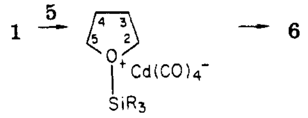
9 would have become favorable at the lower pressure and temperature.

The $Co_2(CO)_8$-catalyzed reaction of tetrahydrofurans having substituents at various positions has been studied, and the results are given in Table I. Generally, incorporation of carbon monoxide took place at 25 °C and 1 atm with benzene or dichloromethane as the solvent. The product distributions in the cases where formation of isomers was possible were greatly effected by the substitution patterns. The results suggest that the regiochemistry would be determined in the ring-opening step of an appropriate silyloxonium ion (**10**) by $Co(CO)_4^-$. For 2-methyltetrahydrofuran (run 2) the ring opening at C-5 (a primary center) is likely to involve S_N2-like attack of $Co(CO)_4^-$, while cleavage at C-2 (a secondary center) would be accounted for by assuming the development of partial positive charge at C-2 in the transition state.[15,16] Since the development of the partial positive charge is expected to be highly enhanced at a tertiary center, it was not surprising to observe 2,2-dimethyltetrahydrofuran (run 3) undergoing exclusive cleavage at C-2 (a teritary center) to give a mixture of products (2-methyl-5-(diethylmethylsiloxy)pentane, 26%, 2-methyl-5-(diethylmethylsiloxy)-2-pentene, 47%, 2-methyl-5-(diethylmethylsiloxy)-1-pentene, 26%) without incorporation of carbon monoxide.[17] Introduction of substituents at the C-3 position of THF has resulted in the incorporation of carbon monoxide predominantly (run 6) or exclusively (run 7) at C-5, probably due to sterically unfavorable approach of $Co(CO)_4^-$ to C-2 in the oxonium ion corresponding to **10**. The presence of a byproduct having an unsaturated bond in run 5 may be ascribed to β-hydride elimination from the intermediate similar to **8**. In such a case, the use of $HSiMe_3$ instead of $HSiEt_2Me$ was found to be effective in suppressing the byproduct formation (run 5). The less bulky $HSiMe_3$ would undergo oxidative addition (see **8** and **9** in Scheme I) more easily than $HSiEt_2Me$ to give the desired product exclusively.



10

The present work not only demonstrates a new method of using carbon monoxide under mild conditions but also suggests a new room-temperature entry to alkylcobalt carbonyls.[10] It should be also noted that the overall transformation described is formally a nucleophilic introduction of an oxymethyl group which is not an easy task from the viewpoint of organic synthesis.[18] Further studies are in progress.

Acknowledgment. This work was supported in part by Grant-in-Aid for Special Project Research No. 57118002 provided by The Ministry of Education, Science, and Culture, Japan. We gratefully acknowledge Shin-Etsu Chem. Ind. Ltd., for generous gift of chlorosilanes.

Registry No. 1, 109-99-9; 4, 87481-75-2; $MeEt_2SiO(CH_2)_4CH(CH_3)OSiEt_2Me$, 87481-76-3; $MeEt_2SiO(CH_2)_3CH(CH_3)CH_2OSiEt_2Me$, 87481-77-4; $MeEt_2SiOCH(CH_3)CH_2CH_2CH(CH_3)CH_2OSiEt_2Me$ (isomer 1), 87481-79-6; $MeEt_2SiOCH(CH_3)CH_2CH_2CH(CH_3)CH_2OSiEt_2Me$ (isomer 2), 87481-80-9; $MeEt_2SiOCH(CH_3)CH_2CH_2C(CH_3) = CHOSiEt_2Me$, 87481-81-0; $MeEt_2SiOCH_2CH_2CH(CH_3)CH_2CH_2OSiEt_2Me$, 87481-82-1; $MeEt_2SiO(CH_2)_3C(CH_3)_2CH_2OSiEt_2Me$, 87494-50-6; $HSiEt_2Me$, 760-32-7; CO, 630-08-0; $Co_2(CO)_8$, 10210-68-1; 2-methyl-5-(diethylmethylsiloxy)pentane, 87481-83-2; 2-methyl-5-(diethylmethylsiloxy)-2-pentene, 87481-84-3; 2-methyl-5-(diethylmethylsiloxy)-1-pentene, 87481-85-4; 2-methyltetrahydrofuran, 96-47-9; 2,2-dimethyltetrahydrofuran, 1003-17-4; *cis*-8-oxabicyclo[4.3.0]nonane, 13149-01-4; 2,5-dimethyltetrahydrofuran, 1003-38-9; 3-methyltetrahydrofuran, 13423-15-9; 3,3-dimethyltetrahydrofuran, 15833-75-7; *cis*-[[2-[2-[(diethylmethylsilyl)oxy]ethyl]cyclohexyl]methoxy]diethylmethylsilane, 87481-78-5.

Supplementary Material Available: Spectral and analytical data (6 pages). Ordering information is given on any current masthead page.

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[15] For example, see: Goldsmith, D. J.; Kennedy, E.; Campbell, R. G. *J. Org. Chem.* **1975**, *40*, 3571.

[16] In the reaction of 2-methyltetrahydrofuran with $Me_3SiMn(CO)_5$, only one product arising from C-5 cleavage was isolated after chromatographic purification.[14]

[17] Generally, a tertiary alkylcobalt carbonyl, if formed, would undergo β-hydride elimination rather than CO insertion.

[18] (a) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. (b) Paulsen, H.; Sumfleth, E.; Sinnwell, V.; Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 2055. (c) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1983**, *24*, 3163, 3165. (d) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 212 and references cited therein.

Cyclopentanones from Nucleophilic Addition/Carbonylation to $(\eta^4$-Diene$)Fe(CO)_3$ Complexes

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Summary: The addition of carbon nucleophiles to (1,3-diene)iron tricarbonyl complexes produces (homoallyl)$Fe(CO)_3$ anionic complexes; as reported earlier, CO is incorporated at 1.5 atm to give acyliron anionic complexes. With most open-chain 1,3-diene ligands, further cyclization occurs, producing cyclopentanone derivatives with the anionic substituent in the 3-position. The yields are good if the nucleophiles are sufficiently reactive, while the primary limitation is the resistance to ring closure with multiply substituted dienes. With 2-substituted 1,3-dienes, the cyclopentanone product is formed with a specific cis relationship of the substitutents at C-3 and C-4. Through deuterium labeling studies, a mechanism involving β-hydride elimination/readdition is demonstrated as the final stage of the cyclopentanone formation.

The addition of a reactive carbon nucleophile to an $(\eta_4$-1,3-diene$)Fe(CO)_3$ complex (e.g., **1**)[2] produces an intermediate that has the expected chemical properties of the homoallyl complex **2**.[3] For example, with $(\eta^4$-1,3-cyclohexadiene$)Fe(CO)_3$, addition of $LiC(CH_3)_2CN$ in the presence of CO gives a new intermediate, with the properties of an acyliron tricarbonyl anion, such as **3**.[5] However, for most open-chain 1,3-dienes, the process does not stop at **3** but leads to cyclopentanones with the anion unit in the C-3 position (after protonation, e.g., **4**). Herein, we

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[1] (a) NIH Graduate Trainee, 1980–1981; EXXON Fellow, 1982–1983. (b) Based in part on the Junior Paper of J.K.L.

[2] For a study of the scope of anion addition, see: Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363–372.

[3] We are aware of no previous examples of $(\eta^3$-but-3-en-1-yl$)Fe(CO)_3$ anion complexes such as **2**, although close parallels with the $RFe(CO)_3L$ anionic complexes can be expected.[4]

[4] Complex **2** is structurally related to the first intermediate in Collman's reaction, the organoiron tetracarbonyl anion. For a discussion, see: Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342–347.

[5] Semmelhack, M. F.; Herndon, J. W.; Springer, J. *J. Am. Chem. Soc.* **1983**, *105*, 2497–2499.

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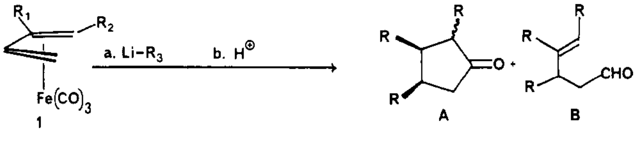
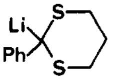
Table I. Formation of Cyclopentanones by Addition/Carbonylation with (η^4-1,3-Diene)Fe(CO)$_3$ Complexes

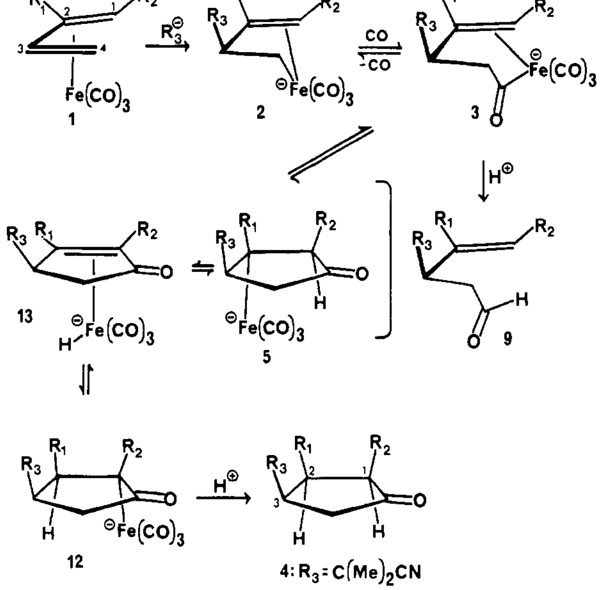


entry	diene complex	LiR_3	% yield A	% yield B
1	$R_1, R_2 = H$	$LiC(CH_3)_2CN$	85[f]	0
2	$R_1, R_2 = H$	$LiC(CH_3)_2CO_2Et$	72	0
3	$R_1, R_2 = H$	$LiC(CH_3)_2CO_2Li$[a]	57	0
4	$R_1, R_2 = H$	$LiCH(CH_3)CO_2$-*t*-Bu[a]	54	0
5	$R_1, R_2 = H$	$LiC(OR)CN(C_4H_9)$	75[b]	0
6	$R_1, R_2 = H$	$LiCHPH_2$	62	0
7	$R_1, R_2 = H$		79	0
8	$R_1 = CH_3, R_2 = H$	$LiC(CH_3)_2CN$	79	0
9	$R_1 = H, R_2 = CH_3$	$LiC(CH_3)_2CN$	93	6
10	$R_1 = OMe, R_2 = H$	$LiC(CH_3)_2CN$	70[c]	8
11	$R_1\text{-}R_2 = (CH_2)_4$	$LiC(CH_2)_2CN$	0	71[d,f]
12	$R_1, R_2 = CH_3$	$LiC(CH_3)_2CN$	0	65[d]
13	$R_1 = H, R_2 = OMe$	$LiC(CH_3)_2CN$	0	28[d]
14	(1,3-cyclohexadiene)	$LiC(CH_3)_2CN$	0	84[d]

[a] Hexamethylphosphoric triamide was used as a cosolvent. [b] The yield is based on the diketone isolated after hydrolysis of the cyanohydrin acetal functionality. [c] The yield is the sum of the yields of **4d** and **6**. [d] Ceric ammonium nitrate was not used; the product was isolated by chromatography directly after protonation. [f] From ref 5.

report initial studies on the scope and limitations of this new example of the general [4 + 1] strategy of cyclopentanone synthesis.[6]

Table I presents the examples with six different diene ligands and a variety of anions. Most of the work involves the simplest case (η^4-1,3-butadiene)Fe(CO)$_3$, **1a**. In a typical procedure, a slow stream of CO is passed over a stirred solution of $LiC(CH_3)_2CN$ (2.3 mmol)[13] in THF (10 mL) at −78 °C. The CO is allowed to exit through a needle. A solution of **1a** (2.3 mmol) in THF (0.5 mL) is added dropwise over a period of 1 min. The gas exit needle is withdrawn, and the pressure of CO is increased to approximately 8–15 psi above 1 atm.[14] The mixture is stirred for 2 h at −78 °C, allowed to warm to 25 °C, and cooled again to −78 °C, and trifluoroacetic acid (1.0 mL, 13 mmol) is added. The solution is stirred for 5 min at −78 °C and then poured into aqueous acetone. Solid ceric ammonium nitrate is added in small portions until further addition produces no further gas evolution (CO). The mixture is partitioned between water and ether and from the ether solution is isolated a colorless oil. Short-path distillation (bath temperature 80–110 °C/0.8 torr) gives 3-(2-cyano-2-methylprop-1-yl)cyclopent-2-en-1-one (**4a**) 78% yield.[15]



series a, $R_1 = R_2 = H$; b, $R_1 = CH_3$, $R_2 = H$; c, $R_1 = OCH_3$, $R_2 = H$; d, $R_1 = H$, $R_2 = CH_3$; e, $R_1 = R_2 = CH_3$; f, $R_1, R_2 = (CH_2)_4$

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(6) General approaches to five-membered rings were rare until recently.[7] Methodology for cyclopentanones related to the subject of this paper, involving an alkyne, an alkene, and CO was developed by Pauson[8] and recently applied in complex synthesis by Magnus.[9] More specifically, intermediates such as **2** may be involved in a quite different iron-promoted ring-forming strategy of McMurry,[10] Merour,[11] and Collman.[12]

(7) For a review with leading references see: Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141–170.

(8) Paulson, P. L.; Khand, I. U. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 2–14.

(9) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477–2478.

(10) McMurry, J. E.; Andrus, A. *Tetrahedron Lett.* **1980**, 4687–4690.

(11) Merour, J. Y.; Roustan, J. L.; Charrier, C.; Collin, J.; Benaim, J. *J. Organomet. Chem.* **1973**, *51*, C24–C26.

(12) Komoto, R. G. Ph.D. Dissertation, Stanford University, 1974; referred to in ref. 4.

(13) Procedures for anion generations. (a) Nitrile and ester–stabilized anions. To a 0.2 M solution of lithium diisopropylamide (1.4 mol equiv) in tetrahydrofuran at −78 °C under argon was added via syringe the appropriate nitrile or ester (1.5 mol equiv) over a period of 30 s. The solution was used immediately in the reaction with the iron complex (1.0 mol equiv). (b) Sulfur and phenyl–stabilized anions. to a 0.2 M solution of diphenylmethane, thioanisole, or 2–phenyl–1,3–dithiane (1.4 mol equiv) in tetrahydrofuran at −78 °C under argon was added via syringe a solution of *n*–butyllithium in hexane (1.3 mol equiv) over a period of 2 min. The solution was allowed to stir 1.5 h at −78 °C and used immediately in the reaction with the iron complex (1.0 mol equiv).

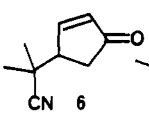
(14) The apparatus used was a one-neck flask equipped with magnetic stirrer and septum. After the iron complex 1 was mixed with the nucleophile at −78 °C, an additional septum was put in place and secured by copper wire in order to maintain the modest positive pressure.

(15) Characterization data: ^{1}H NMR ($CDCl_3$) δ 1.6–2.2 (m, 7 H, H at C-2, 3, 4, 5), 1.34 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 215.5 (s), 122.7 (s), 45.4 (d), 40.6 (t), 38.2 (t), 25.4 (t), 35.9 (s), 25.1 (q), 24.3 (q); IR (neat) 2900 (m), 2240 (m), 1740 (s), 1460 (m), 1405 (m), 1395 (m), 1370 (m), 1260 (s) cm^{-1}; GC–MS 151, 89, 83, 69, 56, 55 (B). Anal. Calcd for $C_9H_{13}N$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.55; H, 8.68; N, 9.09.

Several entries in Table I deserve special mention. The complex **1b** of isoprene produces a single product (entry 8) which has been identified as the cis-3,4-disubstituted cyclopentanone **4b** in good yield.[16] The formation of the less stable cis isomer is consistent with kinetically controlled anti addition at C-3 of the diene ligand to give **2b**, followed by rapid migration to a carbonyl ligand (**2b**) and intramolecular alkene insertion (to give **5b**). As before with the prototype case of (η^4-1,3-cyclohexadiene)Fe(CO)$_3$,[5] if the anion–diene adduct is allowed to warm above about 0 °C, rearrangement occurs to give a new intermediate (presumably an (η^3-allyl)Fe(CO)$_3$ anion) which does not readily incorporate CO.[5] The analogous complex **1c** of 2-methoxy-1,3-butadiene[17] does not give cyclopentanones following the typical procedure. However, at higher CO pressures (50 psi),[18] the cyclopentanone **4c** is formed accompanied by the corresponding cyclopentenone **6** from loss of MeOH. This process is potentially very useful, as gentle base treatment gives selective conversion to **6** (72%) and more vigorous conditions generate exclusively **7** (88% from a mixture of **4c** and **6**).[19]

The complex **1d** of (*E*)-piperylene produces a mixture of cyclopentanones from anion addition at C-3 (**4d**, mixture of epimers) and at C-2 (**8**) in approximately equal amounts. However, with the diene ligands bearing carbon substituents at both C-1 and C-2 (in **1e** and **1f**), ring closure to form cyclopentanones is not observed; the simple aldehydes (**9e,f**) predominate from CO incorporation and protonation.[5] Similarly, from (*Z*)-1-methoxy-1,3-butadiene (complex **10**) only the open-chain aldehyde **11** is obtained.

An important selectivity rule is suggested by these results. With the asumption that CO is acting as an efficient trapping agent for the first-formed addition product (i.e., **2**), the series in Table I and our earlier work[5] show no exception to the rule that nucleophile addition is always preferred at an internal position. Steric effects seem small; for example, the internal positions (C-2, C-3) in piperylene are equally reactive. The success of the cyclopentanone formation depends critically on the structure of the diene; it is efficient so far only with monosubstituted dienes.



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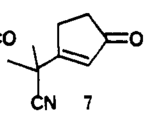

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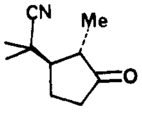

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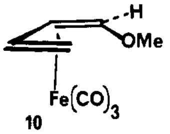

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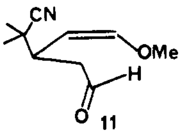
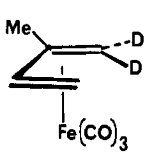


11



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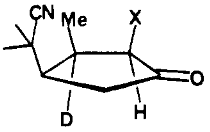

15: X = D
16: X = H

The postulated initial cyclopentanone intermediate **5** appears to rearrange rapidly to the enolate–iron derivative **12**. The rearrangement involves a stereospecific hydrogen transfer, presumably via β-hydride elimination/readdition through **13**. Starting from (η^4-1,1-dideuterio-2-methyl-1,3-butadiene)Fe(CO)$_3$ (**14**),[20] reaction with LiC(CH$_3$)$_2$CN according to the typical procedure gives a single dideuterio product that has been assigned structure **15**, based on spectral data.[21] The hydrogen (deuterium) rearrangement is consistent with cis-β-hydride elimination and retention of configuration during protolytic cleavage of the final anionic iron intermediate **12**. Work is in progress to define further the selectivity and generality of this cyclopentanone synthesis.

Acknowledgment. We acknowledge financial support from the National Science Foundation through research Grant CHE 82-04339 and an NIH graduate traineeship (to J.W.H). We also wish to thank Ms. Mary Baum for helpful discussions with regard to NMR spectral analysis.

Registry No. 1 (R$_1$ = H, R$_2$ = OMe), 62341-63-3; **1a**, 12078-32-9; **1b**, 32731-93-4; **1c**, 62341-64-4; **1d**, 32732-71-1; **1e**, 58356-41-5; **1f**, 32732-60-8; **4a** (R$_3$ = C(CH$_3$)$_2$CN), 85251-31-6; **4a** (R$_3$ = C(CH$_3$)$_2$CO$_2$Et, 87533-75-3; **4a** (R$_3$ = C(CH$_3$)$_2$CO$_2$Li), 87533-76-4;

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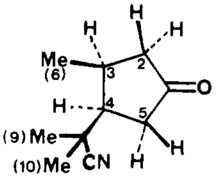
[16] ^{1}H NMR (CDCl$_3$, 250 MHz): δ 2.63 (ddq, 1 H, J = 7.3, 5.7, 7.3 Hz, H at C-3), 2.41 (dd, 1 H, J = 17.5, 7.3 Hz, H at C-2 trans to methyl group), 2.39 (d, 7 H, J = 11.6 Hz, H at C-5 cis to substituent), 2.37 (d, 1 H, J = 9.0 Hz, H at C-5 trans to substituent), 2.10 (ddd, 1 H, J = 11.6, 9.0, 5.7 Hz, H at C-4), 2.10 (d, 1 H, J = 17.5 Hz, H at C-2 cis to methyl group), 1.47, 1.49 (2s, 6 H, H at C-9, 10), 1.14 (d, 3 H, J = 7.3 Hz, H at C-6); Irradiate δ 1.14 δ −2.63 (dd, J = 5.7, 7.3 Hz); irradiate δ 2.63, δ −2.41 (br d, J = 17.5 Hz), 2.10 (dd, J = 11.6, 9.0 Hz).

The structure was assigned as cis based on the coupling constants between the proton at C-3 and those at C-2 and C-4. With use of the Karplus equation, the coupling constants suggest the following dihedral angles: between the protons at C-3 and C-4 is 31°; between C-3 and C-2 (trans) is 90°; between C-3 and C-2 (cis) is 41°. If the bulky isobutyronitrile group is allowed to adopt a pseudoequatorial conformation, then the calculated dihedral angles agree with those based on a Dreiding model. In a molecular model of the trans compound, if either of the dihedral angles between the protons at C-3 and C-4 or C-3 and C-2 (trans) are set at 90°, then both will be approximately 90°; the protons at C-3 and C-2 (cis) cannot be forced into a dihedral angle of 90° without placing unreasonable strain in the system.



[17] A sample of 2-methoxy-1,3-butadiene was prepared from 1,3,3-trimethoxybutane according to the procedure of Norris. Norris, R. A.; Verbanc, J. J.; Hennion, G. F. *J. Am. Chem. Soc.* **1938**, *60*, 1159–1160. Norris' results could not be repeated in our hands unless the amount of catalyst was reduced by a factor of 20. Reaction with Fe(CO)$_5$ in benzene with ultraviolet irradiation produced the desired complex **1c**.

[18] The apparatus used to contain 50 psi of CO was a medium-pressure glass bomb equipped with a syringe port adapter (Kontes "Griffen-Worden" vessel, borosilicate).

[19] If the reaction mixture from entry 10 was extracted with 10% aqueous potassium hydroxide solution, then the 4-substituted 2-cyclopenten-1-one **6** was obtained. Treatment of the product from entry 10 with *p*-toluenesulfonic acid in refluxing chloroform (10 min) led to formation of exclusively the 3-substituted 2-cyclopenten-1-one **7**.

[20] 1,1-Dideuterioisoprene was prepared from (methyl-d_3)triphenylphosphonium iodide and methyl vinyl ketone under standard Wittig conditions. A solution of the labeled isoprene (approximately 5 g) in ether was mixed with diiron nonacarbonyl (33.8 g, 30% excess) at 25 °C under argon. After being heated at reflux for 3 h, the mixture was concentrated and complex **14** was isolated by chromatography: ^{1}H NMR (CDCl$_3$) δ 5.28 (dd, 1 H, J = 6.7, 9.0 Hz, H at C-3), 2.17 (s, 3 H, H at C-5), 1.65 (dd, 1 H, J = 6.7, 2.6 Hz, H at C-4, trans), 0.02 (dd, 1 H, J = 9.0, 2.6 Hz, H at C-4, cis). Absorptions for residual H at C-1 (δ 1.81 and 0.27) are also detected, approximately 0.2 H together. Mass spectral analysis (EI) showed the product to consist of 61% d_2, 34% d_1, and 5% d_0.

[21] Referring to the ^{1}H NMR spectral data for the unlabeled isomer **4b**,[16] the assignment of structure **15** is based on the disappearance of the doublet at δ 2.10 and the appearance of a singlet at δ 1.14 (CH$_3$ at C-6). The mass spectrum showed the product to consist of 64% d_2, 31% d_1, and 5% d_0.

Treatment of the product with sodium methoxide in methyl alcohol briefly at 25 °C produced a monodeuterio isomer characterized as **16** by the singlet at δ 1.14 for the CH$_3$ at C-4 and a mass spectral pattern showing 0% d_2, 78% d_1, and 22% d_0.

4a (R_3 = $CH(CH_3)CO_2$-*t*-Bu), 87533-77-5; **4b**, 87533-78-6; **4c**, 87533-80-0; **4d**, 87533-79-7; **9** (R_1 = H, R_2 = OMe, R_3 = $C(CH_3)_2CN$), 87533-83-3; **9e**, 87533-82-2; **9f**, 87533-81-1; **14**, 87555-32-6; **15**, 87533-85-5; $LiC(CH_3)_2CN$, 50654-53-0; $LiC(CH_3)_2CO_2Et$, 42492-52-4; $LiC(CH_3)_2CO_2Li$, 16423-62-4; $LiCH(CH_3)CO_2$-*t*-Bu, 35717-09-0; 2-(3-oxo-cyclopent-1-yl)-2-phenyl-1,3-dithiane, 66124-79-6; α,α-dimethyl-5-formylcyclohex-2-ene-acetonitrile, 87533-84-4; (η^4-1,3-cyclohexadiene)tricarbonyliron, 12152-72-6; 2-phenyl-2-lithio-1,3-dithiane, 53178-41-9.

Insertion of Zerovalent Metals into the C–N Bonds of N,N′-Bridged Porphyrins

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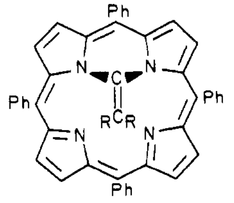
Summary: Treatment of the N,N′-bridged tetraphenylporphyrin ($TPPC{=}C(p\text{-}ClC_6H_4)_2$) with $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ yields the metallocarbene complexes $TPPM\{C{=}C(p\text{-}C_6H_4Cl)_2\}$ in which both N–C bonds are broken, while a similar reaction with $Ni(CO)_4$ yields $TPP\{C{=}C(p\text{-}C_6H_4Cl)_2\}Ni$ in which only one N–C bond is broken.

Recent work has demonstrated that the pyrrolic nitrogen atoms in metalloporphyrins have considerable reactivity. Examples of this include the reversible transfer of alkyl or aryl groups between the metal and nitrogen in iron or cobalt porphyrins[1] and the reversible insertion of carbene ligand, which initially resided on the iron, into an Fe–N bond.[2] We report here that the C–N bonds of N,N′-bridged porphyrin 1[3,4] are reactive toward insertion of low-valent metals and that, depending on the metal, one or both of the C–N bonds can be broken. The only previous report of reaction of N,N′-dialkylated porphyrins with metal ions have resulted in the formation of porphyrin complexes that utilize the unalkylated nitrogens as donors and that leave the N,N′ bridge intact.[5] The oxidative addition of C–N bonds to low-valent transition metals is a rare occurrence.



1, R = *p*-ClC_6H_4

Our results are summarized in Scheme I. Treating the N,N′-bridged porphyrin 1 with an excess of $Fe_3(CO)_{12}$ in boiling tetrahydrofuran solution for 1–2 h followed by concentration, chromatography on silica gel with benzene as eluent, and crystallization from dichloromethane/acetonitrile yields the red carbene complex 2 in 90% yield. The spectroscopic properties of 2 (electronic spectrum, 416 (ϵ 1.29 × 10^5), 520 (1.44 × 10^4), 542 nm (sh); ^1H NMR 8.70 (s, 8 H), 8.12 (s, 4 H), 7.7 (m, 16 H), 6.43 (d, *J* = 7.9 Hz, 4 H), 4.01 ppm (d, *J* = 7.9 Hz, 4 H)) are in good agreement with previous observations of this material obtained by a path reported earlier.[6,7] The reaction between 1 and an equimolar quantity of $Ru_3(CO)_{12}$ under similar conditions yields the red carbene complex 3 that elutes as the first chromatographic band, in 40% yield.[8] The spectroscopic properties of this new substance (electronic spectrum, 416 (ϵ 7.19 × 10^4), 522 (1.52 × 10^4) 542 nm (sh); ^1H NMR spectrum 8.67 (s, 8 H), 8.09 (s, 4 H), 7.69 (s, 8 H), 7.67 (s, 8 H), 6.42 (d, *J* = 8.0 Hz, 4 H), 3.99 ppm (d, *J* = 8.0 Hz, 4 H)) are similar to those of its iron analogue 2.

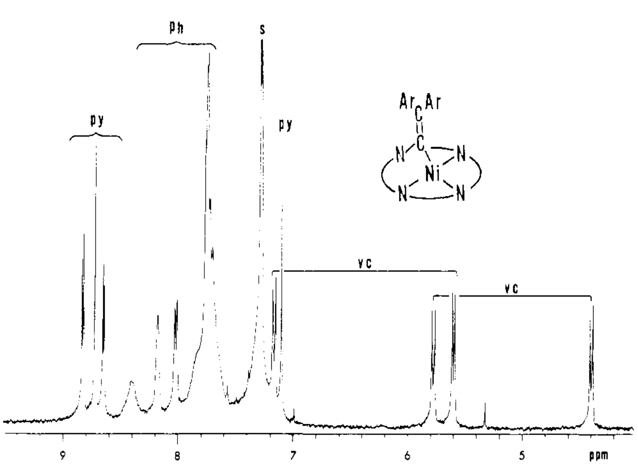
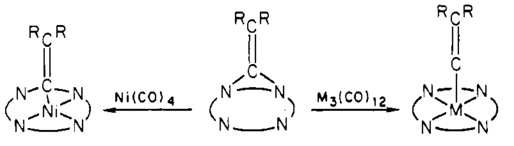


Figure 1. The 360-MHz ^1H NMR spectrum of **4** in chloroform-*d* solution at 21 °C. Peaks are labeled as follows: py, pyrrole protons; Ph, phenyl protons of the tetraphenyl porphyrin; VC, phenyl protons of the *p*-chlorophenyl groups; S, residual, undeuterated solvent resonance.

Scheme I



4 1 2, M = Fe
3, M = Ru

The reaction of 1 with $Ni(CO)_4$ takes a different course, in which only one of the C–N bonds is broken. Treatment of 1 with excess $Ni(CO)_4$ in boiling tetrahydrofuran yields, under similar workup, dark green crystals of 4 in 90% yield.[9] The molecular composition of 4 is established from its field-desorption mass spectrum which exhibits a multiplet at *m/e* 916 (for $^{58}Ni^{35}Cl_2$) due to the parent ion and weak features at *m/e* 670 due to nickel(II) tetraphenylporphyrin, and at *m/e* 246 due to $(p\text{-}ClC_6H_4)_2C_2$. The ^1H NMR spectrum is shown in Figure 1. The two *p*-chlorophenyl groups of the vinyl bridge appear as two quartets that have chemical shifts upfield of normal phenyl resonances because of ring current shifts from the por-

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(7) This reaction completes the cycle $TPPFe\{C{=}C(C_6H_4Cl)_2\}$ → $\{TPPC{=}C(C_6H_4Cl)_2\}FeCl$ → 1 → $TPPFe\{C{=}C(C_6H_4Cl)_2\}$.

(8) Anal. Calcd for $C_{58}H_{36}Cl_2N_4Ru$: C, 72.50; H, 3.78; N, 5.83; Cl, 7.38. Found: C, 72.73; H, 4.09; N, 6.72; Cl, 7.20.

(9) Anal. Calcd for $C_{58}H_{36}Cl_2N_4Ni$: C, 75.84; H, 3.95; N, 6.10; Cl, 7.72. Found: C, 75.65; H, 4.18; N, 5.92; Cl, 7.78.

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