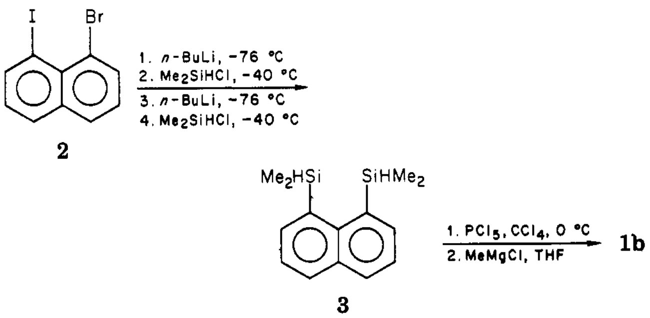
Scheme I



was logical then that interest should accrue to the silicon, germanium, and tin analogues of **1a**. Recently, the heavier congeners, **1c**[3] and **1d**,[4] have been prepared and fully characterized, including structural determinations by X-ray crystallography[5] and conformational analyses by NMR spectroscopy.[6] Both compounds show deviations from planarity but are significantly less distorted than **1a**, i.e., **1a** $\gg$ **1c** > **1d**.[5] The rotation barriers decrease in the same order,[6,7] a trend opposite to that predicted.[8] Most useful would be a study of **1b** for comparison purposes.

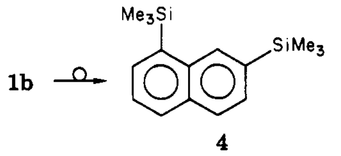
In this communication we report the successful synthesis of the elusive member of this series, 1,8-bis(trimethylsilyl)naphthalene (**1b**), and its facile rearrangement to the 1,7-isomer **4**. Earlier work[4] describing the preparation of **1b** from 1,8-dilithionaphthalene was reinvestigated,[9] and it was found that the product of that reaction was actually 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane.

Our approach to the synthesis of **1b** was a stepwise lithiation–silation procedure similar to one we recently described for the preparation of disilaacenaphthenes.[10] In this case we used the smaller dimethylchlorosilane as the silating agent to generate **3**. The structure of **3** was deduced from elemental analysis and mass spectral and ^{1}H NMR data. Chlorination of both Si–H functions with PCl_5[11] followed by methylation led to **1b** (Scheme I). This compound was obtained in ~25% yield (isolated, >98% pure) based on **2**.

The structure of **1b** is deduced mainly from spectroscopic data: ^{1}H NMR (90 MHz, CCl_4, acetone) δ 0.32 (s, 18 H, $SiCH_3$), 7.30–7.90 (m, 6 H, aromatic); ^{13}C NMR (90 MHz, $CDCl_3$) δ 3.18 (CH_3), 123.51, 130.34, and 136.26 (proton bearing aromatic carbons), 133.26, 139.70, and 141.26 (quaternary carbons). The off-resonance decoupled spectrum showed a quartet at δ 3.18 and doublets at δ 123.51, 130.34, and 136.26 supporting these assignments. The spectrum of **1b** was compared to that of the germanium analogue **1c** and found to be very similar.

Compositional data on **1b** were also obtained. Anal. Calcd for $C_{16}H_{24}Si_2$: C, 70.51; H, 8.88; Si, 20.61. Found: C, 70.49; H, 8.87; Si, 20.65. Mass spectral analysis (70 eV) showed an intense peak at 272, assignable to the molecular ion, M^+, and the base peak at 257, $M - CH_3^+$.

1,8-Bis(trimethylsilyl)naphthalene is a white crystalline solid (mp 64–66 °C) which can be purified by crystallization from methanol or by preparative gas chromatography. It was in using the latter technique that we accidentally discovered that **1b** rearranges to the 1,7 isomer **4** at temperatures above 150 °C. When the column (6 ft × 0.25 in., 5% SE-30 on Chromosorb W) is kept above 200 °C, the isomerization is quantitative. Complete conversion to **4** can also be effected by heating a solution of **1b** in carbon tetrachloride at 150 °C for 1 h. The structural assignment is based on mass spectral data and the comparison of its NMR spectrum with that of an authentic sample. This appears to be a simple thermal reaction although we have not yet ruled out the presence of traces of acid that could catalyze the isomerization. Relevant to this is the known acid-catalyzed rearrangement of 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane to 2-(2-naphthyl)-2,4,4-trimethyl-2,4-disilapentane,[12] a reaction originally believed[4] to be the **1b** → **4** transformation we report here.



Determination of the molecular structure of **1b** by diffraction methods, conformational analysis by NMR, and further study of the 1,8 → 1,7 rearrangement are now in progress.

Acknowledgment. We are most grateful to Kurt Mislow for the discussions that led to our undertaking this project and for generously supplying samples and spectra of 1,8-bis(trimethylgermyl)naphthalene and 1,7-bis(trimethylsilyl)naphthalene. We also thank Vern Feil for the ^{13}C NMR spectra. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. **1b**, 65197-00-4; **2**, 4044-58-0; **3**, 78685-92-4; **4**, 65197-02-6.

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(2) Handal, J.; White, J. G.; Franck, R. W.; Yuh, U. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 3345.

(3) Cozzi, F.; Sjöstrand, U.; Mislow, K. *J. Organomet. Chem.* **1979**, *174*, C1.

(4) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *141*, 1973.

(5) Blount, J. F.; Cozzi, F.; Damewood, J. R., Jr.; Iroff, L. D.; Sjöstrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 99.

(6) Anet, F. A. L.; Donovan, D.; Sjöstrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 1748.

(7) Anderson, J. E.; Franck, R. W.; Mandella, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 4608.

(8) Hutchings, M. G.; Watt, I. *J. Organomet. Chem.* **1979**, *177*, 329.

(9) Wroczynski, R. J.; Baum, M. W.; Kost, D.; Mislow, K.; Vick, S. C.; Seyferth, D. *J. Organomet. Chem.* **1979**, *170*, C29.

(10) Kiely, J. S.; Boudjouk, P. *J. Organomet. Chem.* **1979**, *182*, 173.

(11) Mawaziny, S. *J. Chem. Soc. A* **1970**, *9*, 1641.

(12) Sjöstrand, U.; Cozzi, F.; Mislow, K. *J. Organomet. Chem.* **1979**, *179*, 323.

Carbon-to-Carbon Migration of the Dimetallic Group in Dinuclear Cobalt Alkylidene Complexes

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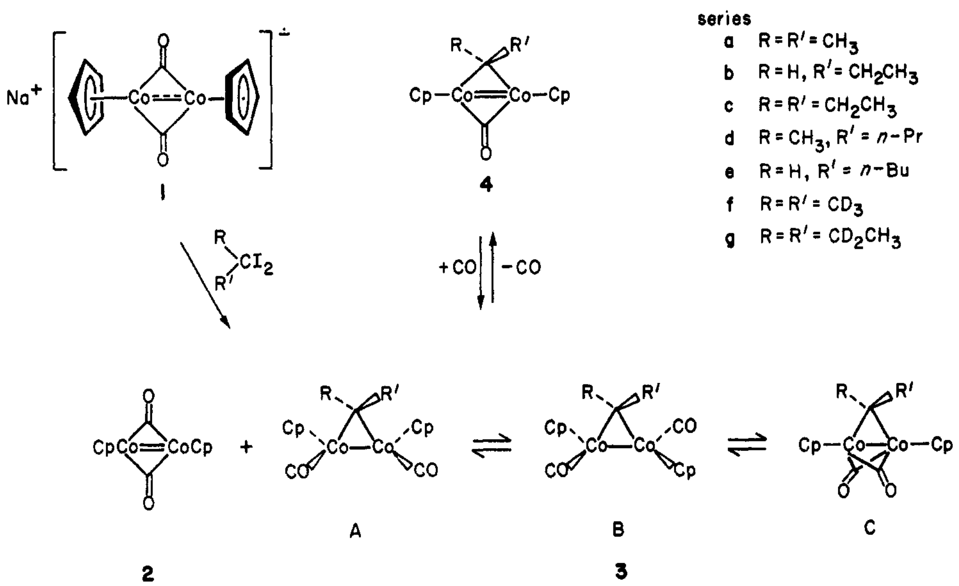
Received June 30, 1981

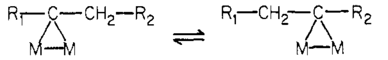
Summary: A series of terminal and internal (μ-alkylidene)cobalt complexes (**3a–g**) has been prepared. These complexes have the empirical formula $(\mu\text{-}CR_1R_2)(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2$. Isomers having doubly bridging, cis terminal, and trans terminal carbonyl groups have been detected spectroscopically, the relative amounts of each isomer depending in a sensitive way upon the alkylidene substituents. Complexes **3** in which both R and R′ are alkyl groups lose one molecule of CO, forming the corresponding unsaturated dinuclear complexes **4**. Upon

Scheme I



thermolysis, the internal alkylidene complexes 3 (R and R' = *n*-alkyl) lead to alkenes. However, they also undergo a surprising rearrangement to terminal alkylidene complexes 3 (R = H, R' = *n*-alkyl'). Isotope labeling studies have provided evidence that both metal/hydrogen migration and π/π-allyl interconversion are involved as primary steps in this rearrangement.

We wish to report that μ-alkylidene complexes in the cobalt series having general structure 3, R and R' = *n*-alkyl (Scheme I), undergo a new type of fundamental organometallic transformation: migration of the dinuclear metal group from carbon to carbon along the chain (eq 1), ultimately leading to monosubstituted alkylidene complexes 3 (R = H, R' = *n*-alkyl').



$$R_1-\underset{M-M}{C}-CH_2-R_2 \rightleftharpoons R_1-CH_2-\underset{M-M}{C}-R_2 \qquad (1)$$

We reported earlier that reaction of radical anion 1 with methylene iodide led to μ-methylene complex 3 (R = R' = H). This material reacts with alkenes by an autocatalytic mechanism, leading in the case of ethylene to propene and $CpCo(CO)(C_2H_4)$ as final products.[1] We have now found that the radical anion/diiodide reaction appears to be general for *gem*-diiodides and that both internal and terminal dinuclear alkylidene complexes can be prepared by this procedure. Thus, addition of 1.5 equiv of the appropriate *gem*-diiodide to a suspension of the sodium salt of 1 in THF resulted in immediate color changes from pale green to blue-green (due to the formation[2] of neutral dimer 2) and then to red-brown. Evaporation of solvent and chromatography of the residues on alumina under air-free conditions, followed by recrystallization from pentane, in every case afforded the corresponding (μ-alkylidene)-bis-((η^5-cyclopentadienyl)carbonylcobalt) (3a–g) in 20–50% yield.[3]

The structures and reactions of complexes 3 are extremely sensitive to steric factors. As reported earlier, the μ-CH_2 complex exists completely as the coordinatively saturated, terminally CO-bonded structures A and B (Scheme I). The ratio of trans and cis isomers (B/A) is 95:5 at room temperature; reactions of the μ-CH_2 complex take place without detectable buildup of other isomers. When R = R' = *n*-alkyl, the alkyl groups are equivalent in the ^1H NMR spectrum, indicating that the terminal CO isomer having the Cp groups trans to one another (isomer B) again predominates. However, IR shows both terminal (for example, when R = R' = Me, $\nu_{CO} = 1937$ cm^{-1}) and bridging (1813, 1853 cm^{-1}) carbonyl groups, indicating the presence of both isomers B and C (presumably equilibrating rapidly on the NMR time scale) in solution. In the complexes where R and R' are different (i.e., **3b**,**d**,**e**), only CO terminal structures are seen when one group is H; when both are alkyl, again IR shows that both terminal and bridging isomers are present in solution.

Also isolated in the reactions of secondary *gem*-diiodides, in approximately 3% yield, were small amounts of structurally related complexes. On the basis of spectral and analytical properties[4] their structures can be assigned as μ-alkylidene-μ-carbonyl-bis(η^5-cyclopentadienyl)cobalt) (4). These form purple, air-sensitive crystals, and in solution they react with excess CO immediately and quantitatively to form the corresponding saturated dimers 3. Complexes 4 are also generated during irradiation of N_2-purged solutions of 3 or simply by heating. Complex **4a**, for example, builds up to a maximum of 17% in the thermal reaction. The fact that these reactions are autocatalytic makes them difficult to monitor well during large-scale runs and thus use preparatively. However, 4 may be isolated in the reaction of 3 with $CpCo(C_2H_4)_2$; **4d**, for example, was obtained in 50% yield in this way.

When a solution of 2-propylidene complex **3a** in benzene-d_6 was heated to 80 °C for 10 h, formation of **4a** was observed after 3 h; following that, decomposition began to occur and propene was produced as the only organic product. However, during NMR monitoring of this reaction we were also surprised to discover that a small amount (7%) of the *terminal* alkylidene complex **3b** appeared during the course of the reaction (cf. Scheme II). Curious to know whether this apparent metal-migration reaction

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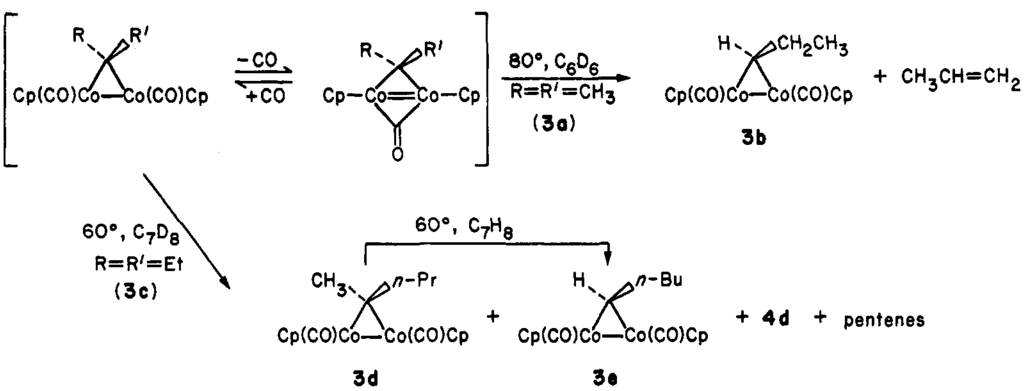
(1) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489.

(2) (a) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1781. (b) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113. (c) Lee, W. S.; Brintzinger, H. *J. Organomet. Chem.* **1977**, *127*, 87.

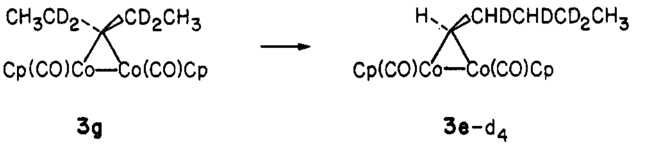
(3) Satisfactory spectral and analytical data have been obtained on each complex. These data are included in the supplementary material for this paper, available in the microfilm edition of the journal.

(4) The first dinuclear cobalt μ-CH_2 complex of this type was discovered in an unexpected reaction between the lithium enolate of acetaldehyde, $CoCl_2$ and pentamethylcyclopentadiene: cf. (a) Halbert, R. T.; Leonowicz, M. E.; Maydonovitch, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5101. For a more recent example, see: (b) Herrmann, W. A.; Huggins, J. M.; Reiter, B.; Bauer, C. *J. Organomet. Chem.* **1981**, *214*, C19–C24.

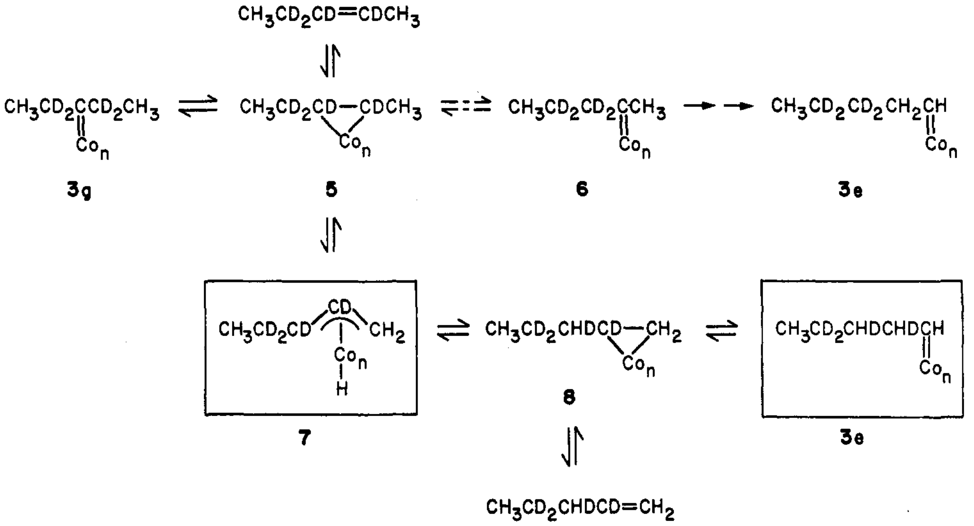
Scheme II



Scheme III



Scheme IV



could occur over a longer carbon chain, we heated a solution of 3-pentylidene complex **3c** under similar conditions. In this case heating even at lower temperature (60 °C) in toluene-d_8 for several hours led to the formation of **4c**, pentenes, a small amount of **3e** (12% at maximum buildup), and traces of **3d** (2%) and **4d** (3%). Heating **3d** at 60 °C for 7 h gave ca. 3% of **3e**, but this rearrangement took place slowly enough that **3d** and **4d** could not have been the sole intermediates in the conversion; i.e., there is apparently a direct path from **3c** (or **4c**) to **3e**. No reverse isomerization was observed on heating **3b** or **3e**; only alkene and intractable organometallic products were formed.

Examination of the time course of these reactions indicated that they are initiated autocatalytically, perhaps by product-assisted removal of a CO ligand, as in the reaction of the parent μ-CH_2 complex with ethylene;[1] for this reason it is difficult to obtain clear-cut information about the mechanism of the metal-migration reaction from kinetic studies. We have therefore turned to isotope labeling studies to probe the mechanism of the rearrangement. Complex **3g** ($\geq$99.5% deuterated at the α-positions) was prepared by conversion of completely α-deuterated 3-pentanone to the corresponding diiodide[5] followed by reaction with radical anion 1. A solution of this material was heated until NMR monitoring showed it had almost all reacted. The product **3e**-d_4 formed was then isolated by column chromatography and its ^1H NMR spectrum examined. This showed[6] clean and specific conversion to the complex labeled as illustrated in Scheme III.

The conversion of **3a** to **3b** obviously involves an overall one-carbon migration of the metal fragment. However, the relative amounts of product complexes formed, and the rates at whcih **3c** and **3d** rearrange seem to discredit **3d** as the sole intermediate in the two-carbon transformation of **3c** to **3e**. The labeling results obtained in the **3g** → **3e** reaction require that in moving the metal fragment from the center to the end of the chain, one hydrogen initially attached to the migration terminus has been transferred to the central carbon and one has been transferred to C-2. In addition, a deuterium initially residing on the α-carbon has also been transferred to the former alkylidene carbon. These data indicate that both (overall) one- and two-carbon migration can occur and that hydrogen, rather than carbon, rearrangement has taken place along with metal migration.

These observations set some quite specific constraints on mechanisms which can be responsible for these migration reactions. In considering such mechanisms, a significant question is whether the dinuclear fragment remains intact during the rearrangement. Although this is in principle determinable by using crossover experi-

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(5) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989.

(6) ^1H NMR (benzene-d_6) of the alkyl region of **3e**: δ 8.13 (t, 1 H, J = 7.9 Hz, proton attached to alkylidene carbon), 2.51 (m, 2 H, H), 1.55 (m, 4 H, H_β and H_γ), 1.04 (t, 3 H, J = 7.1 Hz, terminal methyl group). For **3e**-d_4: δ 8.13 (br d, 1 H), 2.49 (br t, 1 H, H_α), 1.89 (br s, 1 H, H_β), 1.05 (br s, 3 H, terminal methyl group).

ments, in this case the earlier reported propensity of bridging carbene complexes to undergo metal–fragment interchange[1] destroys the molecular integrity necessary for analysis of such experiments. We can therefore write a reasonable mechanism for the migration reaction which accounts for our product and labeling results, but we do not yet know whether the moiety which migrates in the actual reactive species is mono- or dinuclear.

Such a mechanism, illustrated for the observed conversion of **3g** to **3e**-d_4, is shown in Scheme IV. We believe the first step in the process involves migration of metal and a hydrogen atom in opposite directions (perhaps via a β-elimination/reductive elimination sequence), leading to π-complex **5**. Given that one-carbon migration occurs in the closely related rearrangement of **3a**, it may be possible to do the same sort of process in reverse, leading to **6**. However, the labeling results rule out this direct 1,2 metal/H interchange as the *predominant* path in the case of **3g**, because that would lead to the (unobserved) labeling pattern shown in the scheme as resulting directly from **6**. Instead, π-complex **5** apparently more rapidly undergoes insertion into the methyl C–H bond, leading to π-allyl complex **7**. Reductive elimination leads to **8**, and then 1,2 metal/H interchange can occur, leading to the labeling pattern actually found[7] in **3e**.

The π-complexes **5** and **8** are obvious precursors for the pentenes formed as major products in the reaction. However, given the often demonstrated reversibility of π-complex formation between low-valent metals and olefins, if this mechanism is correct, it suggests that free olefin becomes reincorporated into the manifold of intermediates (i.e., there is a viable pathway for conversion of alkenes into dinuclear carbene complexes). If the reentry rate is slow enough, it may be difficult to detect incorporation of olefin in the time required for complete rearrangement of a given internal alkylidene, but we decided to test this prediction. First, we carried out the thermolysis of deuterium-labeled 2-propylidene complex **3f** in the presence of unlabeled propene. Isolation of the terminal alkylidene product **3c** and mass spectral analysis showed that it did, in fact, contain a small but significant amount (ca. 6%) of alkylidene-h_6, without contamination by mixed H/D species which might have arisen by a hydrogen (rather than alkylidene ligand) exchange process. Second, we examined the rearrangement of unlabeled **3c** in the presence of an excess of propene. In this experiment, detectable amounts (ca. 1%) of 1-propylidene complex **3b** appear in place of the 1-pentylidene rearrangement product **3e** formed in the absence of propene.[8]

Whether or not the intermediates in Scheme IV are dinuclear, if stable mononuclear carbene complexes can be prepared with *n*-alkyl chains attached to the alkylidene carbon, it seems likely that carbon-to-carbon migrations analogous to those we have found might occur. In addition, it is perhaps reasonable to point out that the alkylidene/π-complex interconversions illustrated in Scheme IV constitute a mechanism for alkene isomerization. In our particular system it appears that even though this path is accessible, isomerization via π-allyl complexes is more rapid (e.g., **5** is apparently converted to **7** faster than it rearranges to **6**). However, the alkylidene route may in some cases turn out to be the favored pathway. In any case it should certainly now be considered as a viable alternative to the more conventional[9] π-allyl and metal hydride addition/elimination mechanisms.

Acknowledgment. We are grateful for support of this work by the National Science Foundation (Grant No. CHE 79-26291). K.H.T. acknowledges an Ephraim Weiss Scholarship from the University of California, Berkeley.

Registry No. 1, 62602-00-0; **3a**, 79255-80-4; **3b**, 79255-81-5; **3c**, 79255-82-6; **3d**, 79255-83-7; **3e**, 79255-84-8; **3f**, 79255-85-9; **3g**, 79272-65-4; **4a**, 79255-86-0; **4c**, 79255-87-1; **4d**, 79255-88-2; 2,2-diiodopropane, 630-13-7; 1,1-diiodopropane, 10250-52-9; 3,3-diiodopentane, 66688-39-9; 2,2-diiodopentane, 66688-37-7; 1,1-diiodopentane, 66688-35-5; 1,1,1,3,3,3-hexadeuterio-2,2-diiodopropane, 79255-38-2; 2,2,4,4-tetradeuterio-3,3-diiodopentane, 79255-39-3.

Supplementary Material Available: Spectral and Analytical data on complexes **3a–g 4a**, and **4c** (2 pages). Ordering infor-

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[7] It is also obviously important to examine the labeling pattern in the one-carbon migration product **3d** formed from **3g**. However, the small amounts of this material which build up in the thermolysis of **3g** have so far made isolation of enough material for careful NMR analysis very difficult. We are presently investigating the possibility of carrying out this isolation by preparative HPLC; if this is successful, we should be able to test the prediction that the one-carbon migration gives a labeling pattern corresponding to that illustrated in **6** (Scheme IV).

[8] A reviewer has asked whether there is any possibility that the **3b** formed during the rearrangement of **3c** in the presence of propene might be due to the occurrence of some olefin metathesis under the reaction conditions. We feel this interesting possibility is unlikely, since we are unable to detect either metathesized olefins or other alkylidenes (e.g., we see neither the parent complex **3**, R = R′ = H, nor the ethylidene complex **3**, R = H, R′ = Me) during this process.

[9] (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; pp 33–35. See also, for example: (b) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 5811. (d) Green, M.; Hughes, R. P. *J. Chem. Soc., Commun.* **1975**, 619.

Free Radical Reactions of $HCo(CO)_4$

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Received August 4, 1981

Summary: A CIDNP effect has been observed when 1,1-diphenylethylene is reacted at low temperature with $HCo(CO)_4$. This and other chemical evidence clearly demonstrate radical formation.

It has been suggested that the reaction of $HCo(CO)_4$ with 1,1-diphenylethylene[1a] (and related compounds[1b]) proceeds by a radical mechanism (Scheme I), but no evidence for the presence of radicals could be secured. We have restudied this reaction and wish to report the first example of a CIDNP effect observed with $HCo(CO)_4$.

When 1,1-diphenylethylene is injected into a NMR tube containing a CH_2Cl_2 solution of $HCo(CO)_4$ at −78 °C and the tube placed immediately in a ^1H NMR cavity at 31 °C, the CIDNP effect shown in Figure 1 is observed. The proton signal of the methyl group in the product at δ 1.6 shows a doublet emission which quickly changes to a doublet absorption with an upfield shift as the reaction proceeds with the rise in temperature.

The CIDNP effect represents evidence for the intermediacy of the geminate radical pair $\overline{Ph_2\dot{C}CH_3\dot{C}o(CO)_4}$ formed by diphenylethylene abstracting hydrogen from $HCo(CO)_4$ (Scheme I). If it is assumed that the geminate radical pair is derived from a singlet precursor and that the *g* factor for $\dot{C}o(CO)_4$ (2.137 ± 0.01)[2] is larger than that for $Ph_2\dot{C}CH_3$, with a positive coupling constant, *a*, for a $\dot{C}$–CH type radical, application of the Kaptein formulation[3] predicts the observed emission spectrum.

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[1] (a) J. A. Roth and M. Orchin, *J. Organomet. Chem.*, **182**, 299 (1979); (b) T. E. Nalesnik and M. Orchin *ibid.*, **199**, 265 (1980).

[2] R. L. Sweany, *Inorg. Chem.*, **19**, 3512 (1980).

[3] R. Kaptein, *J. Chem. Soc. D.*, 732 (1971). T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976, p 537.