precedent in acyclic and monocyclic systems.[3] We are tempted to associate this novel reactivity with the bridged structure of 2-norbornyl cations.[12] The well-known 6,2-shifts of hydrogen are parallelled by silyl groups, behaving as "super protons".

(12) For recent reviews, see: (a) Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661. (b) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. (c) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (d) Shubin, V. G. *Top. Curr. Chem.* **1984**, *116*, 267. (e) Brown, H. C. *The Nonclassical Ion Problem* (with comments by Schleyer, P. v. R.); Plenum: New York, 1977.

Oxidative Coupling of cis-Carbene Ligands: Synthesis, Structure, and Reactivity of an Iridium(III) Bis(oxacyclopentylidene) Complex

Joseph M. O'Connor* and Lin Pu

Department of Chemistry (D-006)
University of California, San Diego
La Jolla, California 92093

Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19716

The propensity of carbene ligands to engage in useful coupling reactions[1] has stimulated interest in the preparation, structure, and reactivity of mononuclear bis(alkoxycarbene) complexes.[2–4] Herein we report the application of alkynol cyclization methodology to the preparation of an iridium bis(carbene) complex, structural characterization of this complex and unprecedented base-induced carbene ligand coupling chemistry.

Previously we reported the reaction of 3-butyn-1-ol and Ir-(CR=CRCR=CR)(PPh₃)₂(CO)(NCCH₃)⁺BF₄⁻ (R = CO₂CH₃) to generate the carbene complex Ir(C-R=CRCR=CR)(PPh₃)₂(CO)(=C(CH₂)₃O)⁺BF₄⁻.[5] We have now utilized an iridium(III) precursor, 1, containing two labile cis-acetonitrile ligands in reaction with excess 3-butyn-1-ol to generate the first bis(alkoxycarbene) complex of iridium, Ir-(CR=CRCR=CR)(PPh₃)₂(=C(CH₂)₃O)₂⁺BF₄⁻, 2 (R = CO₂CH₃). Bis(carbene) 2 undergoes a remarkable base-induced ligand coupling reaction to give an iridium hydride complex 3 and 2-(2*H*)-furanylidene)tetrahydrofuran, 4, as a single stereoisomer.

When a chloroform solution of 3-butyn-1-ol (230 μL, 3.0 mmol) and bis(acetonitrile) complex 1 (630 mg, 0.54 mmol, 0.02 M)[6] is heated at 50 °C (3.5 h), conversion to bis(carbene) 2 occurs in 87% isolated yield.[7] The ¹H NMR spectrum of 2 in CD₃CN

(1) (a) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1987; Vol. 1. Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984.
(2) Cauchy, D.; Jean, Y.; Eisenstein, O.; Volatron, F. *Organometallics* **1988**, *7*, 829 and references therein.
(3) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172 and references therein.
(4) Struchkov, Y. T.; Aleksandrov, G. G.; Pukhanarevich, V. B.; Sushchinskaya, S. P.; Voronkov, M. G. *J. Organomet. Chem.* **1979**, *172*, 269. Fischer, E. O.; Reitmeier, R.; Ackermann, K. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 669.
(5) (a) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 7578. (b) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2060.
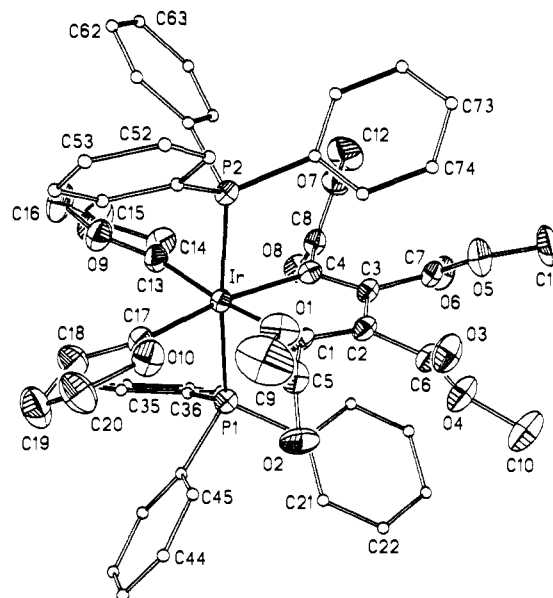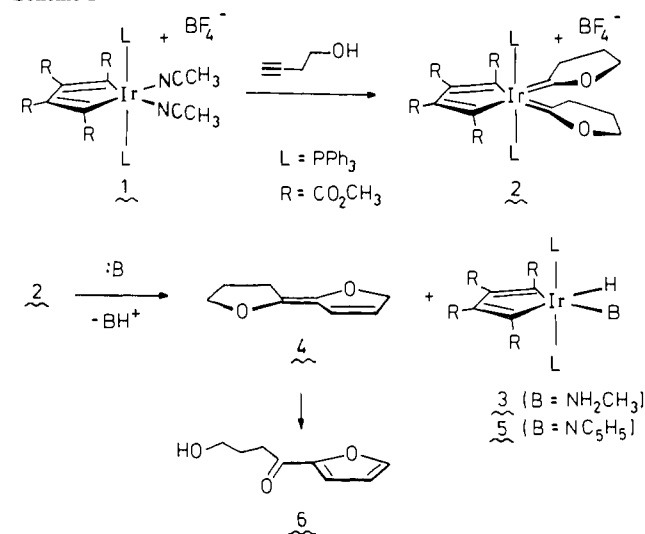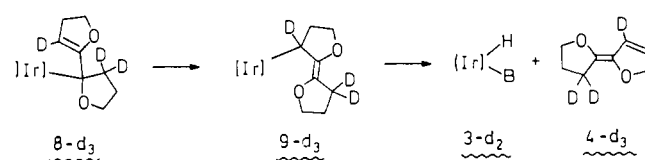(6) Compound 1 is prepared by AgBF₄ abstraction of halide from Ir-(CR=CRCR=CR)(PPh₃)₂Cl in CH₃CN solution.

Figure 1. Molecular structure and labeling scheme for **2**: Ir–C(1), 2.146 (7); Ir–C(4), 2.122 (6); Ir–C(13), 2.033 (8); Ir–C(17), 2.059 (7); C-(1)–Ir–C(4), 77.4 (3); C(1)–Ir–C(13), 174.9 (3); C(4)–Ir–C(13), 98.4 (3); C(1)–Ir–C(17), 94.0 (3); C(4)–Ir–C(17), 170.6 (3); C(13)–Ir–C-(17), 90.4 (3).

Scheme I

Scheme II

consists of one set of resonances for the hydrogens of the 2-oxa-cyclopentylidene ligands, indicative of either a symmetrical static structure or rapid rotation about the iridium carbene bonds on the NMR time scale. In the solid state, the 2-oxacyclopentylidene ligands in 2 are skewed such that the plane of the metallacycle bisects the plane of one carbene ring (C(13)–C(16), O(9)) at an angle of 29.4° and the second carbene ring at an angle of 31.5° (Figure 1).[8]

(7) Characterization data for **1–6** is provided as Supplementary Material.

Complex **2** (1.08 g, 0.88 mmol, 0.09 M) reacts with CH_3NH_2 (34.7 mmol) at 23 °C to give a nearly quantitative yield of the iridium hydride complex **3** (900 mg, 0.87 mmol), $CH_3NH_3{}^+BF_4{}^-$ (101 mg, 0.85 mmol), and the novel carbene coupling product **4** in 92% yield (112 mg, 0.81 mmol).[7,9] Pyridine also reacts with **2** to give **4** and iridium hydride **5**;[7] however, the reaction is much slower (20 h, 55 °C) and the yield lower (46%) than for CH_3NH_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 $CHCl_3$ 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.[7]

When the reaction of **2** (7.9×10^{-3} M) and CH_3NH_2 (0.19 M) in $CDCl_3$ is followed by low-temperature (−5 °C) ^1H NMR spectroscopy, initial conversion of **2** to an intermediate identified as the vinyl ether complex, Ir(CR=CRCR=CR)(PPh₃)₂-(=C̄(CH₂)₃O)(C̄=CHCH₂CH₂O), **7**, is observed.[10] Complex **7** is then cleanly converted to **3** and **4** in a first-order process ($k = 2.4 \times 10^{-4}$ s⁻¹), with no detection of additional intermediates.[11]

Reaction of Ir(CR=CRCR=CR)(PPh₃)₂(=C̄CD₂-CH₂CH₂O)₂⁺BF₄⁻, **2-*d₄***, with CH_3ND_2 in $CDCl_3$ leads to formation of iridium hydride Ir(CR=CRCR=CR)(PPh₃)₂-(ND₂CH₃)(H), **3-*d₂***, with no spectroscopic evidence for the corresponding deuteride **3-*d₃***. In addition, **4-*d₃*** 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-*d₄*** to give a neutral vinyl ether complex **7-*d₃*** followed by migration of the vinyl ether ligand to the adjacent carbene carbon to give **8-*d₃***.[12] A subsequent 1,3-iridium migration to give **9-*d₃*** and β-hydrogen abstraction would then generate **3-*d₂*** and **4-*d₃***.

Mononuclear bis(carbene) complexes have previously been proposed as unobserved intermediates in the carbene coupling reactions of mononuclear mono(carbene) complexes.[13,14] 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.[15]

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): $C_{56}H_{54}O_{10}P_2IrBF_4 \cdot CHCl_3$, 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) Å³, $Z = 2$, D(calcd) = 1.509 g cm⁻³, $\mu = 26.4$ cm⁻¹. Using a pale brown crystal (0.27 × 0.31 × 0.36 mm), 10 702 data were collected (Nicolet R3m, Mo·Kα, 4° ≤ 2q ≤ 50°), 10 346 were unique ($R_{merge} = 0.017$), and 7383 were observed ($3\sigma F_o$) and corrected for absorption ($T_{max}/T_{min} = 1.25$). 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 $CHCl_3$ to separate **3** from $CH_3NH_3{}^+BF_4{}^-$.

(10) For **7** (R = CO₂CH₃): ^1H NMR (CD₂Cl₂, −15 °C) δ 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** (3.5×10^{-2} M) and CH_3NH_2 (0.29 M) in $CDCl_3$ at −5 °C is monitored by ^1H NMR spectroscopy conversion of **7** to **3** and **4** occurs with an observed first order rate constant of 2.5×10^{-4} s⁻¹.

(12) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

(13) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. Connor, J. A.; Lloyd, J. P. *J. Chem. Soc. A* **1970**, 3237. Fischer, E. O.; Dötz, K. H. *J. Organomet. Chem.* **1972**, *36*, C4. Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

(14) Macomber, D. W.; Hung, M. H.; Verma, A. G.; Rogers, R. D. *Organometallics* **1988**, *7*, 2072.

(15) Huy, H. T.; Lefloch, P.; Louis, J. M.; Fetizon, M. *J. Organomet. Chem.* **1986**, *311*, 79.

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

Seung-Wook Ham, Wonghil Chang, and Paul Dowd*

*Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260*

Received December 8, 1988

The semilocalized 1,3-diradical **1**[1,2] bridges the gap between delocalized trimethylenemethane diradicals[3] and localized 1,3-
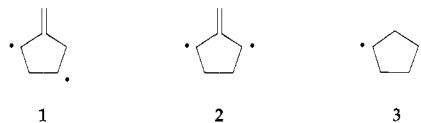
diradicals.[4] We have now observed the electron spin resonance spectrum of the triplet **1**, and, since the experiments were carried out in the five-membered ring series, the physical and spectroscopic properties of **1** can be compared directly to the known diradicals **2** of Platz et al.[5a] and **3** of Buchwalter and Closs.[4] Indeed, there is a direct reactive link between the triplet diradical isomers **1** and **2** involing 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 $PdCl_2$ and carbon monoxide in methanol.[6,7] The product mixture contained diester **5** (35%) and chloro ester **6** (18%), which were separated by column chromatography on silica gel.[8] Conversion of **6** to the desired azo compound **9** followed the sequence shown in Scheme I.[8]

The photolytic decomposition of the azo compound **9** was
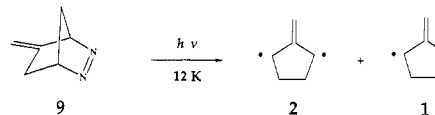
carried out with use of a 1000 W Hg (Xe) lamp in conjunction with a monochromator set at 340 ± 10 nm. The outcome of the photolysis depended upon the temperature, the composition of the matrix, the duration of photolysis, and the concentration of starting azo compound **9**. Irradiation of **9** at 77 K yielded only the rearranged trimethylenemethane **2** ($D' = 285$ G).[5] Irradiation at 15 K in ethanol or glycerol glass also yielded the trimethylenemethane diradical rearrangement product **2**,[5] 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.; Corns, 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⁻¹. Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

(6) (a) 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.