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Zinc-Induced Cyclizations of δ-Iodoacetylenes

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Summary: **Reaction of δ-iodoacetylenes with zinc resulted in substantial formation of (1-iodoalkylidene)cyclopentanes, presumably via radical intermediates. These results represent the first documented example of an iodine atom-transfer cyclization in the course of the formation of an organometallic reagent.**

We have long been interested in intramolecular reactions of free radicals and organometallic reagents possessing appropriately situated acetylene functions.[1] Such species can be obtained from the corresponding halides, which are readily available by classical acetylene chemistry. Cyclization reactions of free radicals of this type have been developed extensively over the past few years and have found numerous applications in synthesis, particularly for the construction of cyclopentane systems.[2] The compatibility of many functional groups with this radical chemistry is often a key consideration in these uses. Although the intramolecular carbometalations of acetylenes have been demonstrated with a variety of organometallic reagents,[3-9] these reactions have found limited utility in the synthesis of complex molecules. The advantage over the free-radical methodology of generating a more elaborate organometallic intermediate, capable of diverse further transformations, has not been generally exploited, owing in part to the incompatibility of ancillary functionality. Recent advances[10] in the accessibility of organozinc compounds and in the applications of these less reactive organometallic reagents in synthetic chemistry have prompted an examination of the reactions of alkynyl iodides of type 1 with zinc.

Results

Reactions of iodides 1 were generally performed with a 2-fold excess of acid-washed zinc[11] powder in dry benzene containing DMF at 50–60 °C. Reaction mixtures were either stirred magnetically or subjected to ultrasound agitation from a common laboratory cleaner. In most instances, the zinc was pretreated with a small amount of iodomethane for surface activation and removal of traces of water. The course of these reactions was monitored over several hours by quantitative gas chromatographic techniques, which generally showed good material balance. Hydrolysis, product isolation, and spectroscopic characterization followed.

Acetylenic iodide **1a**, with an alkyl substituent as the other group on the triple bond, eventually proved to be the most informative example studied. Thus, **1a** produced cyclic vinyl iodide **2a** in significant amounts, as well as the expected reduced acetylene **3a** and the regioselectively cyclized hydrocarbon **4a**. The amount of cyclic iodide **2a** varied in an important manner with the reaction conditions. For example, in a reaction of **1a** with zinc powder that was magnetically stirred at 58 °C, a 23% yield of cyclic iodide **2a** was present at a point where essentially all of starting iodide **1a** had been consumed. An increase in the yield of **2a** to 39% was observed when the reaction was sonicated rather than stirred. The substitution of a standard zinc–copper couple[12] further enhanced the yield of **2a** to 53%. Vinyl iodide **2a** was shown to be unreactive to zinc–copper couple, accounting for its accumulation in the reaction mixture. Control experiments demonstrated that pretreatment of the zinc with iodomethane did not significantly affect the amount of **2a** formed, nor did the use of ultrapure zinc, suggesting that transition-metal impurities are not of the utmost importance in this process.

On the other hand, iodomethane pretreatment did have a major influence on the nature of acyclic reduced species present in the reaction mixture. This was determined by treatment of the final reaction mixture with molecular iodine to reconvert any acyclic organozinc reagent **5a** back to starting iodide **1a**. In this manner, it was shown that employment of the iodomethane pretreatment resulted in essentially all of the acyclic species (>98%) being present as organozinc **5a** prior to the addition of water. Considerable and variable amounts of the acyclic acetylene **3a** were formed (50–70%) before hydrolysis in different experiments without this preliminary step. These observa-

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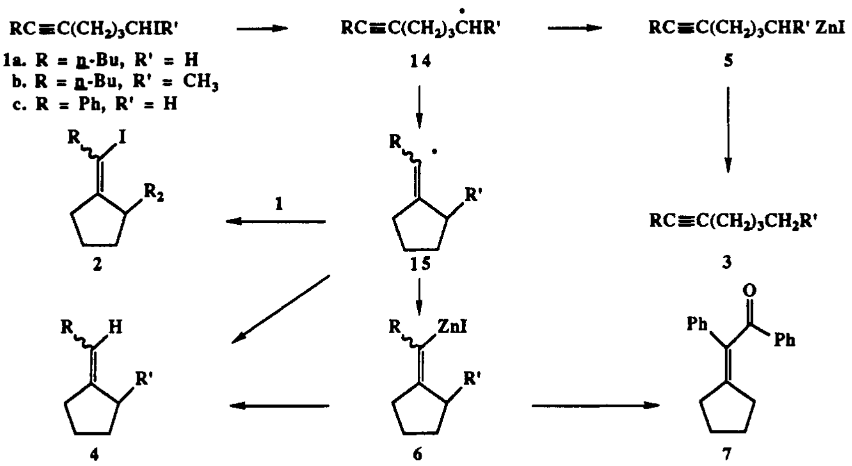
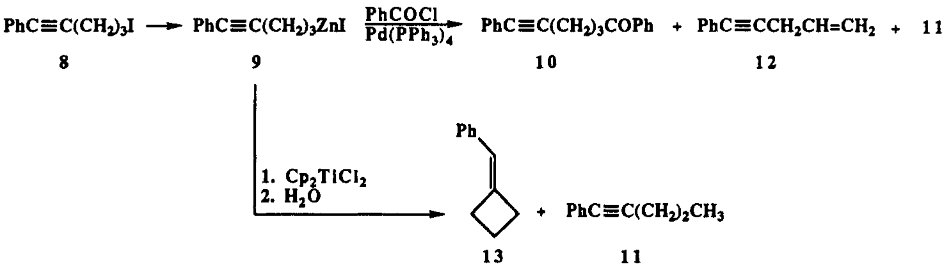
Scheme I



Scheme II



tions are consistent with premature reaction of organozinc reagent **5a** with unavoidable traces of water in the reaction mixtures. Disappointingly, no substantial cyclization of acyclic organozinc **5a** to its cyclic isomer **6a** could be demonstrated, even upon prolonged heating. This result illustrates the lower reactivity of organozinc **5a** with respect to the corresponding lithium and magnesium reagents.[1d-f,4,7]

The zinc-induced cyclization of **1a** to vinyl iodide **2a** appears to be related to the atom-transfer free-radical cyclization recently exploited by Curran.[13] Indeed, transformation of **1a** to **2a** was effected cleanly in 75% yield by irradiation in the presence of bis(tributyltin). Confirmation of the idea that a free-radical chain process is involved in the reaction of **1a** with metallic zinc was provided by an experiment in which styrene was added. Under these circumstances, the formation of cyclic iodide **2a** was almost completely suppressed, presumably by the scavenging of chain-propagating free radicals by styrene. The only important product in this reaction was the acyclic acetylene **3a**, which was largely present as organozinc **5a** as shown by its reaction with iodine.

Related results were found with the homologous secondary iodide **1b** upon reaction with zinc under ultrasound activation. In this instance, a 1.1:1 mixture of the isomeric (*E*)- and (*Z*)-vinyl iodides of structure **2b** was formed in 30% yield. The remainder of the product mixture consisted of acyclic acetylene **3b** and a 1.1:1 mixture of the isomeric cyclic hydrocarbons **4b**. The relative amounts of the two isomers of both **2b** and **4b** were invariant throughout the course of the reaction, as was the ratio of acyclic to cyclic hydrocarbons. The latter rules out cyclization of an intermediate organozinc. Treatment of **1b** with bis(tributyltin) gave the same 1.1:1 ratio of isomeric iodides **2b** in 93% yield.

Several experiments were also conducted with the related phenyl-substituted alkynyl iodide **1c**. Treatment of **1c** with zinc generated cyclic iodide **2c** in as much as 13% yield when the reaction was performed at 0 °C. However, this more activated vinyl iodide was itself converted into the corresponding vinylzinc reagent **6c** under these conditions, as shown by monitoring the products from **1c** as a function of time or by independent examination of cyclic iodide **2c** under similar reaction conditions. Unfortunately, this complication prevented an assessment of the potential cyclization of acyclic organozinc species **5c** with an activating phenyl substituent. Nonetheless, the overall process provides for a relatively clean conversion of **1c** to cyclic organozinc intermediate **6c**, which can be utilized in subsequent synthetic transformations.[14] For example, reaction of **6c** with iodine provided cyclic iodide **2c** in 87% overall yield based on **1c**, whereas acylation with benzoyl chloride in the presence of a Pd(0) catalyst gave conjugated ketone **7** in 85% yield.[15]

A brief study of the lower homologue **8** demonstrated that the acyclic organozinc reagent **9** could be obtained cleanly but that cyclization did not occur either during the formation of the organometallic or upon subsequent heating. This result is in accord with the lack of intramolecular addition of acetylenic radicals with this relative disposition of functions.[1d,2] Acyclic organozinc species **9** could be acylated with benzoyl chloride in the presence of catalytic Pd(0) to give ketone **10** in 72% yield; small amounts of alkyne **11** and enyne **12** were also isolated in this reaction. Most interestingly, cyclization of acyclic organozinc **9** could be induced by the addition of Cp_2TiCl_2;[3a,16] hydrolysis after heating for 6 h gave a 70:30

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[14] Knochel[6a] has observed cyclizations (attributed to radical processes) upon reaction of **1c** with zinc in THF as the solvent.

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mixture of cyclic (**13**) and acyclic (**11**) hydrocarbons. Further examination of the effects of titanium reagents in intramolecular additions to acetylenes would appear to be warranted.

Finally, several other metal powders were screened as potential promoters of the atom-transfer cyclization. Exposure of the more reactive secondary iodide **1b** to acid-washed chromium, copper, or iron powder under the conditions used with zinc did not initiate the reaction. However, an excess of cadmium powder promoted the facile conversion of secondary iodide **1b** to the usual 1.1:1 mixture of *E* and *Z* cyclic iodides **2b** (55% yield) after 1.5 h in refluxing benzene; no appreciable reduction to hydrocarbon products was observed with this less reactive metal. A similar transformation of primary iodide **1a** provided cyclic iodide **2a** in 47% yield, albeit at a substantially slower rate.

Discussion

The chemistry observed in the reactions of **1** with metallic zinc is attributed to the intervention of free-radical intermediates,[17] as is generally assumed with the more reactive metals lithium and magnesium.[18] Thus, reduction of **1** at the zinc surface produces acyclic radical **14**, some of which escapes into the solution. Further reduction of **14**, either prior to leaving or upon back-diffusion to the metal surface,[18a] generates the acyclic organozinc **5**. The fact that acyclic hydrocarbon **3** was not observed prior to hydrolysis in experiments employing iodomethane pretreatment of the zinc suggests that hydrogen abstraction by **14** is not a competitive process under these reaction conditions. However, the facile cyclization of **14** to vinyl radical **15** is a viable competing reaction.[2d] Thermodynamically favorable and kinetically rapid[2a,13] atom transfer of iodine from **1** to **15** yields cyclic iodide **2** and regenerates acyclic radical **14**, which propagates the radical-chain process. Other possible modes of reaction for **15** include reduction to organozinc **6** at the metal surface and hydrogen abstraction from suitable donors to give cyclic hydrocarbon **4** directly. It has been convincingly argued[19] that very few radicals need be generated in solution in order to obtain high yields of radical products such as **2**, so long as the chain lengths of the radical-chain processes are on the order of 100 or so. This is a reasonable scenario, given the high rate constants for both cyclization and iodine transfer. Furthermore, only a small increase in the number of acyclic radicals in solution, whether from sonochemically induced diffusion[17d] or a change in the morphology of the zinc surface,[20] can lead to the formation of substantially more cyclic iodide **2**. Thus, iodine atom transfer is shown to be an important process during the formation of an organometallic reagent for the first time. This phenomenon further complicates the understanding of this complex transformation, at least with alkyl iodides. It is interesting that cadmium, which does not lead to the formation of organometallic compounds under the conditions used,[21] also induces atom-transfer cyclization.

From a synthetic point of view, it was disappointing that the acyclic organozinc **5** did not undergo cyclization to the vinyl organozinc **6**. However, Knochel has recently shown that organozinc reagents of type **5** (prepared in THF solution from iodides **1**)[22] can be converted to the corresponding cyclic organocopper species by transmetalation with $Li_2Cu(CH_3)_2CN$.[5] Given the much greater synthetic utility of the organocopper reagents, this appears to be the method of choice in synthetic applications.

Experimental Section

General Considerations. ^1H NMR spectra were recorded on $CDCl_3$ solutions using either a Varian XL-300, a Varian VXR 400s, or a Bruker AM-500 spectrometer; ^{13}C NMR spectra were also recorded on these instruments. Analytical gas chromatography was performed on either a Varian 3700 or a Hewlett-Packard 5890 instrument equipped with a flame-ionization detector and a Hewlett-Packard Model 3390 or Model 3396 integrator. The analytical columns used were 50 m × 0.25 mm × 0.25 μm DB-5, 30 m × 0.32 mm × 0.25 μm DB-1701, and 50 m × 0.20 mm × 0.25 μm HP-5 fused silica capillary columns. Benzene was distilled from CaH_2 under a nitrogen atmosphere. Dry dimethylformamide (DMF) was obtained by distillation from BaO and stored over 4-Å molecular sieves. Zinc powder was supplied from MCB Manufacturing Chemists, Mallinckrodt, Inc., or Aldrich Chemical Co. This zinc was acid-washed or converted into a zinc–copper couple by literature methods.[11,12] Zinc of 99.99% purity was donated by La Vielle Montagne, 12110 Aubin, France, and used as received. Cadmium powder was purchased from Aldrich. Sonication was accomplished by the partial immersion of the reaction flask into a Bransonic 220 laboratory cleaner filled with water. Flash chromatography was performed on silica gel of 230–400 mesh supplied from Merck.

General Procedure for Metal-Promoted Cyclizations. The metal (2.3 equiv) in a two-neck round-bottomed flask was flame-dried under a rapid flow of nitrogen. Benzene and DMF (15:1) were added, followed by 0.2 equiv of iodomethane. The mixture was sonicated or stirred for 2–3 h at the indicated temperature to ensure that the iodomethane had been consumed. A GC standard (decane for **1a** and **1b**, dodecane for **1c**) and ca. 1.0 equiv of iodide **1** were introduced. Aliquots were removed periodically, hydrolyzed, and analyzed by GC. The products were characterized by isolation or GC retention-time comparison with authentic samples and in some cases by GC–MS comparison.

Reaction of 1a with Zinc. A. A slurry of 150 mg (2.3 mmol) of Zn and 44 mg (0.31 mmol) of iodomethane in 3 mL of benzene containing 0.2 mL of DMF was sonicated at 50 °C for 3 h before iodide **1a** (262 mg, 1.0 mmol) was added. After 6 h, iodine (600 mg, 4.2 mmol) in 3 mL of THF was introduced. GC analysis of aliquots gave the following relative amounts of **1a**:**2a**:**3a**:**4a**: 2 h (<1:39:50:11), 4 h (<1:38:48:14); after reaction with iodine (53:37:<1:10).

B. Iodide **1a** (949 mg, 3.6 mmol) was added to a sonicated slurry of zinc–copper couple (600 mg, 9.5 mmol) at 50 °C in 12 mL of benzene containing 0.8 mL of DMF. (The zinc–copper couple had been pretreated under sonochemical conditions at 50 °C for 2 h with 91 mg of iodomethane.) Aliquots provided the following relative amounts of **1a**:**2a**:**3a**:**4a**: 1 h (<1:53:35:21), 12 h (<1:53:30:16), 24 h (<1:54:27:17), 72 h (<1:56:25:18).

C. Iodide **1a** (234 mg, 0.85 mmol) was added to a magnetically stirred slurry of Zn (150 mg, 2.3 mmol) at 58 °C in 3 mL of benzene containing 0.2 mL of DMF. (The zinc had been pretreated with 26 mg of iodomethane at 58 °C for 2 h.) Aliquots provided the following relative amounts of **1a**:**2a**:**3a**:**4a**: 1 h (6:22:43:10), 2.5 h (2:23:51:15).

D. Iodide **1a** (238 mg, 0.88 mmol) was added to a sonicated slurry of Zn (150 mg, 2.3 mmol) in 3 mL of benzene containing 0.2 mL of DMF at room temperature. The bath temperature had increased to 50 °C after 1 h. After 4 h, iodine (640 mg, 2.4 mmol)

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(21) For a leading reference on direct organocadmium formation see: Burkhardt, E. R.; Rieke, R. D. *J. Org. Chem.* **1985**, *50*, 416.

(22) The careful examination of **1a** under Knochel's conditions[6] also showed the generation of **2a** during organozinc formation.

in 3 mL of THF was added. GC analysis gave the following relative amounts of **1a**:**2a**:**3a**:**4a**: 0.5 h (21:26:39:2), 1.5 h (4:29:53:5), 2.5 h (1:28:53:8); after reaction with iodine (29:25:30:7).

E. Iodide **1a** (243 mg, 0.89 mmol) was added to a sonicated slurry of 99.99% zinc (150 mg, 2.3 mmol) at room temperature. The temperature of the bath had risen to 50 °C after 1 h. After 4 h, the mixture was cooled to room temperature and iodine (640 mg, 2.4 mmol) was introduced. GC analysis gave the following relative amounts of **1a**:**2a**:**3a**:**4a**: 0.5 h (57:9:26:<1), 1.5 h (11:27:52:3), 2.5 h (3:27:52:4); after reaction with iodine (20:25:42:4).

F. Iodide **1a** (254 mg, 0.95 mmol) and styrene (88 mg, 0.85 mmol) were added to a slurry of zinc (150 mg, 2.3 mmol) in 3 mL of benzene containing 0.2 mL of DMF. The mixture was stirred at 58 °C for 4 h. The mixture was cooled to room temperature, and iodine (600 mg, 2.4 mmol) in 3 mL of THF was introduced. GC analysis gave the following relative amounts of **1a**:**2a**:**3a**:**4a**: 1 h (31:2:55:<1), 2 h (8:2:78:1), 3 h (3:2:84:2); after reaction with iodine (70:1:17:2).

Reaction of 2a with Zinc–Copper Couple. To a sonicated mixture of 150 mg (2.3 mmol) of zinc–copper couple in 3 mL of benzene containing 0.2 mL of DMF at 50 °C (pretreated with 47 mg of iodomethane) was added 119 mg (0.45 mmol) of **2a**. GC analysis of aliquots removed after 1.75, 4, and 6 h showed no reaction of **2a**.

Reaction of 1c with Zinc. To a sonicated mixture of 150 mg (2.3 mmol) of zinc in 3 mL of benzene containing 0.2 mL of DMF at 0 °C (pretreated with 34 mg of iodomethane) was added 291 mg (1.0 mmol) of **1c**. GC analysis gave the following amounts of **1c**:**2c**:**3c**:**4c**: 10 min (53:7:13:9), 30 min (23:13:16:34), 1 h (13:12:15:50), 2 h (5:7:14:67).

Reaction of 2c with Zinc–Copper Couple. To a sonicated mixture of 150 mg (2.3 mmol) of zinc–copper couple in 3 mL of benzene containing 0.2 mL of DMF at 50 °C (pretreated with 50 mg of iodoethane) was added a 15:1 mixture of **2c**:**4c**. GC showed an 11:1 mixture of **2c**:**4c** after 2 h, which was transformed to a 7:1 mixture of **2c**:**4c** after 5 h.

Reaction of 1b with Zinc. Iodide **1b** (248 mg, 0.89 mmol) was added to a sonicated slurry of zinc in 3 mL of benzene containing 0.2 mL of DMF at 50 °C (pretreated with 31 mg of iodomethane). GC analysis showed that the ratios of isomers of **2b** and **4b** remained constant throughout the course of the reaction at 1.1:1 for both **2b** and **4b**. The following relative amounts of **1b**:**2b**:**3b**:**4b** were observed: 0.17 h (<1:27:42:17), 1.5 h (<1:29:40:25).

Reaction of 1b with Cadmium. A mixture of **1b** (229 mg, 0.82 mmol) and cadmium powder (1.0 g, 9.0 mmol) in 3 mL of benzene containing 0.2 mL of DMF was refluxed for 1.5 h. Saturated NH_4Cl solution was added, and the organic phase was washed with brine, dried (Na_2SO_4), and concentrated. Flash chromatography with pentane as eluant gave 126 mg (55%) of a 1.1:1 isomeric mixture of (*E*)- and (*Z*)-**2b**.

Reaction of 1a with Cadmium. A mixture of **1a** (254 mg, 0.96 mmol) and cadmium powder (1.0 g, 9.0 mmol) in 3 mL of benzene containing 0.2 mL of DMF was refluxed for 10 h. The mixture was cooled to room temperature, and saturated NH_4Cl solution was added. The organic phase was dried (Na_2SO_4) and concentrated. Flash chromatography using pentane as eluant gave 120 mg (47%) of **2a**.

(1-Phenylphenacylidene)cyclopentane (7). To 150 mg of zinc powder in 3 mL of benzene containing 0.2 mL of DMF (pretreated with 57 mg of iodomethane) was added 270 mg (0.95 mmol) of **1c**. The mixture was heated at 58 °C for 5 h and cooled to room temperature, and a mixture of 189 mg (1.35 mmol) of benzoyl chloride and 240 mg (0.2 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene was introduced. After 2 h, saturated NH_4Cl solution was added and the organic phase was washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography using an ether/pentane gradient gave 206 mg (85%) of **7**: mp 61–63 °C; ^{1}H NMR δ 7.91 (m, 2), 7.49–7.20 (m, 8), 2.60–2.52 (m, 2), 2.40–2.32 (m, 2), 1.69 (m, 4); ^{13}C NMR δ 198.2, 149.7, 138.0, 137.2, 132.7 (2), 129.6 (2), 128.5 (2), 128.3 (3), 128.1, 126.9, 32.9, 26.4, 26.3; IR 1659, 1599 cm^{-1}; MS *m/z* (relative intensity) 262 (100), 261 (45), 233 (45), 129 (43), 128 (29), 115 (39), 105 (55); exact mass 262.136, calcd for $C_{19}H_{18}O$ 262.1358.

(1-Iodobenzylidene)cyclopentane (2c).[1b] A mixture of 253 mg of **2c** and 150 mg of zinc in 3 mL of benzene containing 0.2 mL of DMF (pretreated with 36 mg of iodomethane) was heated at 55 °C for 4.5 h. After the mixture was cooled to room temperature, 600 mg of iodine in 3 mL of THF was introduced. Water and pentane were added to the mixture, and the organic layer was washed with brine, dried (Na_2SO_4), and concentrated. Flash chromatography with pentane as eluant gave 219 mg (87%) of **2c**: ^{1}H NMR δ 7.40–7.18 (m, 5), 2.50–2.45 (m, 2), 2.34–2.30 (m, 2), 1.82–1.74 (m, 4).

1,6-Diphenyl-5-hexyn-1-one (10). A mixture of 582 mg (2.2 mmol) of **8** and 300 mg (4.6 mmol) of zinc in 9 mL of benzene containing 0.5 mL of DMF (pretreated with 66 mg of iodomethane) was heated at 60 °C for 4.5 h. The mixture was cooled to room temperature, and a solution of 332 mg (2.35 mmol) of benzoyl chloride and 190 mg (0.2 mmol) of $Pd(PPh_3)_4$ in 3 mL of benzene was added. After 1.5 h, saturated NH_4Cl solution was added and the organic phase was washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography using 1:1 ether/pentane as eluant gave 388 mg (72%) of **10**: ^{1}H NMR δ 8.00 (m, 2), 7.56–7.27 (m, 8), 3.17 (t, 2, J = 7 Hz), 2.57 (t, 2, J = 7 Hz), 2.07 (quint, 2, J = 7 Hz); ^{13}C NMR δ 199.3, 136.8, 132.8, 131.4 (2), 128.3 (2), 128.0 (2), 127.8 (2), 127.5, 123.6, 89.2, 81.3, 37.1, 23.0, 18.8; IR 2210, 1682 cm^{-1}; MS *m/z* (relative intensity) 248 (16), 220 (15), 128 (100), 120 (40), 105 (90); exact mass 248.123, calcd for $C_{18}H_{16}O$ 248.1202. Also isolated was 95 mg (28%) of a 70:30 mixture of **11** and **12**.

Reaction of 8 with Zinc and Cp_2TiCl_2. A mixture of **8** (596 mg, 2.21 mmol) and zinc (200 mg, 3.1 mmol) in 9 mL of benzene containing 0.5 mL of DMF (pretreated with 66 mg of iodomethane) was heated at 58 °C for 15 h. GC analysis of a hydrolyzed aliquot showed only **11**. Cp_2TiCl_2 (630 mg, 2.5 mmol) in 5 mL of THF was added. After 6 h, saturated NH_4Cl solution was added and the organic phase was washed with brine, dried ($MgSO_4$), and concentrated. GC and ^{1}H NMR measurements showed a 70:30 mixture of **13**[23]:**11** in good yield. In a separate experiment, attempted reaction of an organometallic intermediate with benzaldehyde gave an 85:15 mixture of **13**:**11**, from which the cyclic hydrocarbon **13** was isolated in 55% yield: ^{1}H NMR δ 7.38–7.30 (m, 2), 7.26–7.15 (m, 3), 6.13 (m, 1), 3.10 (m, 2), 2.94 (m, 2), 2.16 (quint, 2, J = 8 Hz); IR 1675 cm^{-1}.

(1-Iodopentylidene)cyclopentane (2a).[24] A solution of 231 mg (0.88 mmol) of **1a** and 50 mg (0.09 mmol) of bis(tributyltin) in 3 mL of benzene was heated to reflux with an infrared lamp for 2 h. Concentration and chromatography using hexane as eluant gave 173 mg (75%) of **2a**: ^{1}H NMR δ 2.42 (t, 2, J = 7 Hz), 2.35–2.25 (m, 4), 1.82 (quint, 2, J = 7 Hz), 1.66 (quint, 2, J = 7 Hz), 1.55–1.42 (m, 2), 1.37–1.25 (m, 2), 0.92 (t, 3, J = 7 Hz); IR 1645 cm^{-1}.

1-(1-Iodopentylidene)-2-methylcyclopentane (2b). In a similar fashion, 471 mg (1.69 mmol) of **1b** and 20 mg (0.03 mmol) of bis(tributyltin) gave 438 mg (93%) of a 1.1:1 isomeric mixture of (*E*)- and (*Z*)-**2b**. The stereochemical assignment is based on an nuclear overhauser effect (NOE) experiment involving irradiation of the exocyclic allylic methylene (=CIC*H*$_2$), where enhancement of the methinyl proton (C*H*CH$_3$) was observed for only the *E* isomer. Signals in the ^{1}H NMR spectrum are assigned as follows: *E* isomer δ 2.87 (m, 1), 2.48–2.16 (m, 4), 1.91–1.22 (m, 8), 1.01 (d, 3 J, = 7 Hz), 0.93 (t, 3, J = 7 Hz); *Z* isomer δ 2.68 (m, 1), 2.48–2.16 (m, 4), 1.91–1.22 (m, 8), 1.04 (d, 3, J = 7 Hz), 0.92 (t, 3, J = 7 Hz). ^{13}C NMR: δ 153.1, 152.3, 99.9, 96.7, 45.2, 41.7, 40.9, 40.8, 37.5, 35.1, 33.3, 32.5, 31.3, 30.6, 25.0, 22.6, 21.7, 21.5, 20.0, 18.4, 14.1 (2). IR: 1645 cm^{-1}. GC–MS (*m/z* (relative intensity)): *E* isomer 278 (10), 151 (11), 109 (44), 95 (100), Exact mass 278.055; *Z* isomer 278 (10), 151 (29), 109 (37), 95 (100), exact mass 278.053; calcd for $C_{11}H_{19}I$ 278.0533.

1-Pentylidene-2-methylcyclopentane (4b). A mixture of 200 mg (0.72 mmol) of **2b** and 220 mg (0.75 mmol) of Bu_3SnH was gently warmed. Vacuum transfer gave 50 mg (55%) of a 1.3:1 mixture of (*E*)- and (*Z*)-**4b**. The stereochemical assignment is based on an NOE experiment involving irradiation of the methyl groups on the cyclopentane ring, where enhancement of the vinyl proton was observed for only the *E* isomer. IR: 2980, 2860, 1440 cm^{-1}; GC–MS (*m/z* (relative intensity)): *Z* isomer 152 (48), 109 (30), 96 (18), 95 (100), 82 (31), 81 (57), 67 (43), exact mass 152.161;

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E isomer 152 (33), 109 (30), 96 (20), 95 (100), 82 (30), 81 (63), 67 (44), exact mass 152.157; calcd for $C_{11}H_{20}$ 152.1566. Signals in the NMR spectra are assigned as follows. ^{1}H NMR: *Z* isomer δ 5.16 (m, 1), 2.65 (m, 1), 2.38–2.10 (m, 2), 2.06–1.93 (m, 2), 1.89–1.48 (m, 4), 1.33–1.28 (m, 2), 1.18–1.09 (m, 2), 0.93 (d, 3, J = 7 Hz), 0.88 (t, 3, J = 7 Hz); *E* isomer δ 5.10 (m, 1), 2.38–2.10 (m, 3), 2.06–1.93 (m, 2), 1.89–1.48 (m, 4), 1.33–1.28 (m, 4), 1.01 (d, 3, J = 7 Hz), 0.88 (t, 3, J = 7 Hz). ^{13}C NMR: *Z* isomer δ 147.9, 120.4, 35.1, 34.6, 33.3, 29.1, 28.8, 24.1, 22.5, 19.1, 14.1; *E* isomer δ 147.8, 119.4, 38.8, 35.6, 32.4, 32.0, 29.0, 24.0, 22.4, 20.7, 14.1.

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Registry No. 1a, 42049-41-2; **1b**, 136954-13-7; **1c**, 57718-12-4; **2a**, 94012-69-8; (*E*)-**2b**, 136954-14-8; (*Z*)-**2b**, 136954-15-9; **2c**, 57718-22-6; **3a**, 1942-46-7; **3b**, 2294-72-6; **3c**, 1129-65-3; **4a**, 53366-55-5; (*E*)-**4b**, 136954-16-0; (*Z*)-**4b**, 136954-17-1; **4c**, 4410-77-9; **7**, 136954-18-2; **8**, 34886-50-5; **10**, 136954-19-3; **11**, 4250-81-1; **13**, 5244-75-7.

Variable-Temperature One- and Two-Dimensional ^{13}C NMR Studies on $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$: Mechanism of Carbonyl Migration

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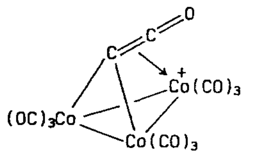
Summary: The 125.7-MHz ^{13}C NMR spectrum of $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ at −90 °C exhibits a 1:2:1:2:2 carbonyl pattern consistent with the triply bridged structure found in the solid state. The coalescence behavior of the ^{13}CO resonances can be simulated by invoking a mechanism in which a completely bridge-opened structure is required; local rotation of each $Co(CO)_3$ vertex is shown to be rapid. 2D-EXCHANGE spectroscopy is used as an independent probe for the fluxional processes and shows that, in accord with the bridge-opened model, all carbonyl sites do not exchange at the same rate. It is also demonstrated that rotation about the cobalt–phosphorus and P–C_{ipso} bonds is slowed on the NMR time scale.

The fluxional behavior of carbonyl ligands on metal cluster surfaces has attracted much attention for a considerable number of years. Some very fine experimental data have emerged; especially notable are the ingenious and elegant experiments carried out to elucidate the carbonyl scrambling mechanisms in heavy metal clusters.[1] Moreover, the thought-provoking ideas of Johnson and Benfield may give us cause to reevaluate our models of fluxionality in metal clusters.[2] Nevertheless, the situation is much less clear for carbonyl-capped tricobalt systems in which not only local rotation of $Co(CO)_3$ vertices but also intermetallic carbonyl migrations have such low barriers that the ^{13}CO NMR spectrum in solution is almost invariably a single line even at very low temperatures. Very recently, the 9-fold degeneracy of the carbonyl ligands in $[Co_3(CO)_9CC{=}O]^+$ (**1**) and in $Co_3(CO)_9CCH(C_6H_4Cl)_2$ (**2**) has been split to give in each case a 6:3 pattern at low temperature.[3,4] Although these results yield valuable structural information, they do not provide unequivocal answers to mechanistic questions.



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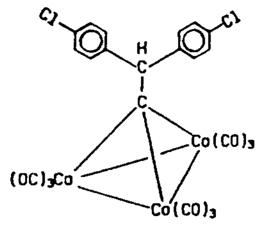

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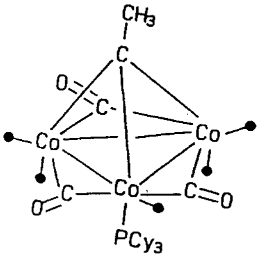
To our knowledge, the only other carbynyl–tricobalt cluster showing well-defined fluxional behavior is $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ which has the triple-bridged structure **3** in the solid state.[5] ^{13}C NMR measurements on **3** at 25 MHz suggested[6] that the low-temperature limiting spectrum would yield a 1:2:1:2:2 pattern for the carbonyl resonances, consistent with the solid-state structure. These data prompted us to initiate a study using high-field instrumentation which might allow a more complete analysis of the molecular dynamics of this system.



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