J. Am. Chem. Soc. **1983**, *105*, 6045-6052 6045

Stereochemistry of Metallacycle Formation in the Double Alkylation of Bis(triphenylphosphine)nitrogen(1+) Bis(η^5-cyclopentadienyl)bis(μ-carbonyl)dicobaltate with α,γ-Diiodoalkanes

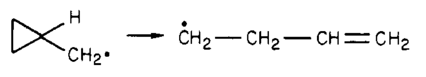
Gilbert K. Yang and Robert G. Bergman*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received March 16, 1983*

Abstract: Alkylation of the dinuclear cobalt radical anion **4** with 1,3-diiodobutane and 2,4-diiodopentane yields three new metallacycles: a methyldicobaltacyclopentane (**11**) and the cis and trans isomers of an α,α'-dimethyldicobaltacyclopentane (**6c** and **6t**). Alkylation of **4** with either of the diastereomeric 2,4-diiodopentanes *meso*-**7** and *dl*-**7** yields identical ratios of **6c** and **6t**. Control studies demonstrate that neither starting diiodide isomerization nor product isomerization can account for this product mixture. This is evidence that at least one of the two alkylation steps proceeds via electron transfer. In contrast, alkylation of **4** with a mixture of (2*R*,3*R*)- and (2*S*,3*S*)-1,3-diiodobutane-*2-d* (*syn*-**12**-*d*) proceeds stereoselectively: a 1:5 ratio of syn/anti metallacycles **11**-*d* is formed. We conclude that the first (intermolecular) step in the double alkylation proceeds by initial electron transfer while the second (cyclization) step proceeds predominantly by S_N2 displacement or by a partly stereospecific electron transfer process of the type recently postulated in certain photosolvolysis reactions.

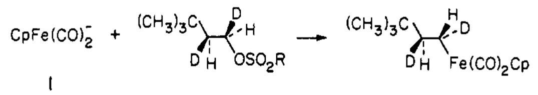
Alkylation of transition-metal anions is one of the most important routes for transition metal–carbon σ bond formation. Consequently, much attention has been devoted to studies of transition-metal anion attack on alkyl halides and sulfonate esters. The goal of many of these studies has been to determine the stereochemistry of the metal–carbon bond formation process and from this to differentiate between mechanisms involving radical intermediates and those involving S_N2 transition states.[1] The nucleophilic species that have been investigated include $Co(DmgH)_2pyr^-$,[2ac] $Mn(CO)_5^-$,[2b] $CpMo(CO)_3^-$,[2c] $Mn(CO)_4PEt_3^-$, and $CpW(CO)_2PEt_3^-$,[2d] with the majority of the studies being performed with $CpFe(CO)_2^-$.[3]

Whitesides et al.[3a] performed a particularly elegant set of experiments utilizing sulfonate esters of *threo-* and *erythro-*3,3-dimethylbutan-*1,2-d*$_2$-1-ol as alkylating agents for $CpFe(CO)_2^-$ (**1**) (shown in Scheme I) and other organometallic nucleophiles. They found that alkylation proceeded primarily with inversion of configuration at carbon. In other work, San Filippo, Krusic, Fagan, and Silbermann[4] treated anion **1** with cyclopropylcarbinyl iodide and bromide (Scheme II). With the iodide two products were obtained, the (cyclopropylcarbinyl)iron complex **2** and the (allylcarbinyl)iron complex **3** in 70% and 30% relative yield, respectively. The latter product was presumed to arise by formation of cyclopropylcarbinyl radical, which is known to rapidly rearrange to allylcarbinyl radical (eq 1). Thus, San Filippo et al. propose that the reaction proceeds by initial electron transfer from **1** to the cyclopropylcarbinyl iodide, yielding cyclopropylcarbinyl radical and iodide ion. With cyclopropylcarbinyl bromide such an electron-transfer path is not available, and even-electron processes (e.g., S_N2 substitution) are probably dominant. Currently, the question of whether S_N2 or electron-transfer processes dominate in the R_3Sn^- system is being hotly debated by a number of research groups.[5]

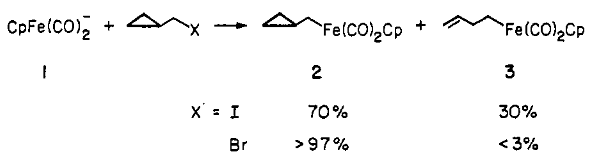


(1)

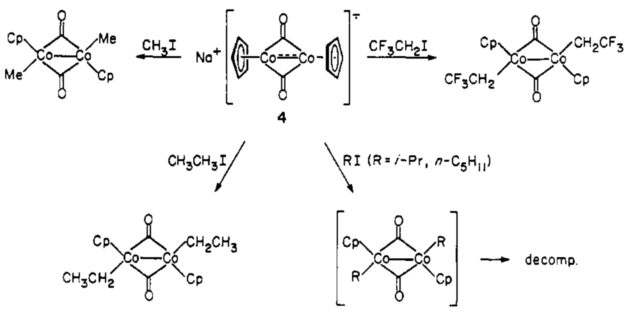
Scheme I



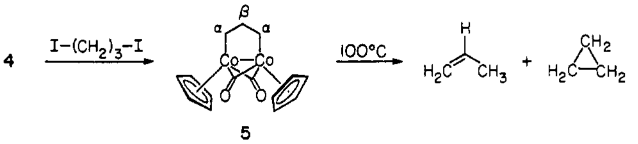
Scheme II



Scheme III



Scheme IV



---

(1) For excellent recent reviews on the stereochemistry of transition metal–carbon sigma bond formation and reactivity, see: (a) Flood, T. C. In "Topics in Inorganic and Organometallic Stereochemistry"; Wiley: New York, 1981; Vol. 12. (b) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434-442.

(2) See, for example: (a) Jensen, F. R.; Madan, V.; Buchanan, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1414. (b) Johnson, R. W.; Pearson, R. G. *J. Chem. Soc., Chem. Commun.* **1970**, *986*. (c) Bock, P. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2826. (d) Dong, D.; Slack, D. A.; Baird, M. C. *J. Organomet. Chem.* **1978**, *153*, 219.

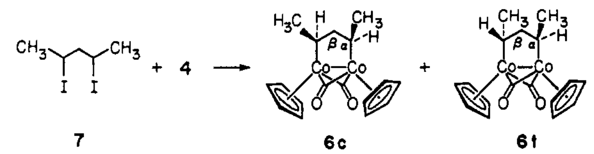
(3) See, for example: (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Chem. Soc.* **1974**, *96*, 2814. Boschetto, D. J.; Whitesides, G. M. *Ibid.* **1971**, *93*, 1529. **1969**, *91*, 4313. (b) Slack, D. A.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1974**, 701; *J. Am. Chem. Soc.* **1976**, *98*, 5539. (c) See ref 2b.

(4) (a) Krusic, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250. (b) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *Ibid.* **1978**, *100*, 4834. San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *Ibid.* **1978**, *100*, 4834.

(5) (a) San Filippo, J., Jr.; Silbermann, J. *J. Am. Chem. Soc.* **1981**, *103*, 5588-5590. (b) Ashby, E. C.; DePriest, R. *Ibid.* **1982**, *104*, 6144-6146. (c) Kuivila, H. G.; Alnajjar, M. S. *Ibid.* **1982**, *104*, 6146-6147.

0002-7863/83/1505-6045$01.50/0 © 1983 American Chemical Society

Scheme V



Our group has recently been studying[6] the alkylation of a dinuclear nucleophile, the dicobalt radical anion **4**. Both the sodium and bis(triphenylphosphine)nitrogen(1+) (PPN) salt of **4** undergo double alkylation with a variety of primary alkylating agents[6,7] (Scheme III) to yield several somewhat thermally sensitive dialkyldicobalt complexes. However, more highly substituted alkylating agents with leaving groups at secondary or tertiary centers or chains longer than ethyl do not yield stable isolable dialkyl complexes.[8] This makes the study of the stereochemistry of the cobalt–carbon bond formation process very difficult in the dialkyldicobalt system.

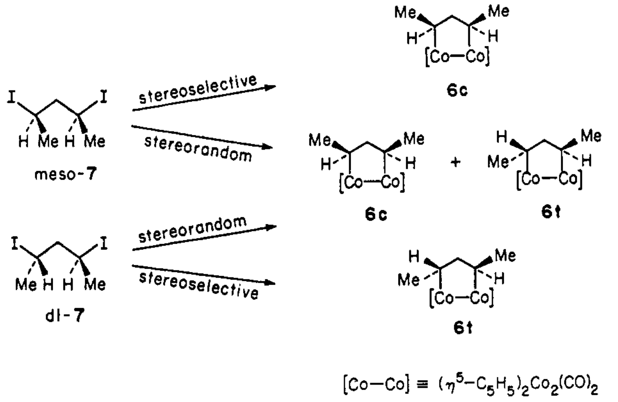
The discovery that the metallacyclopentane **5** prepared from the reaction of radical anion **4** with 1,3-diiodopropane was remarkably thermally stable[9] (Scheme IV) provided the hope that stereochemical studies with α-substituted analogues of **5** would be possible. Additionally the chemical and spectroscopic differences of diastereomeric molecules are typically enhanced by confinement to a ring. Thus we expected that use of a metallacyclic system would combine thermal stability with ease of analyzing product mixtures. On the basis of this expectation, we felt that a study of derivatives of **5** would enable us to determine the stereochemical outcome of the metal–carbon bond formation process in this dinuclear system.

Results and Discussion

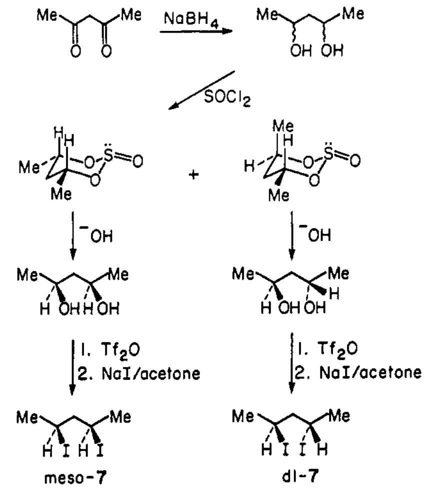
We began our study with the preparation of the α,α-dimethyldicobaltacyclopentane **6** by a route analogous to that used for the preparation[9] of the parent trimethylene-bridged metallacycle **5**. Reaction of radical anion salt PPN·**4** with a mixture of isomers of 2,4-diiodopentane (**7**) in THF gave **6** (Scheme V) as dark green crystals in 27% yield based on cobalt. This material is stable for days under N_2 at room temperature in benzene solution. Solutions of **6** decompose within a day in the air although the solid appears to be indefinitely stable. The ^{1}H NMR spectrum of this compound show that it is a mixture of two isomers, **6c** and **6t**. The trans isomer has a single cyclopentadienyl resonance at δ 4.57. The α-methine hydrogen signals appear as a sextet at 2.57 ppm, and the methyl signals appear as a doublet at 1.06 ppm. The protons on the β-methylenic carbon appear as a triplet at 0.37 ppm. The cis isomer has one cyclopentadienyl resonance at δ 4.58. The methine resonances appear as a multiplet at 2.10 ppm, and the methyl resonances appear as a doublet at 1.12 ppm. The β-methylenic hydrogens are diastereotopic, and their signals appear as two multiplets at 0.38 and 0.15 ppm.

Alkylation of radical anion **4** with the individual meso and *dl* diastereomers of diiodide **7** involves substitution at two carbon centers, either of which may proceed with preservation or loss of stereochemistry. The overall stereochemical possibilities are illustrated in Scheme VI. A completely stereorandom process will yield a mixture of **6c** and **6t** that is identical for both *meso*-**7** and *dl*-**7**. On the other hand, a stereospecific process will yield a single product isomer for *meso*-**7** and the other isomer for *dl*-**7**. Which isomers are actually formed depends upon whether inversion or retention of configuration is occurring at the carbon centers; Scheme VI illustrates only one possibility for the sake of clarity. Since metallacycles **6c** and **6t** have well-separated cyclopentadienyl resonances and well-separated methyl resonances, the relative amount of the two isomers is easily determined by integration of the ^{1}H NMR spectra of the product mixture. From this information we are able to distinguish between stereospecific and stereorandom processes.

Scheme VI



Scheme VII



Preparation of *meso*- and *dl*-7. Diiodides *meso*-**7** and *dl*-**7** were prepared by the route summarized in Scheme VII. The two isomers of 2,4-pentanediol were separated by the method described by Pritchard and Vollmer.[10] Conversion of the diols to the cyclic disulfite esters allows separation of the isomers by annular Teflon spinning-band distillation. Thus the meso diol and the *dl* diol were obtained in >99% and >94% diastereomeric purity, respectively. Replacement of the hydroxyl groups with iodide was achieved by conversion to the bis(trifluoromethanesulfonate) (triflate) ester followed by treatment with NaI in acetone. Even at 0 °C the latter step is very rapid due to the excellent leaving characteristics of the triflate anion. This permitted complete formation of the diiodide before iodide-induced epimerization and consequent loss of stereochemical information at the initially substituted center could occur. Overall, the diastereomeric purities of *meso*-**7** and *dl*-**7** were 93% and 88%, respectively, as estimated by ^{1}H NMR.

Stereochemistry of the Formation of 6 from 4 and 7. The reactions between PPN-**4** and *dl*-**7** and PPN·**4** and *meso*-**7** were run in THF-d_8 in NMR tubes sealed under vacuum. These were prepared by mixing solutions of the two reactants at −76 °C in the NMR tubes which were evacuated, sealed, and then warmed to the appropriate reaction temperature. The reactions were monitored by ^{1}H NMR spectroscopy at the reaction temperature, and the relative amounts of the two isomers of **6** were determined by integration of the cyclopentadienyl and methyl resonances (see Experimental Section for details). The results of these experiments are shown in Table I. Figure 1 shows the methyl region ^{1}H NMR

---

(6) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1781–87; **1976**, *98*, 7436.

(7) White, M. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1056. Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113–20.

(8) White, M. A.; Bergman, R. G., unpublished results.

(9) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694–5; *Organometallics* **1982**, *1*, 1571–1579.

(10) Pritchard, J. G.; Vollmer, R. L. *J. Org. Chem.* **1963**, *28*, 1545–9.

Table I. Reaction of Radical Anion 4 with *meso*- and *dl*-2,4-Diiodopentane. Stereochemistry of the Products

starting material 7	[PPN·4], mM	[diiodide], mM	T,[a] °C	time	% conversn	6c/6t	*dl*-7/meso-7
93% *meso*-7 7% *dl*-7	5.85	11.3	−60	225 h	0.1	50:50	14:86
	5.84	13.2	20	530 min	86	45:55	33:67
12% *meso*-7 88% *dl*-7	5.23	11.6	−60	225 h	0.1	50:50	82:18
	5.31	13.0	20	530 min	93	45:55	74:26

[a] The reactions run at −60 °C were used to determine the product stereochemistry at very low conversions. The precision of both the product ratio and diastereomer ratio is somewhat lower than in the room-temperature reactions.

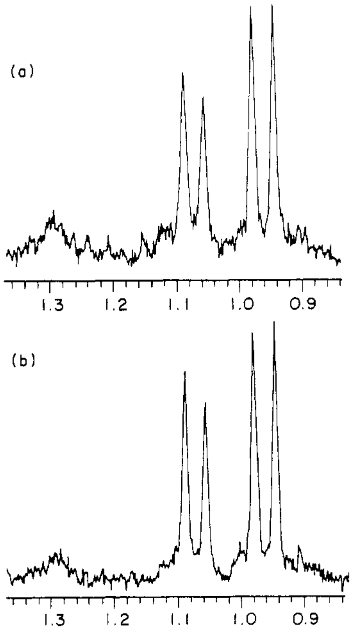


Figure 1. 200-MHz ^{1}H NMR spectra (THF-d_8) of the methyl region of metallacycle 6 formed in the reaction between the radical anion salt PPN·4 and (a) *dl*-2,4-diiodopentane (*dl*-7) and (b) *meso*-2,4-diiodopentane (*meso*-7) at room temperature. The 6t resonance is centered at δ 1.07, and the 6c resonance is centered at δ 0.96 ppm downfield from the Me$_4$Si.

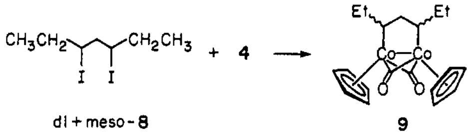
spectra for the room-temperature reactions. The ratio of **6c**/**6t** is 45:55 and is identical for both isomers of diiodide. This indicates that the stereorandom pathway in Scheme VI is followed. This requires that complete loss of stereochemical information is occurring at at least one of the carbon centers.

Control Experiments. To be certain that the randomization process is taking place in the actual formation of the metallacycle, we needed to demonstrate that neither starting material nor product epimerization were occurring. The diastereomeric purity of the remaining diiodide **7** from each reaction mixture was examined in the ^{1}H NMR spectra of the reaction mixtures (Table I). From this it is clear that stereochemical scrambling of diiodide is slow relative to the rate of metallacycle formation. This is therefore not the source of the observed scrambling.

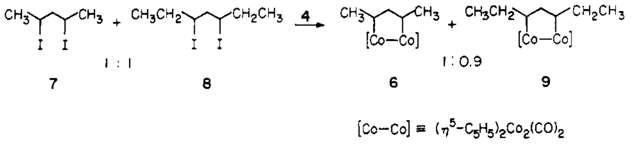
The possibility that the metallacycles themselves were rapidly epimerizing under the reaction conditions was examined in the following way. We wanted to determine if a sample of **6** that is enriched in one isomer would equilibrate to the ratio of 45:55 observed for **6c**/**6t** under conditions identical with those found in the alkylation.

In order to make our test for equilibration as sensitive as possible, we decided to observe the behavior of one of the diastereomers of **6** added to a reaction involving a structurally similar but distinguishable diiodide and radical anion **4**. Thus, a mixture of *dl*- and *meso*-3,5-diiodoheptane (**8**) and **4** (Scheme VIII) yields an organometallic product mixture very similar in appearance to the dimethylmetallacycle **6**. This mixture was fully characterized (see Experimental Section) and is consistent with its being a mixture of *cis*- and *trans*-diethyldicobaltacyclopentanes (**9**). When **4** is alkylated with an approximately equimolar mixture of C$_5$ diiodides **7** and C$_7$ diiodides **8** in THF-d_8, the ^{1}H NMR spectrum of the reaction mixture shows an equal amount of **6** and **9** to within 10%. This is illustrated in Scheme IX. This shows the formation of these two metallacycles occurs at a similar rate and therefore almost certainly by the same mechanism. If reactive species are formed in the alkylation reaction that lead to scrambling of **6**, they should also be present in the C$_7$ model system and would likewise lead to scrambling of any **6** present. Since the diastereomers of the C$_5$ and C$_7$ metallacycles **7** and **9** are resolvable by HPLC, we can analyze a reaction mixture for small amounts of either isomer of either metallacycle.

Scheme VIII

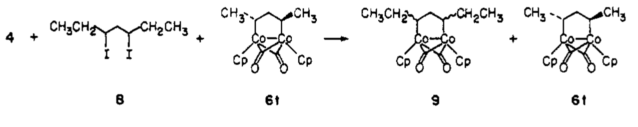


Scheme IX



[Co—Co] ≡ (η^5-C$_5$H$_5$)$_2$Co$_2$(CO)$_2$

Scheme X



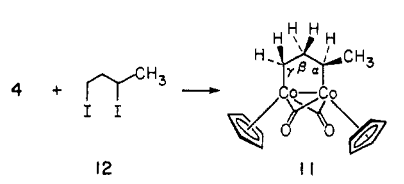
Since we could not prepare the pure isomers of metallacycle **6** synthetically, we used high-pressure liquid chromatography (HPLC) to separate them from a mixture of the two. Separation was accomplished on a semipreparative C$_{18}$ reverse-phase column eluted with 20% H$_2$O in MeOH. The isomers had very similar R_f values and eluted in approximately 10 column volumes. A small amount of each diastereomer was obtained in this manner, each >93% pure by ^{1}H NMR.

Accordingly, to a reaction mixture containing PPN·**4** and a mixture of isomers of C$_7$ diiodides **8** was dissolved 1 mg of >95% isomerically pure C$_5$ metallacycle **6t**. After the reaction was complete, the mixture was worked up and the combined metallacyclic product mixture was analyzed by HPLC. Both isomers of **9** were observed but only the trans isomer of **6** was detected. No **6c** was detectable to within 5%. This result is illustrated in Scheme X. This provides strong evidence that the metallacycles **6** are stereochemically inert under the conditions of their formation.

These two control experiments indicate that we must be observing an epimerization that is mechanistically significant, i.e., that randomization takes place in some reaction step which occurs during, not before or after, the process which converts radical anion **4** and diiodide **7** into **6**.

Synthesis of the α-Methyldicobaltacyclopentane 11. We next set out to investigate the possibility that different amounts of stereochemical scrambling might occur in the initial cobalt–carbon bond formation and the cyclization step. Similar to the preparation of the parent cobaltacycle **5** and the dimethyl derivative **6** the α-methyl cobaltacycle is easily prepared by reaction of PPN·**4** with 1,3-diiodobutane (**12**) in THF (Scheme XI). Dark green crystals of **11** are isolated in 32% yield based on cobalt. Solutions

Scheme XI



of this material in benzene are stable for days under N_2 at room temperature. In the air, these solutions decompose within a day although the crystals appear to be indefinitely stable. The ^1H NMR spectrum of this material (benzene-d_6) exhibits two cyclopentadienyl resonances at δ 4.60 and 4.58 due to the two chemically distinct cyclopentadienyl rings. The alkyl region exhibits clearly separated multiplets for each of the six chemically distinct protons on the alkyl bridge. The proton on the carbon α to the methyl group appears farthest downfield at 2.53 ppm. Signals due to the two methylenic protons on the carbon γ to the methyl group appear at 1.61 and 1.19 ppm. The methyl resonance appears as a doublet at 1.10 ppm. Multiplets at 0.56 and 0.28 ppm are assigned to the β-hydrogens respectively anti and syn to the methyl group (vide infra).

Relative Rate of Reaction of Primary and Secondary Iodides with 4. The formation of the α-methyl metallacycle **11** from 1,3-diiodobutane and radical anion **4** involves the formation of cobalt–carbon bonds to both primary and secondary carbon centers. Since, in general, the reactivities of primary and secondary carbon centers are quite different, it is likely that formation of the primary cobalt–carbon bond occurs first followed by cyclization to form the secondary cobalt–carbon bond.

To assure ourselves that the primary iodide was indeed more reactive than the secondary iodide, the following competition experiments were performed. PPN·**4** dissolved in THF-d_8 was treated with an excess of a roughly equimolar mixture of C_5 diiodide **7** and C_4 diiodide **12**. The solutions were analyzed directly by ^1H NMR. Integration of the Cp resonances corresponding to the dimethyl **6** and the monomethyl **11** metallacycles indicated that primary/secondary diiodide **12** reacted 10 times faster than secondary/secondary **7**. Competition between 1,3-diiodopropane and **7** indicated that the primary/primary diiodide reacted 25 times faster than **7**. Correcting for the statistical factor of 2, an approximately 10-fold increase in reactivity in going from secondary to primary iodides is seen. Similarly, competition between 1,3-diiodopropane and C_4 diiodide **12** demonstrated that the primary/secondary diiodide reacts approximately 75% as fast as the primary/primary diiodide after statistical correction, showing that distant substitution has a small effect on the rate of reaction. This provides good evidence that intermolecular reaction of radical anion **4** at a primary center is more rapid than intermolecular reaction at a secondary center. We conclude that in the reaction of **4** with C_4 diiodide **12**, formation of the primary cobalt–carbon bond occurs first, followed by rapid intramolecular formation of the secondary cobalt–carbon bond.

We sought to capitalize on this difference in reactivity by using it to study the stereochemistry of the second (intramolecular) bond formation step in the metallacycle synthesis. Our plan was to substitute one of the diastereotopic protons at C2 in 1,3-diiodobutane with deuterium. Reaction of this material with radical anion **4** would yield **11**-*d* with a deuterium label at the β-carbon. The product can be analyzed for the stereochemical fate of the label since the resonances at the β-carbon due to the protons syn and anti to the methyl group are distinguishable by ^1H NMR.

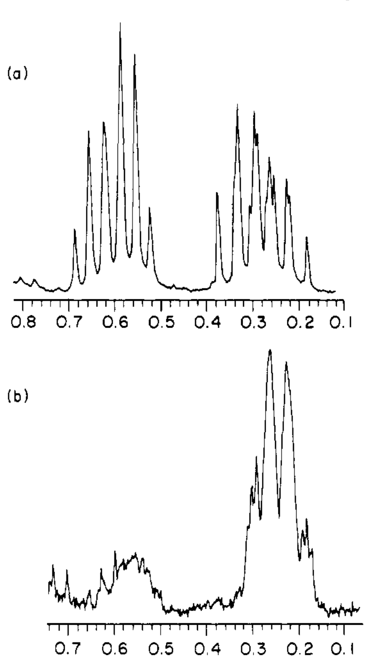
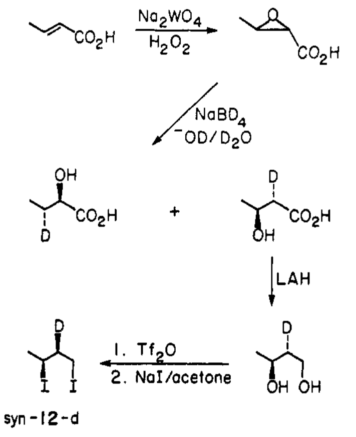
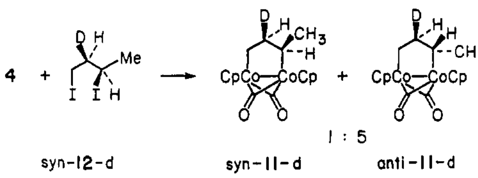


Figure 2. 200-MHz ^1H NMR spectra (benzene-d_6) of the β-methylenic proton region of (a) α-methyldicobaltacyclopentane (**11**) and (b) α-methyldicobaltacyclopentane-*d* (**11**-*d*) formed on reaction of PPN·**4** with (2*S*,3*R*)- and (2*R*,3*S*)-1,3-diiodobutane (*syn*-**12**-*d*). Chemical shifts are recorded in parts per million downfield from Me_4Si.

Scheme XII



Scheme XIII



Preparation of a Mixture of (2*R*,3*R*)- and (2*S*,3*S*)-1,3-Diiodobutane-2-*d* (*syn*-12-*d*). The preparation of *syn*-**12**-*d* is summarized in Scheme XII. A racemic mixture of deuterated 3-hydroxybutanoic acids was prepared by the method of Mohrig et al.[11] Reduction with LAH gave >95% deuterium substituted (2*S*,3*R*)- and (2*R*,3*S*)-butane-2-*d*-1,3-diol with the deuterium label >95% anti. This was converted to the racemic diiodide *syn*-**12**-*d* by treatment with trifluoromethanesulfonic anhydride followed by backside displacement of the ditriflate ester by NaI in acetone. The diiodide was determined to be >90% one diastereomer (2*R*,3*R* and 2*S*,3*S*; this configuration has the 3-iodide and deuterium label syn according to currently recommended nomenclature[12]) by integration of the intensities of the diastereotopic proton resonances.

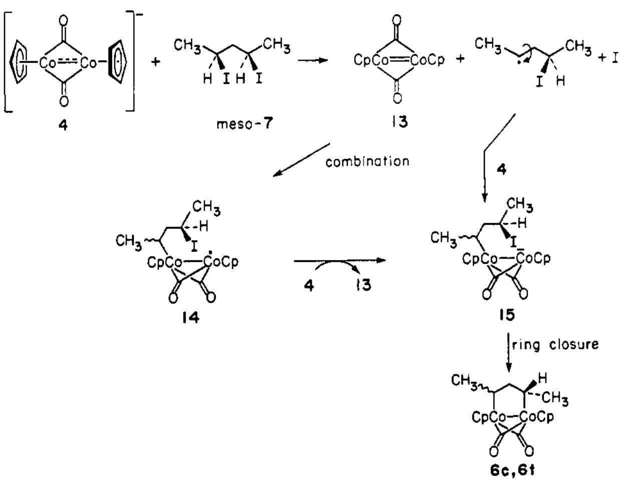
Reaction of *syn*-12-*d* with PPN·4. Stereochemistry at the Secondary Carbon. The reaction of >90% *syn*-**12**-*d* with PPN·**4** was performed at room temperature in THF. ^1H NMR analysis of the deuterated metallacycle **11**-*d* (Scheme XIII) showed the β-methylenic hydrogen resonances at 0.56 and 0.28 ppm in an intensity ratio of 1:5 (Figure 2). Thus, *formation of the second*

---

(11) Mohrig, J. R.; Vreede, P. J.; Schultz, S. C.; Fierke, C. A. *J. Org. Chem.* **1981**, *46*, 4655–8.

(12) Masamune, S.; Ali, Sk. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 557.

Scheme XIV



cobalt–carbon bond proceeds with some stereospecificity. Since the assignment of the resonances is not known, we cannot determine if retention or inversion of configuration at carbon has occurred. However, if we make the reasonable assumption that the stereospecific pathway proceeds with inversion, then we may assign the resonance at 0.28 ppm to the hydrogen syn to the methyl group and the resonance at 0.56 ppm to the hydrogen anti to the methyl group.

Mechanism of the Dialkylation of Radical Anion 4. On the basis of the results of our experiments we propose the mechanism for the dialkylation of **4** summarized in Scheme XIV. Initial attack of **4** at one iodide center proceeds by an electron-transfer process yielding iodide ion, the known neutral dimer[6,13a] **13**, and the 4-iodo-2-pentyl radical.[13b] Loss of stereochemical information occurs here with rapid inversion[14] and rotation at the radical center. The radical then combines with the dimer **13** yielding the paramagnetic alkyldicobalt radical **14**. This material is reduced by another equivalent of **4** to yield the anionic alkyldicobalt complex **15**. Alternatively, the iodopentyl radical may attack another equivalent of **4** to yield **15** directly. Ring closure then proceeds from **15** to give the product. Kaplan and Drury have shown[15a] that the 3-iodopropyl radical closes to cyclopropane with a unimolecular rate constant of 2×10^3 s^{-1} at 111 °C. Closure of the 4-iodo-2-pentyl radical should be even slower. Thus, even if **13** and the iodo radical escape the initial solvent cage, reaction of the radical with free $[CpCo(CO)]_2$ may compete effectively with the formation of cyclopropanes.

Summary and Conclusion

The alkylation of radical anion **4** with α,γ-diiodides proceeds with complicated stereochemistry. The first (intermolecular) alkylation step proceeds with complete randomization of stereochemistry due presumably to an electron-transfer process generating the dimer **13** and γ-iodo radical, which collapse to species **14**. This is then reduced to the 18-electron anion **15**, followed by ring closure with predominant inversion of configuration at carbon. The conventional rationalization of this result would postulate cyclization by intramolecular S_N2 displacement, with some competitive electron transfer.[4] Recent photosolvolysis studies, however, suggest that electron transfer can occur with a moderate degree of inversion stereospecificity.[15b] Such an occurrence in intermediate **15** could result in the observed predominance of inversion in the ring-closure step leading to **6**. It is difficult to distinguish between these competitive S_N2/electron transfer and electron transfer-with-inversion mechanisms using presently available data.

These results extend the understanding of metal–carbon bond formation processes to systems containing two metal centers and to systems capable of forming two metal–carbon bonds. We have found that both stereospecific and stereorandom mechanisms operate, just as they do in mononuclear organometallic systems. Future studies may show whether this mechanistic dichotomy is general for dinuclear compounds.

Experimental Section

General Data. $PPN[CpCo(CO)]_2$ was prepared by the method described by Schore et al.[6] Manipulations of this and other organometallic compounds were performed in a Vacuum Atmospheres 553-2 inert-atmosphere glovebox equipped with a MO-40-1 inert gas purifier. *meso*-2,4-Pentanediol and *dl*-2,4-pentanediol were prepared in >99% and 95% diastereomeric purity by the method described by Pritchard and Vollmer.[10] The ^1H NMR spectra of these compounds and intermediates in their preparation agreed with those found in the literature.[20]

^1H NMR spectra were recorded on either the UCB-200 (200 MHz) or the UCB-250 (250 MHz) Fourier transform NMR instruments at the University of California, Berkeley (UCB), NMR facility and are reported in units of parts per million (δ) downfield from tetramethylsilane (Me_4Si). The internal standard for spectra recorded in chloroform-*d* is Me_4Si. For spectra recorded in benzene-d_6, THF-d_8, methylene chloride-d_2, and deuterium oxide the internal standard is the residual proton resonance occurring at 7.15, 1.73, 5.32, and 4.63 ppm, respectively. Solution infrared spectra were recorded in 0.1-mm NaCl cells on a Perkin-Elmer Model 283 spectrophotometer. Electron-impact mass spectra were recorded at the UCB mass spectral facility on either an AEI MS 12 (low-resolution) or a Kratos MS50 (high-resolution) mass spectrometer. Elemental analyses were performed by the UCB microanalytical laboratory. Melting points were taken in glass capillary tubes in a Thomas-Hoover capillary melting point apparatus and are not corrected. Hydrogen ion concentrations (pH) were estimated with pHydrion pH paper (Micro Essential Laboratory).

High-pressure liquid chromatography (HPLC) was performed on a Beckman Model 324 gradient liquid chromatograph using Altex Ultrasphere-ODS (C_{18} reverse phase, 5-μm packing, 1.0 × 25 cm) or Altex Ultrasphere-Si (silica, 5-μm packing, 1.0 × 25 cm) semipreparative columns. Detection was accomplished with an Altex spectrometer flow cell attached to a Hitachi Model 100-10 spectrophotometer operating at 320 nm and observing the HPLC effluent directly.

Benzene, THF, and toluene were distilled from Na/benzophenone under a nitrogen atmosphere. Hexanes were washed with 5% HNO_3 in concentrated H_2SO_4, followed by aqueous Na_2CO_3 and then H_2O, dried, and then distilled from *n*-BuLi under a nitrogen atmosphere. Hexamethyldisiloxane (HMDS, Aldrich) was dried over 4A sieves and then vacuum transferred. THF-d_8 and benzene-d_6 were stirred over Na/benzophenone and then transferred under vacuum prior to use. All HPLC solvents were "Omnisolve" brand solvents (MCB) and were deaerated with argon prior to use.

Trifluoromethanesulfonic anhydride (Tf_2O) was either purchased from Aldrich and vacuum transferred prior to use or prepared from trifluoromethanesulfonic acid (Aldrich) by distillation from P_2O_5.[16] 3,5-Heptanedione was obtained from Eastman and was used as received. Clean copper wire was prepared by immersing copper wire in concentrated HNO_3 and then washing with water followed by acetone. Unless otherwise noted, all other solvents and reagents were reagent grade and were used as received. Stereochemically labeled diiodides were sensitive to thermal epimerization and were isolated with minimal heating and handling near room temperature. All stereochemically labeled compounds were stored at <−40 °C.

***meso*- and *dl*-2,4-Diiodopentane (*meso*- and *dl*-7).** In a 1-L round-bottom flask were placed 13.2 g of 2,4-dibromopentane (50.8 mmol, CTC Organics) dissolved in 100 mL of acetone and a solution of NaI (38.0 g, 0.25 mol) dissolved in 250 mL of acetone. These were stirred together and heated at reflux over a piece of clean copper wire. After 3 h an aliquot was removed, stripped of solvent under vacuum, and extracted with chloroform-*d*. This solution was filtered into an NMR tube and the ^1H NMR spectrum recorded showed several new peaks near 2 ppm. Two more aliquots were removed after 22 and 27 h and treated as above. The

---

(13) (a) Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5846–59. (b) Attempts to trap the organic radical by the cyclopropylcarbinyl radical rearrangement or the 5-hexenyl radical rearrangement failed when no isolable cobalt alkyls could be obtained upon reaction of radical anion 4 with appropriate substrates. Carter, E. A.; Yang, G. K.; Bergman, R. G., unpublished results.

(14) The rate constant for radical inversion is estimated to be $>10^5$ s^{-1}: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; 1st ed.; Harper and Row: New York, 1976; p 467.

(15) (a) Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 1753. Drury, R. F.; Kaplan, L. *Ibid.* **1973**, *95*, 2217–2221. (b) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7978.

(16) Burdon, J.; Farazmand, I.; Stacey, M.; Tatlow, J. C. *J. Chem. Soc.* **1957**, 2574.

methyl doublet at 1.7 ppm assigned to the starting dibromide had disappeared, and the rest of the spectrum appeared to have reached a steady state. The reaction mixture was cooled and the acetone removed at reduced pressure. The remaining solid was extracted with diethyl ether until the extract was colorless. The combined ether phases were washed with 10% aqueous $Na_2S_2O_3$ and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure and short-path vacuum distillation of the residue from clean copper wire gave 9.7 g (30 mmol, 60% yield from the dibromide) of clear very slightly yellow oil **7** which was >95% pure by NMR: bp 48–51 °C (0.3 mm); ^{1}H NMR (chloroform-*d*) δ 1.91, 2.01 (2 doublets, 6 H, *J* = 6.4, 6.8 Hz), 2.60 (m, 0.3 H), 4.25 (m, 2 H); MS (50 eV) *m*/*e* 41 (base), 324 (M^+).

***cis*- and *trans*-3,5-Dimethyl-1,2-bis(η^5-cyclopentadienyl)-1,2-dicobaltacyclopentanes (6c and 6t).** In a glovebox a 50-mL round-bottom flask was charged with 1.00 g of PPN·**4** (1.19 mmol) and 20 mL of THF. To this mixture was added 1.34 g of a mixture of 2,4-diiodopentane isomers **7** (4.15 mmol). An aliquot removed from the reaction mixture after 2 h was analyzed by infrared spectroscopy, and a new absorption at 1803 cm^{-1} was observed. Similar aliquots were removed from the reaction mixture over time, and after 4 h the absorption at 1690 cm^{-1} due to the starting radical anion **4** had disappeared. Hexanes (30 mL) were added to the mixture to precipitate NaI which was then removed by filtration. The solvent was removed from the resulting solution under vacuum. Chromatography of the residue in the glovebox through a 2 × 15 cm column of alumina II yielded two fractions. The first eluted with 3:1 hexanes/benzene and was the yellow-orange $CpCo(CO)_2$. The second dark green product band eluted with 2:1 hexanes/benzene. The solvent was removed from this fraction under vacuum, and the product was recrystallized from toluene/HMDS at −40 °C. Filtering and drying under vacuum yielded 122 mg (27% based on cobalt) of pure (by NMR) **6c** and **6t**: ^{1}H NMR (benzene-d_6; this material showed the two different isomers **6c** and **6t** in nearly equal amounts): **6t** δ 4.57 (s, 5 H), 2.57 (m, 1 H, *J* = 7 Hz), 1.06 (d, 3 H, *J* = 6.7 Hz), 0.37 (t, 1 H, *J* = 7.1 Hz), **6c** δ 4.58 (s, 5 H), 2.12 (m, 1 H), 1.13 (d, 3 H, *J* = 6.4 Hz), 0.37 (m, 1 H), 0.17 (m, 1 H); IR (THF) 1805 cm^{-1}; MS (50 eV) *m*/*e* 374 (M^+). Anal. Calcd for $C_{17}H_{20}O_2Co_2$: C, 54.56; H, 5.39; Co, 31.50. Found: C, 54.66; H, 5.47; Co, 32.1.

3,5-Heptanediol. This material was prepared from 3,5-heptanedione by the general procedure of Pritchard and Vollmer[10] with the workup procedure described by Fry and Britton.[17] In a 250-mL round-bottom flask containing 30 mL of water were dissolved 2.50 g of $NaBH_4$ (66.1 mmol) and 0.4 g of NaOH (10 mmol). This solution was cooled to 10 °C and stirred. A solution of 7.73 g of 3,5-heptanedione dissolved in 30 mL of methanol was placed in a 50-mL pressure equalizing addition funnel and added dropwise over 1 h to the solution of borohydride. When the addition was complete, the volume of the reaction mixture was reduced to 40 mL under vacuum. Continuous extraction of this solution with ether for 17 h followed by removal of the solvent from the organic layer yielded crude product. Short-path vacuum distillation (24 mm) gave 6.93 g of 3,5-heptanediol (52.5 mmol, 87% based on dione) as a clear colorless viscous oil which was judged to be pure by NMR: bp 127–130 °C (24 mm); ^{1}H NMR (chloroform-*d*) δ 3.72 (m, 1 H), 3.28, 2.68 (2 doublets, 1 H, diastereomeric OH, *J* = 2, 4 Hz), 1.67–1.40 (m, 6 H), 0.93, 0.94 (2 triplets, 6 H, diastereomeric CH_3, *J* = 12, 12 Hz). Anal. Calcd for $C_7H_{16}O_2$: C, 62.60; H, 12.20. Found: C, 63.22; H, 11.91.

3,5-Diiodoheptane (8). In a 100-mL round-bottom flask were placed 20 mL of CH_2Cl_2 (dried over $CaCl_2$) and 2.1 mL of Tf_2O (3.52 g, 12.5 mmol). This was cooled to 0 °C and stirred. Pyridine (2.0 mL, 1.96 g, 24.7 mmol) and 3,5-diheptanediol (0.71 g, 5.4 mmol) were dissolved in 10 mL of CH_2Cl_2 in a 50-mL pressure equalizing addition funnel and added to the stirred anhydride solution over 0.5 h. When the addition was complete, the mixture was filtered through 2-cm bed of silica in a 30-mL frit. The silica was washed with 20 mL of CH_2Cl_2, and the solvent was removed from the combined organic portion under vacuum. The residue was dissolved in 40 mL of acetone and cooled to 0 °C. A 35-mL sample of a 0.5 M solution of NaI in acetone (17.5 mmol) was added dropwise over 0.5 h. The solvent was then removed under vacuum, and the solids were dissolved in water (20 mL). The aqueous mixture was extracted with hexanes (2 × 20 mL) to extract the diiodide product. The hexane portion was then washed with water (2 × 10 mL) followed by 10% aqueous $Na_2S_2O_3$ (10 mL) and more water (10 mL). After the solution was dried ($MgSO_4$) and filtered, the solvent was removed under vacuum, yielding 0.15 g of **8** (8% based on diol) as a clear colorless oil that was judged to be >97% pure by ^{1}H NMR: ^{1}H NMR (benzene-d_6) δ 4.25 (m, 2 H, *dl*), 3.92 (quintet, 2 H, meso, *J* = 7.0 Hz), 2.44 (m, 1 H, meso), 1.82 (m, 1 H, meso), 1.56 (m, 4 H, *dl*), 1.48 (m, 2 H, *dl*), 1.29 (quintet, 4 H, meso, *J* = 6.9 Hz), 0.78, 0.76 (2 triplets, 6 H, meso and *dl*, *J* = 7.1, 7.1 Hz); HRMS (70 eV) calcd for $C_7H_{14}I_2$ *m*/*e* 351.9185, found *m*/*e* 351.9194 (M^+). The ratio of *dl*/*meso*-**8** was calculated to be 27:73 by integration of the ^{1}H NMR resonances at 4.25 and 3.92 ppm.

***cis*- and *trans*-3,5-Diethyl-1,2-bis(η^5-cyclopentadienyl)-1,2-dicobaltacyclopentane (6c and 6t).** In a glovebox 668 mg of PPN·**4** (7.93 × 10^{-4} mol) was slurried in 1 mL of THF in a 25-mL round-bottom flask. To this was added 1.24 g of diiodide **8** (3.52 × 10^{-3}) mol all at once. The reaction mixture soon turned green, and periodic monitoring of the reaction mixture showed absorbances growing in at 2018 and 1963 cm^{-1} ($CpCo(CO)_2$) and 1797 cm^{-1} ($[CpCo(CO)]_2$)[12] and a product absorbance at 1810 cm^{-1}. After 6 h the reaction was judged to be complete by the lack of a starting material absorption at 1690 cm^{-1}. Hexanes (10 mL) were added, and the mixture was filtered. Removal of the solvent under vacuum from the green solution and chromatography of the residue in the glovebox (alumina II, 1:3 benzene/hexanes, 2 × 17 cm) yielded an intense dark green product band. The solvent was removed from this fraction under vacuum, and the product was recrystallized from toluene/pentane at −40 °C. The dark green crystals were filtered, washed with cold pentane, and dried under vacuum: yield 75 mg of **9** which is pure by ^{1}H NMR (24% based on cobalt); ^{1}H NMR (benzene-d_6) δ 4.58 (s, 5 H), 2.6–2.25 (m, 2 H), 1.70–1.40 (m, 4 H), 0.90, 0.85 (2 triplets, 6 H, *J* = 9 Hz), 0.65–0.07 (3 multiplets, 2 H); IR (THF) 1810 cm^{-1}; MS (30 eV) *m*/*e* 402 (M^+). Anal. Calcd for $C_{19}H_{24}O_2Co_2$: C, 56.73; H, 6.01. Found: C, 56.46; H, 5.88.

***meso*-2,4-Diiodopentane (*meso*-7).** *meso*-2,4-Pentanediyl ditriflate was prepared by the method of Beard et al.[18] In a 100-mL round-bottom flask was dissolved 2.8 mL of trifluoromethanesulfonic anhydride (Tf_2O) (1.66 mmol) in 20 mL of CH_2Cl_2 (dried over $CaCl_2$), and this solution was cooled to 0 °C. A mixture of pyridine (1.8 mL, 22.3 mmol, dried over CaH) and 99% pure *meso*-2,4-pentanediol (0.75 g, 7.21 mmol) dissolved in 5 mL of CH_2Cl_2 was added dropwise to the stirred anhydride solution over a period of 40 min. The mixture was filtered through a 2-cm bed of silica held in a 15-mL frit. The frit was washed with 20 cm of CH_2Cl_2, and the combined organic solutions were stripped of solvent under vacuum. The residue was dissolved in 20 mL of cold (0 °C) acetone, and a solution of NaI (21 mmol, 42 mL, 0.5 M in acetone) was added dropwise over 5 min. The mixture changed from pink to yellow during the addition. The solvent was removed under vacuum, and to the residue was added 50 mL of water. The aqueous mixture was extracted with hexanes (2 × 10 mL), and the combined organic layers were then extracted with water (1 × 10 mL) and 10% aqueous $Na_2S_2O_3$ (2 × 10 mL) and then dried over $MgSO_4$. Removal of the solvent under vacuum yielded 1.67 g of slightly yellow oil (72.4% based on diol). ^{1}H NMR showed this to be chemically pure with a ratio of *meso*/*dl*-**7** of 93:7 by integration of the multiplets at 3.80 and 4.07 ppm (benzene-d_6) respectively: ^{1}H NMR (chloroform-*d*) δ 4.21 (m, 2 H), 2.60 (m, 1 H), 2.01 (m, 2 H), 1.90 (d, 6 H, *J* = 6.8 Hz), (benzene-d_6) δ 4.07 (m, *dl* impurity), 3.80 (m, 2 H), 2.28 (m, 1 H), 1.48 (d, *dl* impurity), 1.35 (d, 6 H, *J* = 6.8 Hz); HRMS (70 eV) calcd for $C_5H_{10}I_2$ *m*/*e* 323.8872, found 323.8884 (M^+). The resonances characteristic of *meso*- and *dl*-**7** are well separated in benzene-d_6 allowing the simple determination of diastereomeric purity.

***dl*-2,4-Diiodopentane (*dl*-7).** *dl*-2,4-Pentanediyl ditriflate was prepared by the general method of Beard et al.[18] In a 100-mL round-bottom flask equipped with a magnetic stirring bar was stirred Tf_2O (4.70 g, 16.6 mmol) dissolved in 25 mL of CH_2Cl_2 (dried over $CaCl_2$). This mixture was cooled to 0 °C, and a solution of 95% diastereomerically pure *dl*-2,4-pentanediol (0.75 g, 7.21 mmol) and pyridine (1.8 mL, 22.3 mmol, dried over CaH) dissolved in 5 mL of CH_2Cl_2 was added dropwise over 0.5 h. When the addition was complete, the orange mixture was filtered through 2 cm of silica in a 15-mL frit. The silica was then washed with 10 mL of CH_2Cl_2, and the combined organic solution was stripped of solvent under vacuum. Care was taken that the ditriflate mixture was kept at or below 0 °C. The residue was dissolved in 20 mL of ice cold acetone and stirred. A solution of NaI (21 mmol, 42 mL, 0.5 M in acetone) was added dropwise over 3 min. When the addition was complete, the solvent was removed under vacuum, again taking care to keep the solution at or below 0 °C. The residue was dissolved in 20 mL of water and the mixture then extracted with hexanes (10 mL). The layers were separated, and the hexanes layer was washed with water (1 × 10 mL) followed by $Na_2S_2O_3$ (1 × 10 mL, 10% aqueous) and then dried over $MgSO_4$ at −60 °C. Filtering and removal of the solvent under vacuum gave *dl*-2,4-diiodopentane as a slightly yellow oil: yield 1.72 g (5.31 mmol, 74% based on diol) of chemically pure (NMR) **7**; ^{1}H NMR (benzene-d_6) δ 4.09 (sextet, 2 H, *J* = 6 Hz), 3.77 (sextet, *J* = 6 Hz, meso impurity) 1.48 (d, 6 H, *J* = 7 Hz), 1.33 (m, 2 H, includes resonances from meso impurity); HRMS (70 eV) calcd for $C_5H_{10}I_2$ *m*/*e* 323.8872,

---

(17) Fry, A. J.; Britton, W. E. *J. Org. Chem.* **1973**, *38*, 4016.

(18) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673.

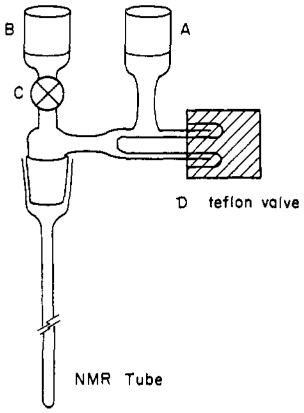


Figure 3. Adapter used to introduce solutions of *meso*- and *dl*-**7** to solutions of PPN·**4** frozen in NMR tubes.

found 323.8862 (M^+). Integration of the resonances at 4.09 and 3.77 ppm indicates a *dl*/*meso*-**7** ratio of 88:12.

Reaction of PPN·4 with *meso*-7 and *dl*-7. Stereochemical Experiments. These alkylations were run identically. For example: in a glovebox PPN·**4** (3.5 mg, 4.15 μmol) was weighed directly into an NMR tube sealed to a ground glass joint. To the tube was added THF-d_8 (0.71 mL) and HMDS (0.5 μL) as an internal standard. The tube was connected to the adapter shown in Figure 3 and then agitated until all of the PPN·**4** had dissolved. With valve D closed and a septum on joint B the apparatus was brought out of the drybox and attached to a vacuum manifold via joint A. The contents of the NMR tube were then frozen in liquid nitrogen. A solution of diiodide *meso*-**7** (8.03 μmol, 0.803 M in THF-d_8, 10 μL) was added through septum B and open stopcock C via a syringe with a needle long enough to reach into the NMR tube. After the solution was added and frozen, stopcock C was closed and the tube was evacuated by opening valve D. The tube was then sealed under vacuum. The reactants were initially warmed to −76 °C and thoroughly mixed. Further warming to −60 °C or room temperature allowed the reaction to proceed at the appropriate temperature. ^{1}H NMR spectra were recorded in probes equilibrated to the reaction temperature. Integration of the Cp region near 5 ppm or the methyl region near 1.1 ppm gave the observed ratios of **6c** and **6t**. The diiodide methyl resonances were diagnostic of their relative concentrations and integration of these gave estimates of the extent of diiodide scrambling.

Separation of Dimethylmetallacyclopentanes 6c and 6t by HPLC. Diastereomeric mixtures of **6c** and **6t** were found to give some separation by HPLC (reverse phase, acetonitrile/water). After further experiments utilizing different columns and conditions (silica/hexanes, reverse phase, methanol/water) the optimal conditions were found to be reverse phase, 80:20 methanol/water, and flow rates of 3 mL min^{-1}. Typical retention times were 35 min for **6c** and 36.5 min for **6t**. The samples were injected as saturated solutions in toluene (10 μL, ca. 0.1 mg/injection). Repeated injection and collection of the individual peaks gave small samples of the separate diastereomers whose ^{1}H NMR spectra were used in the assignment of the retention times. By integration of the methyl resonances the sample of **6t** obtained in this manner was found to be >99% diastereomerically pure and **6c** was >93% diastereomerically pure.

Control Experiment. Reaction of PPN·4 with 3,5-Diiodoheptane in the Presence of 6t. HPLC Analysis of the Products. In a 100-mL round-bottom flask was placed 1 mg of the trans dimethylmetallacycle **6t** (2.7 μmol). PPN·**4** (11 mg, 13 μmol) and 3 mL of THF were placed in the flask, and this mixture was stirred with a magnetic stirring bar until all of the solid material had dissolved. At this point 3,5-diiodoheptane (17 mg, 48 μmol) was added. Aliquots were removed from this mixture periodically, and the infrared spectra of these solutions were recorded directly. A peak at 1802 cm^{-1} was observed to grow in as the starting radical anion absorption at 1690 cm^{-1} diminished. After 4.25 h the infrared spectrum showed that nearly all of radical anion **4** had reacted. Hexanes (20 mL) was added, and this solution was then filtered. Removal of the solvent under vacuum and chromatography (air free conditions, alumina II, 1:3 benzene/hexanes, 0.5 × 5 cm column) yielded a dark green fraction that contained the metallacycles. The solvent was removed from this solution under vacuum, and the residue was subjected to HPLC analysis under the conditions used for separation of the diastereomers. Comparison of this mixture with known samples of dimethylmetallacycle **6** indicated that no **6c** was present to within ±5%.

1,3-Diiodobutane (12). In a 1-L round-bottom flask equipped with a magnetic stirring bar 1,3-dibromobutane (37.8 g, 0.175 mol) and NaI (80.0 g, 0.53 mol) were dissolved in 700 mL of methyl ethyl ketone. This solution was heated at reflux for 6 h after which time a 0.5-mL aliquot was removed by syringe. The solvent was removed under vacuum from this aliquot and the residue extracted with chloroform-*d*. The ^{1}H NMR spectrum of this solution showed a lack of the methyl doublet at δ 1.74 assigned to the starting dibromide. Shorter reaction times monitored in a similar manner were found to give incomplete substitution. The brown reaction mixture was cooled and then filtered. The solvent was removed under reduced pressure, yielding an oil that was dissolved in diethyl ether (70 mL) and extracted with $Na_2S_2O_3$ (3 × 30 mL, 10% aqueous). The ether layer was dried over $MgSO_4$, and the solvent was then removed under reduced pressure. Distillation of the remaining oil at reduced pressure (2 mm) yielded 41.7 g (0.135 mol, 77% based on dibromide) of oily yellow diiodide **12** judged to be >95% pure by NMR. The yellow color was removed by letting the product stand over mercury and clean copper wire and then filtering: bp 57–59 °C (2 mm) [lit.[19] 80–82 °C (5 mm)]; ^{1}H NMR (chloroform-*d*) δ 1.97 (d, 3 H, *J* = 6.8 Hz), 2.07 (m, 1 H), 2.28 (m, 1 H), 3.23 (m, 1 H), 3.33 (m, 1 H), 4.24 (m, 1 H), (methylene-d_2 chloride) δ 4.26 (m, 1 H), 3.37 (m, 1 H), 3.23 (m, 1 H), 2.27 (m, 1 H), 2.04 (m, 1 H), 1.96 (d, 3 H, *J* = 7 Hz); MS (70 eV) *m/e* 55 (base), 310 (M^+).

3-Methyl-1,2-bis(η^5-cyclopentadienyl)-1,2-dicobaltacyclopentane (11). In a glovebox 1,3-diiodobutane (1.15 g, 3.71 mmol) was added to a stirred suspension of PPN·**4** (2.00 g, 2.37 mmol) in 20 mL of THF. After 20 min infrared analysis of an aliquot removed from the reaction mixture showed new peaks growing in at 1804 and 1790 cm^{-1}. After 2 h the absorption at 1690 cm^{-1} due to the starting radical anion **4** had disappeared, indicating the reaction was complete. Hexanes (20 mL) were added to the reaction mixture, and the precipitated NaI was filtered off. The solvent was removed under vacuum, giving a green residue. Air-free chromatography through a 4 × 17 cm column of alumina II (1:4 benzene/hexanes) gave a red-orange band that eluted first ($CpCo(CO)_2$) followed by a dark green product band. This fraction was collected, and the solvent was removed under vacuum. The product was recrystallized from toluene/hexanes as dark-green needles that were filtered, washed with cold hexanes, and dried under vacuum. Further cooling of the supernatant yielded a second crop of crystals for a total of 0.274 g of product metallacycle **11** (0.76 mol, 32% yield based on cobalt) which was judged to be pure by NMR: ^{1}H NMR (benzene-d_6) δ 4.60 (s, 5 H), 4.58 (s, 5 H), 2.53 (m, 1 H), 1.62 (q, 1 H, *J* = 7.7 Hz), 1.18 (m, 1 H), 1.08 (d, 3 H, *J* = 6.6 Hz), 0.60 (m, 1 H), 0.28 (m, 1 H); IR (THF) 1806 cm^{-1}; mp (under N_2) 138–140 °C dec; MS (30 eV) *m/e* 39 (base), 360 (M^+). Anal. Calcd for $C_{16}H_{18}O_2Co_2$: C, 53.56; H, 5.04; Co, 32.72. Found: C, 53.50; H, 4.96; Co, 33.5.

Epoxidation of Crotonic Acid. This epoxidation was performed on twice the scale of the procedure described by Mohrig et al.[11] The product *trans*-2,3-epoxybutanoic acid (pure by ^{1}H NMR) was obtained in 16.2% yield based on crotonic acid (lit.[11] 36%): ^{1}H NMR (chloroform-*d*) δ 11.0 (br, 1 H), 3.29 (q of d, 1 H, *J* = 5.1, 1.7 Hz), 3.24 (d, 1 H, *J* = 1.6 Hz), 1.44 (d, 3 H, *J* = 5.1 Hz), (deuterium oxide) δ 2.95 (d, 1 H, *J* = 2 Hz), 2.90 (q of d, 1 H, *J* = 5.1, 2 Hz), 1.13 (d, 3 H, *J* = 5.1 Hz); mp 85.0–87.0 °C (lit.[21] 84.5–85 °C).

Synthesis of a Mixture of (2*S*,3*S*)- and (2*R*,3*R*)-3-Hydroxybutanoic-*2-d* Acid and (2*S*,3*S*)- and (2*R*,3*R*)-2-Hydroxybutanoic-*3-d* Acid. Reduction of the epoxide was performed on one-half the scale described by Mohrig et al.[11] The product obtained was a very slightly yellow oil (66.6% based on epoxide (lit.[11] 52%)). ^{1}H NMR showed this product oil to be a pure mixture of 2-hydroxybutanoic-*3-d* acid and 3-hydroxybutanoic-*2-d* acid in a 6:94 relative ratio. For the desired (2*S*,3*S*)- and (2*R*,3*R*)-3-hydroxybutanoic-*2-d* acid the vicinal coupling constant between H(C2) and H(C3) was 9 Hz. This agrees with the literature[11] value and is consistent with the stereochemical assignment; ^{1}H NMR (chloroform-*d*) δ 6.9 (br, 1 H), 4.25 (d of q, 1 H, *J* = 9, 6.4 Hz), 2.49 (br d, 1 H, *J* = 9 Hz), 1.27 (d, 3 H, *J* = 6.3 Hz), 1.00 (d, *J* = 7.3 Hz, 2-hydroxy impurity, 6% relative area to 1.27 ppm resonance), (deuterium oxide) δ 4.04 (d of q, 1 H, *J* = 8.2, 6.8 Hz), 2.29 (br d, 1 H, *J* = 8.3 Hz), 1.04 (d, 3 H, *J* = 6.3 Hz), 0.75 (d, *J* = 7.5 Hz, 2-hydroxy impurity, 6% relative area to 1.04 ppm resonance). [^{1}H NMR of 3-hydroxybutanoic acid (Aldrich) (chloroform-*d*) δ 5.3 (br, 1 H), 4.23 (m, 1 H), 2.53 (m, 2 H), 1.26 (d, 3 H, *J* = 6.3 Hz).] Integration shows that the deuterium incorporation at C2 in the deuterated material is 49–50%, i.e., 98–100% C2-d_1.

(2*S*,3*R*)- and (2*R*,3*S*)-Butane-*2-d*-1,3-diol. In a 250-mL round-bottom flask equipped with a magnetic stirring bar was placed 125 mL of dry THF and 1.40 g of $LiAlH_4$ (36.8 mmol, Alfa). While this was stirred, a mixture of deuterated hydroxybutanoic acids (2.58 g, 24.5 mmol) prepared as described above was dissolved in THF (40 mL) and placed in a 30-mL pressure equalizing addition funnel. This solution was

---

(19) Hass, H. B.; Huffman, H. C. *J. Am. Chem. Soc.* **1941**, *63*, 1233.
(20) Cazaux, L.; Maroni, P. *Bull. Soc. Chim. Fr.* **1972**, *2*, 773.
(21) Payne, G. B.; Williams, P. H. *J. Org. Chem.* **1959**, *24*, 54.

added dropwise to the $LiAlH_4$ slurry over 25 min under a gentle stream of N_2. The reaction was followed by removal of 1-mL aliquots that were treated as follows. After being quenched with 10% aqueous NH_4Cl and acidified with 6 M HCl, the mixture was extracted with ether (3 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed under vacuum. The residue was taken up in chloroform-*d*. ^1H NMR showed product peaks at δ 4.1, 3.85, and 1.7 and starting material resonances at 2.45 and 4.24 ppm. After 4.5 h the reaction was complete. The reaction mixture was quenched with 10% aqueous NH_4Cl and then stripped of solvent under vacuum. The white residue was dissolved in 20 mL of 6 M HCl and continuously extracted for 12 h. Removal of solvent from the extract under vacuum yielded 1.93 g of slightly yellow product oil (80% based on hydroxy acid) that was determined by NMR to contain only the 1,2- and 1,3-diols: ^1H NMR (chloroform-*d*) δ 4.09 (m, 1 H), 3.75 (m, 2 H), 2.63 (br s, 2 H), 1.69 (m, 1 H), 1.25 (d, 3 H, $J = 6.2$ Hz), 1.20 (t, 1,2-diol impurity), 0.93 (d, 1,2-diol impurity), (benzene-d_6) δ 3.69 (m, 1 H), 3.48 (m, 2 H), 1.92 (br s, 2 H), 1.37 (br m, 1 H, CHD), 0.97 (d, 3 H, $J = 6.2$ Hz); ^1H NMR of an authentic sample of 1,3-butanediol (MCB) (benzene-d_6) δ 3.70 (m, 1 H), 3.50 (m, 2 H), 2.18 (br d, 1 H, $J = 4$ Hz), 1.96 (br t, 1 H, $J = 4.5$ Hz), 1.41 (m, 1 H), 1.24 (m, 1 H), 0.97 (d, 3 H, $J = 6$ Hz). Integration of the ^1H NMR spectrum showed that the ratio of 1,2-diol to 1,3-diol was 1:14. Integration of the 1.6–1.0 ppm region (benzene-d_6) shows that the 1.37 ppm resonance in the labeled 1,3-diol is >93% of the total area, indicating >93% diastereomerically pure deuterium substitution.

The ditosylate derivative of the 1,3-diol was prepared to obtain a mass spectrum of the deuterated material. A mixture of the labeled C4 diols (0.95 g, 10.5 mmol) was placed in a 50-mL round-bottom flask equipped with a magnetic stirring bar. Pyridine (14 mL, dried over CaH_2) was added, and this mixture was cooled to 0 °C. To this stirred mixture *p*-toluenesulfonyl chloride (4.34 g, 22.8 mmol, TsCl, MCB) was added in small quantities over 20 min. After 3 h HCl (40 mL, 6 M) was added and an oily product appeared. This oil was separated from the aqueous mixture and chromatographed on silica (230–400 mesh, 2 × 21 cm, 7:2:1 petroleum ether/CH_2/diethyl ether). After 75 mL of solvent was allowed to elute, 22 fractions (20 mL each) were collected. The 1,2-ditosylate eluted in fractions 10 and 11 while the 1,3-ditosylate eluted in fractions 13–22. Each fraction was examined by TLC using the same solvent system on silica plates. Removal of the solvent under vacuum from the combined 1,3-ditosylate fractions and recrystallization from warm EtOH yielded white needles of (2*R*,3*S*)- and (2*S*,3*R*)-1,3-butaneditosylate-*2-d* which was determined to be pure by NMR: yield 0.883 g (21% based on diol); ^1H NMR (chloroform-*d*) δ 7.75 (d, 4 H, $J = 8.2$ Hz), 7.34 (m, 4 H), 4.69 (quintet, 1 H, $J = 6.4$ Hz), 3.98 (m, 2 H), 2.46 (br s, 6 H), 1.93 (br q, 1 H, $J = 6$ Hz, CHD), 1.24 (d, 3 H, $J = 6.4$ Hz); mp 56–57 °C (lit.[22] 58–59 °C); MS (70 eV) 399 (M^+), 398 ($M^+ - 1$, 6% of M^+). By examination of the ^1H NMR and mass spectra the ratio of d_0:d_1:d_2 ditosylates is 4.5:92.7:2.7.

(2*R*,3*R*)- and (2*S*,3*S*)-1,3-Diiodobutane-*2-d* (*syn*-12-*d*). In a 50-mL round-bottom flask equipped with a magnetic stirring bar were placed 0.13 g of deuterated 1,3-butanediol (1.44 mmol), 0.30 mL of pyridine (0.29 g, 3.7 mmol, dried over CaH), and 20 mL of CH_2Cl_2 (dried over $CaCl_2$). After the mixture was cooled to 0 °C and stirred, a solution of Tf_2O (0.91 g, 10.0 mmol) dissolved in 10 mL of CH_2Cl_2 was added dropwise from a 50-mL pressure equalizing addition funnel. This mixture was stirred for 10 min and then filtered through a 2-cm bed of silica in a 15-mL frit. The silica was washed with 20 mL of CH_2Cl_2, and the solvent was removed from the combined organic solution. The residue was dissolved in 20 mL of cold (0 °C) acetone and stirred in an ice bath. To this was added NaI (20 mL, 0.5 M in acetone, 10 mmol) dropwise over 5 min. After the addition was complete, the solvent was quickly removed under vacuum at 0 °C and the residue was dissolved in 20 of water. The aqueous mixture was extracted with hexanes (2 × 20 mL), and the combined hexanes portion was washed with 10% aqueous $Na_2S_2O_3$ and then dried ($MgSO_4$). Filtering and removal of the solvent under vacuum yielded 0.17 g of slightly yellow product **12**-*d* (40% based on diol): ^1H NMR (methylene-d_2 chloride) δ 4.45 (m, impurity) 4.25 (m, 1 H), 3.36 (m, 1 H), 3.23 (m, 1 H), 2.03 (br m, 1 H, CHD), 1.94 (d, 3 H, $J = 7$ Hz), 1.93 (t, impurity). Integration shows that impurities account for 15% of all proton resonances. No resonances consistent with the 1,2-diiodides were seen. Integration of the region between 2.4 and 1.9 ppm indicated that the deuterium label was >95% stereospecifically syn.

Alkylation of Radical Anion 4 with *syn*-12-*d*. This alkylation was performed identically with the preparation of the unlabeled metallacycle **11**. The monodeuterated metallacycle **11**-*d* was isolated after chromatography by removal of the solvent from the metallacycle fraction (28% yield based on cobalt): ^1H NMR (benzene-d_6) δ 4.59 (s, 5 H), 4.57 (s, 5 H), 2.56 (br quintet, 1 H, $J = 7$ Hz), 1.56 (br t, 1 H, $J = 7.5$ Hz), 1.22 (br t, 1 H, $J = 8.3$ Hz), 1.15 (d, 3 H, $J = 6.4$ Hz), 0.56 (br m, 0.17 H), 0.28 (br q, 0.83 H). The excess diiodide *syn*-**12**-*d* was collected in the first column fraction and the diastereomeric purity of the deuterium label was found by ^1H NMR (methylene-d_2 chloride) to be >75% intact.

Competition Experiments. All the competition experiments were performed identically. For example, in a glovebox PPN·**4** (5.2 mg, 6.17 μmol) was placed in a small vial. THF-d_8 (0.4 mL) was added to dissolve the radical anion **4**. In another vial 1,3-diiodopropane (18.8 mg, 63.5 μmol) and 1,3-diiodobutane (52.6 mg, 170 μmol) were dissolved in THF-d_8. The diiodide solution was then quickly added to the solution of anion **4**, and the vial was capped and periodically shaken. After 3.5 h the reaction mixture was filtered into an NMR tube and the ^1H NMR spectrum was recorded. Integration of the Cp region showed a relative area of 108:104 for the C_3 primary/primary diiodide product and the C_4 primary/secondary diiodide product. Correcting for molar ratios and statistical ratios the primary carbon center of the C_4 diiodide reacts 0.72 times as fast as the primary center of the C_3 diiodide.

Acknowledgment. Partial support of this work was provided by NSF grant CHE79-26291. We are grateful to Prof. Stanley J. Cristol for calling our attention to the work of his group on the stereochemistry of electron transfer processes in photosolvolysis reactions.

Registry No. PPN·**4**, 58635-28-5; **6c**, 86632-45-3; **6t**, 86688-16-6; *meso*-**7**, 22495-59-6; *dl*-**7**, 22464-33-1; *dl*-**8**, 86632-37-3; *meso*-**8**, 86632-38-4; *cis*-**9**, 86632-46-4; *trans*-**9**, 86688-17-7; **11**, 86632-47-5; *syn*-**11**-*d*, 86632-48-6; *anti*-**11**-*d*, 86707-51-9; **12**, 18371-24-9; *syn*-**12**-*d*, 86632-39-5; TF_2O, 358-23-6; $CpCo(CO)_2$, 12078-25-0; 2,4-dibromopentane, 19398-53-9; 3,5-heptanediol, 86632-40-8; 3,5-heptanedione, 7424-54-6; *meso*-2,4-pentanediylditriflate, 86632-41-9; *meso*-2,4-pentanediol, 3950-21-8; *dl*-2,4-pentanediylditriflate, 86632-42-0; *dl*-2,4-pentanediol, 1825-14-5; 1,3-dibromobutane, 107-80-2; crotonic acid, 107-93-7; *trans*-2,3-epoxybutanoic acid, 13737-02-5; 3-hydroxybutanoic-*2-d* acid, 79069-08-2; 2-hydroxybutanoic-*3-d* acid, 86632-43-1; butane-*2-d*-1,3-diol, 86688-15-5; 1,3-butaneditosylate-*2-d*, 86632-44-2.

---

[22] Laasko, T. M.; Reynolds, D. D. *J. Am. Chem. Soc.* **1951**, *73*, 3518–20.