaction of  $\text{Ir}(\text{CR}=\text{C}(\text{R})\text{CR}=\text{CR})(\text{PPh}_3)_2(=\text{CCD}_2\text{CH}_2\text{CH}_2\text{O})_2^+\text{BF}_4^-$ , **2-d**, with  $\text{CH}_3\text{ND}_2$  in  $\text{CDCl}_3$  leads to formation of iridium hydride  $\text{Ir}(\text{CR}=\text{C}(\text{R})\text{CR}=\text{CR})(\text{PPh}_3)_2(\text{ND}_2\text{CH}_3)(\text{H})$ , **3-d**, with no spectroscopic evidence for the corresponding deuteride **3-d**. In addition, **4-d** is formed with deuterium incorporated only into the sites indicated (Scheme II). One mechanism consistent with all current information involves initial deprotonation of an oxacyclopentylidene ligand in **2-d** to give a neutral vinyl ether complex **7-d**, followed by migration of the vinyl ether ligand to the adjacent carbene carbon to give **8-d**.<sup>12</sup> A subsequent 1,3-iridium migration to give **9-d** and  $\beta$ -hydrogen abstraction would then generate **3-d** and **4-d**.

Mononuclear bis(carbene) complexes have previously been proposed as unobserved intermediates in the carbene coupling reactions of mononuclear mono(carbene) complexes.<sup>13,14</sup> To our knowledge the oxidative *cis*-carbene ligand coupling reported here represents one of the first examples of bis(carbene) ligand coupling of any type in an isolable mononuclear bis(carbene) complex.<sup>15</sup>

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**Supplementary Material Available:** Tables of characterization data for all new compounds, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters (8 pages); table of observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

(8) (a) Crystal data for **2** (293 K):  $\text{C}_{56}\text{H}_{54}\text{O}_{10}\text{P}_2\text{IrBF}_4\text{CHCl}_3$ , triclinic,  $P\bar{1}$ ,  $a = 12.951$  (2) Å,  $b = 13.371$  (2) Å,  $c = 18.071$  (4) Å,  $\alpha = 78.42$  (2)°,  $\beta = 79.27$  (2)°,  $\gamma = 78.14$  (1)°,  $V = 2966$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D(\text{calcd}) = 1.509$  g cm<sup>-3</sup>,  $\mu = 26.4$  cm<sup>-1</sup>. Using a pale brown crystal (0.27 × 0.31 × 0.36 mm), 10 702 data were collected (Nicolet R3m, Mo-K $\alpha$ ,  $4^\circ \leq 2\theta \leq 50^\circ$ ), 10 346 were unique ( $R_{\text{merge}} = 0.017$ ), and 7383 were observed ( $3\sigma F_o$ ) and corrected for absorption ( $T_{\text{max}}/T_{\text{min}} = 1.25$ ).  $R(F) = 4.35\%$ ,  $R(wF) = 4.87\%$ . (b) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

(9) The reaction workup involved evaporation of solvent and distillation ( $10^{-2}$  mmHg, 65 °C) of **4** from the brown residue. The residue was then washed with  $\text{CHCl}_3$  to separate **3** from  $\text{CH}_3\text{NH}_3^+\text{BF}_4^-$ .

(10) For **7** ( $\text{R} = \text{CO}_2\text{CH}_3$ ):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , -15 °C)  $\delta$  4.14 (t,  $J = 8.0$  Hz, 2 H), 3.69 (br s, 1 H), 3.44 (s, 3 H), 3.33 (s, 3 H), 3.26 (br, t,  $J = 9$  Hz), 3.21 (s, 3 H), 3.17 (s, 3 H), 2.91 (t,  $J = 8$  Hz, 2 H), 2.22 (br, t,  $J = 9$  Hz), and 1.28 (p,  $J = 8$  Hz, 2 H).

(11) When similar reaction of **2** ( $3.5 \times 10^{-2}$  M) and  $\text{CH}_3\text{NH}_2$  (0.29 M) in  $\text{CDCl}_3$  at -5 °C is monitored by  $^1\text{H}$  NMR spectroscopy conversion of **7** to **3** and **4** occurs with an observed first order rate constant of  $2.5 \times 10^{-4} \text{ s}^{-1}$ .

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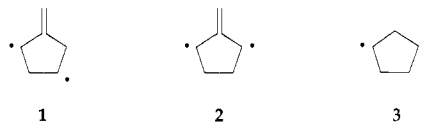
#### 4-Methylenecyclopentane-1,3-diyl: First Direct Observation of a Semilocalized Homotrimethylenemethane 1,3-Diradical

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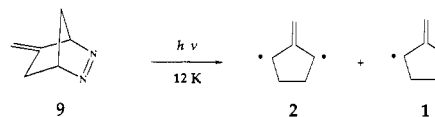
The semilocalized 1,3-diradical **1**<sup>1,2</sup> bridges the gap between delocalized trimethylenemethane diradicals<sup>3</sup> and localized 1,3-



diradicals.<sup>4</sup> We have now observed the electron spin resonance spectrum of the triplet **1**, and, since the experiments were carried out in the five-membered ring series, the physical and spectroscopic properties of **1** can be compared directly to the known diradicals **2** of Platz et al.<sup>5a</sup> and **3** of Buchwalter and Closs.<sup>4</sup> Indeed, there is a direct reactive link between the triplet diradical isomers **1** and **2** involving an apparent 1,2-hydrogen atom shift.

The azo precursor to **1** was prepared as follows (Scheme I): The adduct **4** of cyclopentadiene and di-*tert*-butyl azodicarboxylate was treated with  $\text{PdCl}_2$  and carbon monoxide in methanol.<sup>6,7</sup> The product mixture contained diester **5** (35%) and chloro ester **6** (18%), which were separated by column chromatography on silica gel.<sup>8</sup> Conversion of **6** to the desired azo compound **9** followed the sequence shown in Scheme I.<sup>8</sup>

The photolytic decomposition of the azo compound **9** was



carried out with use of a 1000 W Hg (Xe) lamp in conjunction with a monochromator set at  $340 \pm 10$  nm. The outcome of the photolysis depended upon the temperature, the composition of the matrix, the duration of photolysis, and the concentration of starting azo compound **9**. Irradiation of **9** at 77 K yielded only the rearranged trimethylenemethane **2** ( $D' = 285$  G).<sup>5</sup> Irradiation at 15 K in ethanol or glycerol glass also yielded the trimethylenemethane diradical rearrangement product **2**,<sup>5</sup> but evident in the wings of the spectrum was a weaker pair of lines corresponding to a diradical with  $D' = 635$  G. It seemed likely that this was the 1,3-semilocalized diradical **1**, partly masked by the more stable trimethylenemethane rearrangement product **2**. Photolysis of **9** in chloroform, isopentane, or methylcyclohexane matrices yielded

(1) For a thermal rearrangement involving the singlet state of **1**, see: Andrews, G. D.; Baldwin, J. E. *J. Org. Chem.* **1988**, *53*, 4624.

(2) Semilocalized (allyl + p) diradicals have been observed by the following: (a) Jain, R.; Sponsler, M. B.; Combs, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356. (b) Jain, R.; McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 552.

(3) Reviews: Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 151.

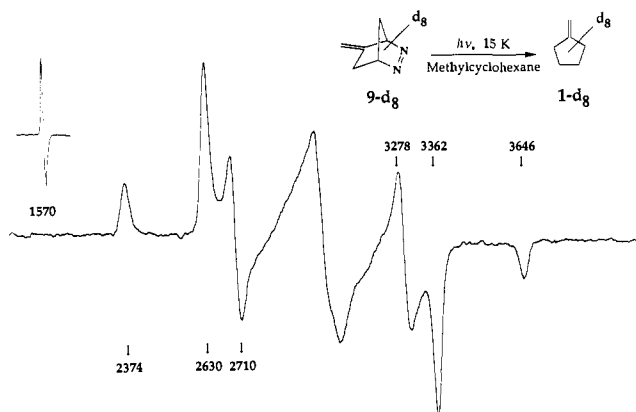
(4) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

(5) (a) Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5726. (b) The parent trimethylenemethane has  $D = 0.025$  cm<sup>-1</sup>. Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

(6) Stille, J. K.; Divakaruni, R. *J. Org. Chem.* **1979**, *44*, 3474. Stille, J. K.; James, D. E. *Transition Metal Catalyzed Carbonylation of Olefins. The Chemistry of Functional Groups, Supplement A. Double Bonded Functional Groups*, Patai, S., Ed.; Wiley: New York, 1976; p 1099.

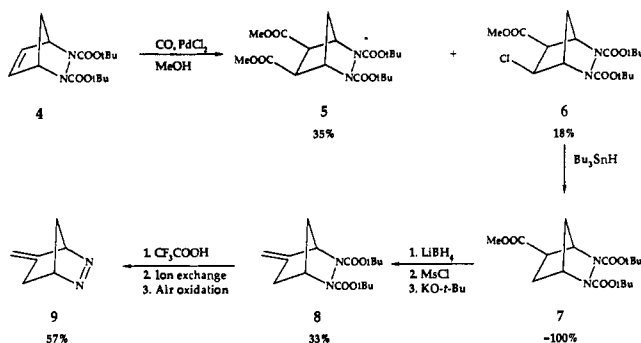
(7) Tsuji, J.; Morikawa, M. *Tetrahedron Lett.* **1963**, 1061. Tsuji, J.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4851.

(8) All new substances gave satisfactory spectral data.



**Figure 1.** ESR spectrum of  $1-d_8$  showing the line positions and the splitting expected of the  $x$  and  $y$  lines. The inset shows the  $\Delta m = 2$  transition at 1570 G.

### Scheme I



the desired semilocalized diradical **1** as the major product.<sup>9</sup> The ESR spectrum of the perdeuterated diradical  $1-d_8$  from photolysis of  $9-d_8$  in methylcyclohexane glass was also examined. The zero-field parameter  $E$  is not fully resolved in the  $1-h_8$  spectrum but is readily extracted from the spectrum of the perdeuterated derivative  $1-d_8$  (Figure 1). Thus, for **1**,  $D = 0.0591 \pm 0.0006 \text{ cm}^{-1}$  and  $E = 0.00254 \pm 0.00003 \text{ cm}^{-1}$ . The  $D$  value for **1** is approximately halfway between that of **2** ( $0.0265 \text{ cm}^{-1}$ )<sup>5a,b</sup> and **3** ( $0.084 \text{ cm}^{-1}$ )<sup>4</sup> and somewhat smaller than those for semilocalized four-membered ring diradicals.<sup>2</sup> The small value of  $E$  is typical of four- and five-membered ring diradicals<sup>2,4</sup> (e.g., **2**,  $E = 0.00550$ ; **3**,  $E = 0.0020$ ).

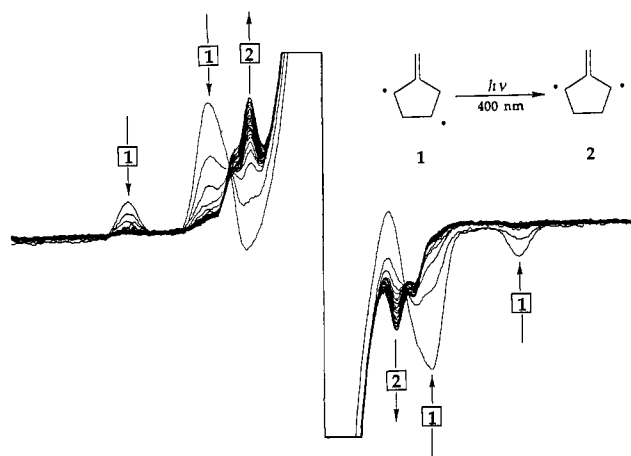
Determination of the Curie law behavior of **1** yields a straight line; therefore, **1** is a ground-state triplet.<sup>10</sup> The triplet **1** decomposes irreversibly at 40 K limiting the range of the Curie-Weiss plot.

The transformation from **1** to **2** is a triplet-triplet conversion. Therefore, the conversion of the semilocalized triplet diradical **1** to the more highly delocalized trimethylenemethane triplet **2** can be followed entirely using ESR (Figure 2). It was established in this way that in the isopentane matrix the rearrangement of **1** to **2** is a *photochemical reaction*.<sup>11</sup> The first photoproduct from the irradiation at 340 nm of **9** is the semilocalized diradical **1**. Continued irradiation of the diradical **1** at 340 nm results in a

(9) Cf.: Adam et al. (Adam, W.; Gunther, E.; Hössel, P.; Platsch, H.; Wilson, R. M. *Tetrahedron Lett.* 1987, 28, 4407) who reported photolysis of the 7,7-dimethyl-5-methylene-2,3-diazabicyclohept-2-ene in the presence of oxygen. They detected very little peroxide which would be indicative of trapping of diradical intermediates. Thus, the low-temperature ESR method may have the advantage, over oxygen trapping, of forestalling untoward decomposition pathways of the diradicals which would obscure their formation.

(10) It is also possible that singlet and triplet are degenerate.

(11) The very interesting rearrangement of 2,3-diazabicyclo[2.2.1]hept-2-ene-7-spirocyclopropane apparently also proceeds by a 1,2-hydrogen migration to yield a trimethylenemethane.<sup>2b</sup> The 1,2-shift is ascribed to a tunneling reaction from a vibrationally excited precursor. We cannot rule out the tunneling reaction, but, as in our experiments, deuterium substitution had little effect on the outcome of the reaction.<sup>2b</sup> Accordingly, a photoreaction might be important in this instance as well.



**Figure 2.** Photochemical isomerization of triplet **1** to triplet **2** by irradiation of 400 nm and 15 K. The matrix is methylcyclohexane.

decrease in **1** and an increase in the more stable triplet **2**. The chromophore in this transformation is probably the allyl radical which absorbs over the range 210–400 nm.<sup>12</sup> By irradiating the sample at 400 nm, triplet **1** was converted smoothly to **2** with isosbestic behavior (Figure 2). The azo compound **9** shows no sensitivity to light at 400 nm, so its photolysis does not intrude at that wavelength. This rules out the direct conversion of **9** to **2** which can, in principle, occur at 340 nm.

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## Selective Hydrocracking of Monosaccharide Carbon-Carbon Single Bonds under Mild Conditions. Ruthenium Hydride Catalyzed Formation of Glycols

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Carbohydrates exhibit unusually rich chemical functionality but limited stability. Homogeneous transition-metal catalysts should offer the unique combination of high selectivity and reactivity needed to effectively manipulate these important substrates. We show here how this relatively unexplored catalyst-substrate combination can be exploited to (a) accomplish the facile hydrocracking of specific C-C single bonds and (b) provide a foundation for new approaches to biomass conversion.

Fructose is readily hydrogenated (100 °C, 20 atm H<sub>2</sub>, *N*-methyl-2-pyrrolidinone solvent) in the presence of 0.02 equiv of H<sub>2</sub>Ru(PPh<sub>3</sub>)<sub>4</sub> (eq 1, Table I expt 1).<sup>1</sup> The expected products,

