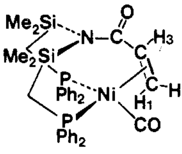
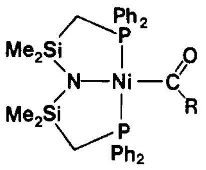
more slowly than that of **1a** or **1b** to give, after 3 h, a mixture of two identifiable products. The rearranged Ni(0) derivative **2c** is obtained as the major product[7] in ~90% yield (by ^{1}H NMR spectroscopy) as well as another Ni(0) derivative, **3**; this latter complex[8] can be separated and obtained pure as yellow microcrystals by careful, repeated recrystallizations from hexane. **3** is formulated as an η^2-acryloyl complex wherein the rearranged ligand binds in a novel tridentate fashion. Consistent with this proposed structure for **3** are the ^{1}H NMR data[8] that show four resonances for the diastereotopic silyl methyl groups due to the chirality of the coordinated acryloyl ligand. In addition, the resonances of the coordinated olefin are shifted upfield and are split by two inequivalent phosphorus nuclei. The infrared spectrum has only one very strong terminal carbonyl stretch at 1950 cm^{-1} as well as a strong band at 1625 cm^{-1} ascribed to ν_{CO} of the η^2-acryloyl function. Additional support for this formulation comes from the ^{31}P{^{1}H} NMR spectrum which consists of an AX doublet of doublets (δ_A 16.38, δ_X = −1.38, J_{AX} = 57.9 Hz) for the inequivalent phosphines.



3

The phenylnickel derivative **1d** also produces a mixture of compounds in its reaction with carbon monoxide; after 7 h at ambient conditions, the Ni(0) derivative,[9] **2d**, and the nickel–benzoyl complex,[10] **4d**, were obtained as an approximately 1:1 mixture in quantitative yield (by ^{1}H NMR spectroscopy). Predictably, no product due to coordination of the *N*-benzoyl fragment, analogous to **3**, is observed. Identification of these products was made possible by a Pasteur-type separation of the colorless crystals of **2d** from the orange prisms of **4d**. As anticipated, the reaction of pure **4d** with additional CO resulted in the formation of the *N*-benzoylnickel(0) species, **2d**. If the reaction of the phenylnickel complex **1d** with CO is monitored by ^{1}H NMR spectroscopy, the nickel(II) benzoyl derivative **4d** is formed rapidly and quantitatively at room temperature (<30 min); however, the subsequent reaction to form **2d** is much slower, going to completion in approximately 2 days.



4a, R = CH_3
b, R = $CH_2CH{=}CH_2$
c, R = $CH{=}CH_2$
d, R = C_6H_5

The palladium–methyl analogue, **1e**, does not measurably react with atmospheric pressures of CO, even after 3 days. However, higher pressures (20 atm) generate quantitative yields (^{1}H NMR spectroscopy) of the palladium acetyl complex, $[Pd(COCH_3)N(SiMe_2CH_2PPh_2)_2]$;[11] further reaction with CO was not observed. Indeed, no other transition metal incorporating this ligand system[12] rearranges like that of the nickel derivatives with CO.

The mechanism for this fascinating rearrangement must involve initial formation of the acylnickel species **4** followed by, in a subsequent step, reductive elimination of the nickel(II) amide acyl to give the nickel(0) products. By monitoring[13] the reaction of **1a** or **1b** with carbon monoxide at −40 °C by either ^{31}P{^{1}H} or ^{1}H NMR spectroscopy, we observe very straightforward conversions, via the acyl species **4a** and **4b**, to the nickel(0) products **2a** and **2b**. We are at present investigating the kinetics of this rearrangement and the effect of other ligands on this process.

Acknowledgment. Financial support for this research was generously provided by the Department of Chemistry, the Natural, Applied and Health Sciences Fund (UBC), and the Natural Sciences and Engineering Research Council of Canada. P.A.M. thanks the Walter C. Sumner Foundation for a Memorial Fellowship.

Registry No. 1a, 81603-07-8; **1b**, 82865-00-7; **1c**, 81610-99-3; **1d**, 81603-09-0; **1e**, 81603-11-4; **2a**, 82865-01-8; **2b**, 82865-02-9; **2c**, 82865-03-0; **2d**, 82865-04-1; **3**, 82865-05-2; **4a**, 82865-06-3; **4b**, 82865-07-4; **4d**, 82865-08-5; CO, 630-08-0.

---

(7) Although **2c** is the major product, it has not yet been obtained analytically pure due to contamination by **3**. **2c**: ^{1}H NMR (C_6D_6) $SiCH_3$, δ −0.08 (s), CH_2P, 1.85 (br s), H_1, 6.17 (dd, $J_{1,3}$ = 17.0, $J_{1,2}$ = 2.0 Hz), H_2, 5.38 (dd, $J_{2,3}$ = 10.2 Hz), H_3, 5.99 (dd), $P(C_6H_5)$, 6.95 (m, para/meta), 7.15 (m, ortho); IR (CH_2Cl_2, cm^{-1}) ν_{CO}, 1966 (s), 1935 (s), $\nu_{COCH{=}CH_2}$, 1700 (m).

(8) **3**: ^{1}H NMR (C_6D_6) $SiCH_3$, δ 0.65 (d, $^4J_{H,P}$ = 0.98 Hz), 0.35 (d, $^4J_{H,P}$ = 0.98 Hz), −0.35 (s), −0.65 (s), CH_2P, 1.22 (m), H_1, 4.34 (m, $J_{1,3}$ = 11.72, $J_{1,P1}$ = 6.59, $J_{1,P2}$ = 1.46 Hz), H_2, 3.89 (m, $J_{2,3}$ = 7.57, $J_{2,P1}$ = 5.62, $J_{2,P2}$ = 4. 15 Hz), H_3, 4.14 (m, $J_{3,P1}$ = 13.92, $J_{3,P2}$ = 3.17 Hz), $P(C_6H_5)$, 6.70, 6.98 (m, para/meta), 7.48, 7.92 (m, ortho). Anal. Calcd for $C_{34}H_{39}NNiO_2P_2Si_2$: C, 60.89; H, 5.82; N, 2.09. Found: C, 60.86; H, 6.00; N, 1.82. This type of π complex with α,β-unsaturated amides is known; see: Yamamoto, T.; Igarashi, K.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 7448.

(9) **2d**: ^{1}H NMR (C_6D_6) δ $SiCH_3$, δ −0.03 (s), CH_2P, 1.93 (br s), $P(C_6H_5)$ and COC_6H_5, 6.92 (m), 7.52 (m); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2000 (s), 1935 (s), ν_{COPh} 1680 (m). Anal. Calcd for $C_{39}H_{41}NNiO_3P_2Si_2$: C, 62.57; H, 5.48; N, 1.87. Found: C, 63.00; H, 5.73; N, 1.65.

(10) **4d**: ^{1}H NMR (C_6D_6) $SiCH_3$, δ −0.01 (s), 0.45 (s), PCH_2, 1.54 (dt, J_{gem} = 13.7, J_{app} = 6.5 Hz), 1.80 (J_{app} = 5.0 Hz), $P(C_6H_5)_2$ and COC_6H_5, 6.75 (m), 7.12 (m), 7.28 (m), 7.90 (m), 8.21 (m); IR (KBr, cm^{-1}) ν_{NiCOPh} 1602 (m). Anal. Calcd for $C_{37}H_{41}NNiOP_2Si_2$: C, 64.16; H, 5.92; N, 2.02. Found: C, 64.31; H, 5.98; N, 2.16. The proton NMR data are consistent with restricted rotation of the NiCOPh group about the Ni–C bond, presumably due to the interaction of the nickle–benzoyl moiety with the phenyl substituents on the phosphorus donors. Heating **4d** to >70 °C causes broadening and coalescence of the proton NMR resonances (and some formation of the starting nickel–phenyl complex **1d**).

(11) $[Pd(COCH_3)N(SiMe_2CH_2PPh_2)_2]$: mp 153 °C; ^{1}H NMR ($C_6D_6$) $SiCH_3$, δ 0.24 (s), CH_2P, 1.75 (t, J_{app} = 6.25), $COCH_3$, 1.64 (t, $^4J_{H,P}$ = 2.20 Hz), $P(C_6H_5)$, 7.02 (m, para/meta), 7.74 (m, ortho); IR (CH_2Cl_2, cm^{-1}) ν_{COCH_3} 1640 (m). Anal. Calcd for $C_{32}H_{39}NOP_2PdSi_2$: C, 56.72; H, 5.76; N, 2.07. Found: C, 57.03; H, 5.64; N, 2.41.

(12) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J., manuscript in preparation. Rhodium and iridium complexes of hybrid multidentate ligands are described.

(13) The acyl derivatives **4a** and **4b** can be prepared in situ by shaking an NMR tube of the nickel–alkyl derivatives **1a** or **1b** under 1 atm of CO at −78 °C for 5–10 min; the tube was then sealed under CO with a torch. At −40 °C the conversion of **4a** to **2a** has a half-life of ~30 min. **4a**: ^{1}H NMR (C_7D_8, −80 °C) $SiCH_3$, δ 0.16 (br s), 0.63 (br s), CH_2P, 1.19 (br m), $COCH_3$, 1.41 (br t, $^{13}COCH_3$, $^2J_{^{13}C}$ = 4.5 Hz), $P(C_6H_5)$, 6.81 (br m, para/meta), 8.34 (br m, ortho); ^{31}P {^{1}H} (C_7D_8, −40 °C, relative to external $P(OMe)_3$ at 141.0 ppm) 27.8 ppm (s). As with **4d**,[10] the ^{1}H NMR is consistent with restricted rotation of the $NiCOCH_3$ group about the Ni–C bond at low temperatures.

Oxidative Conversion to a Terminal Carbene Ligand of a Bridging Carbene in a Dinuclear Iron–Cobalt Complex

John R. Matachek and Robert J. Angelici*

Department of Chemistry and Ames Laboratory
U.S. Department of Energy,[1] Ames, Iowa 50011

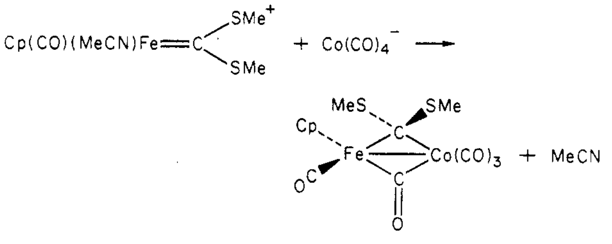
Received August 24, 1982

Summary: We report the synthesis of a new carbene-bridged dinuclear complex, Cp(CO)Fe(μ-CO)[μ-C(SMe)$_2$]-

$Co(CO)_3$, 1, and its reactions with oxidizing agents. With a variety of oxidizing agents (I_2, Br_2, Ph_3C^+, Cp_2Fe^+, and $C_7H_7^+$), this bridging carbene complex undergoes a two-electron oxidation which results in cleavage of the Fe–Co bond and formation of the terminal carbene complex $Cp(CO)_2Fe[C(SMe)_2]^+$.

Recent interest in the synthesis and reactivity of bridging carbene ligands[2–7] in polynuclear metal complexes derives from the postulated intermediacy of bridging carbenes in the Fischer–Tropsch reaction[2] and reactions of hydrocarbons which are catalyzed heterogeneously by transition metals.[3] Only a few general modes of reactivity for bridging carbenes have been reported: the conversion of μ-CH_2 to CH_3 or CH_4,[4] the transformation of bridging carbenes into bridging carbynes,[4a,e,f,5] the insertion of olefins or acetylenes into the metal–carbene bond,[4b,d,6] and the intramolecular coupling of two bridging carbenes across a single pair of metal atoms.[6a,7] In this communication, we report the synthesis of a new carbene-bridged dinuclear complex, $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Co(CO)_3$, 1, and its reactions with oxidizing agents which lead to cleavage of the Fe–Co bond and conversion of the bridging carbene into a terminal carbene ligand; this reaction represents a new type of reactivity for the bridging carbene group.

Complex 1 is prepared from the terminal dithiocarbene complex $\{CpFe(CO)(NCMe)[C(SMe)_2]\}PF_6$[8] and PPN-$[Co(CO)_4]$[9] by reaction in tetrahydrofuran for 1 h at room temperature:

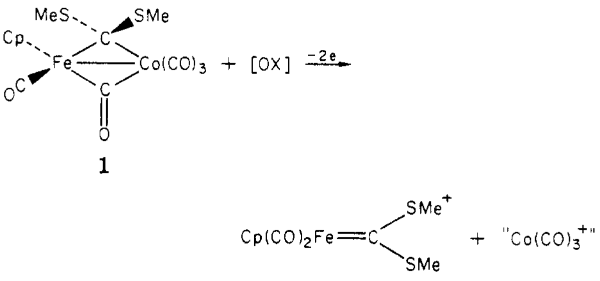


(1)

1

Evaporation of the solvent, hot hexanes extraction of the residue, filtration, and cooling of the solution at −20 °C yield small purple crystals of 1 (83% yield)[10] that are air-stable for weeks. Compound 1 may also be prepared from $\{CpFe(CO)_2[C(SMe)_2]\}PF_6$,[11] although in lower yield. A few dinuclear complexes are reported to contain terminal carbene ligands;[12] however, the carbene-bridged structure of 1 is indicated by the relatively high-field position of the ^{13}C NMR carbene resonance (δ 176.44) as compared to those for related terminal carbenes,[8] the inequivalence of the SMe groups in the ^1H and ^{13}C NMR spectra of 1, and the overall similarity of the IR spectrum in the $\nu(CO)$ terminal region of 1 to that of $Cp(CO)Fe(\mu\text{-}CO)_2Co(CO)_3$.[13]

In a reaction not previously reported for bridging carbene complexes, 1 is readily oxidized to yield a mononuclear terminal dithiocarbene complex of iron, 2. Reactions with 2 equiv of the oxidizing agents I_2, Br_2, $Ph_3C^+PF_6^-$, $Cp_2Fe^+FeCl_4^-$, and $C_7H_7^+BF_4^-$ in CH_2Cl_2 solvent under N_2 give $CpFe(CO)_2[C(SMe)_2]^+$, 2,[11] as the only iron carbonyl containing product. In the reaction with I_2 in the presence of 2 equiv of PPh_3, the cobalt fragment is isolated (41%) as $ICo(CO)_2(PPh_3)_2$, which is identified by comparing its IR spectrum with that of an authentic sample.[14,15] In the absence of PPh_3, no identifiable Co(I) complex is isolated. The yield of the iron product 2 is 91%[16] after 10 min of reaction with 2 equiv of I_2 at room temperature without added PPh_3. The analogous reaction with Br_2 gives a 90% yield of 2 after 5 min. Two equivalents of $C_7H_7^+BF_4^-$ give a 95% yield of 2 after 24 h. After only 1 min, 2 equiv of $Cp_2Fe^+FeCl_4^-$ give a 75% yield of 2, whereas 1 equiv gives a 46% yield. Reactions of $Ph_3C^+PF_6^-$ after 20 min give the following yields with different numbers of equivalents of the oxidizing agent: 23% (0.5 equiv), 77% (1.5 equiv), 90% (2.0 equiv). These reactions establish that 2 equiv of oxidant are required. No intermediates are observed even in reactions involving fewer than 2 equiv.



1

2

(2)

---

(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the office of Basic Energy Sciences, Chemical Sciences Division.

(2) Brady, R. C. III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181–6182.

(3) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490.

(4) (a) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136 and references therein. (b) Sumner, C. E.; Riley, P. E.; Davis, R. E.; Pettit, R. *Ibid.* **1980**, *102*, 1752–1754. (c) Balch, A. L.; Olmstead, M. M.; Farr, J. P. *Inorg. Chim. Acta* **1981**, *52*, 47–54. (d) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489–2491. (e) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. J. *Ibid.* **1981**, *103*, 63–75. (f) Hursthouse, M. B.; Jones, K. M.; Malik, K. M.; Wilkinson, G. *Ibid.* **1979**, *101*, 4128–4139.

(5) (a) Calvert, P. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225–5226. (b) Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *Ibid.* **1980**, *102*, 7787–7789. (c) Howard, J. A. K.; Jeffrey, J. C.; Laguna, M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 1170–1173. (d) Howard, J. A. K.; Jeffrey, J. C.; Laguna, J. M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 751–762. (e) Jeffrey, J. C.; Navarro, R.; Razay, H.; Stone, F. G. A. *Ibid.* **1981**, 2471–2478.

(6) (a) Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roue, J.; Woodward, P. *J. Chem. Soc., Chem. Comm.* **1981**, 862–864. (b) Dyke, A. F.; Knox, S. A. R.; Naishi, P. J.; Taylor, G. E. *Ibid.* **1980**, 803–805. (c) Jeannin, Y.; Dromzée, Y.; Daran, J. C.; Leuisalles, J.; Rose-Munch, F.; Rudler, H. *Ibid.* **1981**, 152–154.

(7) (a) Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922–5923. (b) Maitlis, P. M.; Kiyoshi, I.; Andrews, D. G.; Mann, B. E. *J. Chem. Soc., Chem. Commun.* **1981**, 809–810.

(8) McCormick, F. B.; Angelici, R. J. *J. Organomet. Chem.* **1981**, *205*, 79–89.

(9) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 87–88.

(10) Data for 1: mp 103–104 °C; IR (cyclohexane) $\nu(CO)$ 2037 (m), 1988 (br s), 1836 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.70 (s, 5 H, Cp), 2.70 (s, 3 H, SCH_3), 2.23 (s, 3 H, SCH_3); ^{13}C NMR (CD_2Cl_2, −80 °C, $Cr(acac)_3$) δ 249.59 (s, μ-CO), 212.50 (s, FeCO), 208.77 (s, Co–CO), 201.06 (s, CoCO), 176.44 (s, μ-carbene C), 83.27 (s, Cp), 29.97 (s, SCH_3), 24.85 (s, SCH_3). Anal. Calcd for $C_{13}H_{11}O_5S_2CoFe$: C, 36.64; H, 2.60. Found: C, 36.60; H, 2.93. MS (20 eV), *m/e* 398 $(M - CO)^+$, $(M - 2CO)^+$, $(M - 3CO)^+$, $(M - 3CO - CH_3)^+$, $(M - 3CO - 2CH_3)^+$.

(11) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231–1235.

(12) (a) Rosenblum, M.; Nitay, M.; Priester, W. *J. Am. Chem. Soc.* **1978**, *100*, 3621–3623. (b) Casey, C. P. *Chem. Commun.* **1970**, 1220–1221. (c) Casey, C. P.; Cyr, C. R. *J. Organomet. Chem.* **1973**, *57*, C69–C71. (d) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172–2180. (e) Fischer, E. O.; Offhaus, E. *Chem. Ber.* **1969**, *102*, 2449–2455. (f) Curtis, D. M.; Messerle, L. *J. Am. Chem. Soc.* **1982**, *104*, 889–890. (g) Berry, M.; Martin-Gil, J.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1625–1629. (h) Schubert, U.; Ackermann, K.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *231*, 323–334.

(13) Manning, A. R. *J. Chem. Soc. A* **1971**, 2321–2325.

(14) Aresta, M.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1969**, *3*, 227–231.

(15) The low yield of $ICo(CO)_2(PPh_3)_2$ may be due at least in part to its further reaction with I_2 to unidentified products.

(16) The yield of $CpFe(CO)_2[C(SMe)_2]^+$ was determined by measuring the intensity of the 2058-cm^{-1} $\nu(CO)$ absorption and comparing it with intensities of standard solutions of $\{CpFe(CO)_2[C(SMe)_2]\}PF_6$.

Organometallics 1982, 1, 1543–1545

The variety of oxidizing agents that participate in reaction 2 indicates that the removal of two electrons from the bridging carbene complex 1 is all that is required for its conversion to the terminal carbene complex 2. The only other reported conversion of a bridging to a terminal carbene was communicated very recently;[12f] it involves the shift of the bridging carbene ligand in Cp$_2$Mo$_2$(CO)$_4$(CR$_2$) upon reaction with R$_2$CN$_2$ (R = p-MeC$_6$H$_4$) to a terminal position in the product Cp(CO)$_3$MoMo(CR$_2$)(N$_2$CR$_2$)Cp. The type of bridging to terminal carbene conversion represented by the oxidation in eq 2 may be of more general applicability to a variety of bridging carbene complexes. Oxidation of other complexes with bridging carbenes containing heteroatoms (O, N, S, etc.) capable of stabilizing terminal carbene ligands are likely to yield isolable terminal carbene compounds as observed in reaction 2. On the other hand, oxidation of μ-CH$_2$ and μ-CR$_2$ complexes according to eq 2 would generate unstable terminal carbenes which would be converted rapidly to other products such as olefins, as in the decomposition of Cp(CO)$_2$Fe=CH$_2^+$.[17] In this way, oxidation may activate bridging carbenes to new types of reactivity.

Registry No. 1, 83043-22-5; 2, 69532-10-1; {CpFe(CO)(NCMe)[C(SMe)$_2$]}PF$_6$, 77781-29-4; PPN[Co(CO)$_4$], 53433-12-8; {CpFe(CO)$_2$[C(SMe)$_2$]}PF$_6$, 69532-11-2; ICo(CO)$_2$(PPh$_3$)$_2$, 14767-53-4; Fe, 7439-89-6; Co, 7440-48-4.

---

(17) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* 1977, *99*, 6099–6101.

Regiochemistry of Cycloaddition of (Trimethylenemethane)palladium Intermediates to Muconic Esters

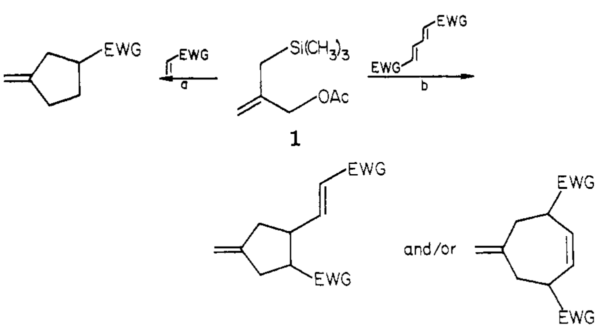
Barry M. Trost,* Thomas N. Nanninga, and Dominic M. T. Chan

McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received June 14, 1982

Summary: The palladium-catalyzed additions of 2-((trimethylsilyl)methyl)allyl acetate to muconic esters produces five- and seven-membered rings, whereas the phenyl-substituted derivative produces only five-membered-ring products.

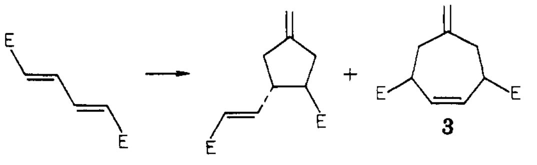
The palladium-catalyzed reaction of 2-((trimethylsilyl)methyl)allyl acetate (1) with electron-deficient olefins provides an exciting approach to methylenecyclopentanes (path a, eq 1).[1,2] Its utility ultimately depends upon its generality. A particularly intriguing problem derives from the use of a diene as an acceptor in which the competition between a seven- and a five-membered ring lurks (path b, eq 1). Exploration of this phenomenon within the context of muconic esters derives from the symmetry of the system and the utility of the resultant methylenecyclopentane for a synthesis of brefeldin A, an antitumor cyclopentanoid macrolide.[3]



(1)

EWG = electron-withdrawing group

Treatment of dimethyl (E,E)-muconate with 1 in the presence of Pd(0) catalysts leads to two products. Spectral analysis clearly assigns the structure of the major product as the methylenecyclopentane 2[4] and the minor product as the methylenecycloheptene 3.[4] The infrared spectrum of 2 showed conjugated and unconjugated ester carbonyl groups at 1735 and 1720 cm^{-1}; the NMR spectrum showed the conjugated double bond [^{1}H NMR δ 6.90 (dd, J = 15.8, 8.1 Hz) and 5.88 (dd, J = 15.8, 1.1 Hz) and ^{13}C NMR at δ 149.3 and 121.3] in addition to the exocyclic methylene group at δ 4.92. On the other hand, 3 only shows an unconjugated ester carbonyl group at 1748 cm^{-1} and an isolated symmetrical vicinal disubstituted double bond [^{1}H NMR δ 6.10 (d, J = 2.4 Hz); ^{13}C NMR δ 130.7] in addition to the exocyclic methylene group [^{1}H NMR δ 4.89; ^{13}C NMR δ 146.7 and 113.9]. The most notable effect on the ratio of the seven- to five-membered rings was temperature—with a higher temperature favoring five- over seven-membered-ring formation.



E = CO$_2$CH$_3$ 2

	2	3	
(Ph$_3$P)$_4$Pd, dppe, THF	1.6	1	(47%[a])
(Ph$_3$P)$_4$Pd, dppe, dioxane	3.8	1	(98%[b])
[(i-C$_3$H$_7$O)$_3$P]$_4$Pd,[c] THF	1.1	1	(89%[b])

[a] Yield based on 1. Actual yield based upon recovered diene would be substantially higher. [b] Yield based upon recovered diene. [c] Catalyst formed in situ by reaction of (i-C$_3$H$_7$O)$_3$P and Pd(OAc)$_2$.

The source of this competition can arise from two different pathways (eq 2). In the first (path A), initial attack occurs at a terminus of the diene unit which can lead to a cisoid (4) or transoid (5) dienolate intermediate in which the former can produce either five- or seven-membered rings but the latter is constrained to form the five-membered ring. If this mechanistic scheme is correct, the ratio of 2 to 3 would depend upon the partitioning of 4 or of 4 and 5. Alternatively, β attack on the diene system (path

---

(1) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* 1979, *101*, 6429; 1981, *103*, 5972.

(2) For a related reaction of cooligomerization of alkylidenecyclopropanes and olefins catalyzed by Pd see: (a) Binger, P.; Bentz, P. *J. Organomet. Chem.* 1981, *221*, C33. (b) Binger, P.; Germer, A. *Chem. Ber.* 1981, *114*, 3325. (c) Binger, P.; Schuchardt, U. *Ibid.* 1981, *114*, 3313. (d) *Ibid.* 1980, *113*, 3334. (e) *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 249. (f) Binger, P. *Synthesis* 1973, 427. For a cooligomerization catalyzed by Ni see: Noyori, R.; Yemakawa, M.; Takaya, H. *Tetrahedron Lett.* 1978, 4823 and earlier references therein.

(3) For some recent total syntheses see: Greene, A. E.; LeDrian, C.; Crabbe, P. *J. Am. Chem. Soc.* 1980, *102*, 7583. Koksal, Y.; Radditz, P.; Winterfeldt, E. W. *Angew. Chem. Int. Ed. Engl.* 1980, *19*, 472. Kitahara, T.; Mori, K.; Matsui, M. *Tetrahedron Lett.* 1979, 3021. Bartlett, P. A.; Green, F. R., III *J. Am. Chem. Soc.* 1978, *100*, 4858. Corey, E. J.; Wollenberg, R. H.; Williams, D. R. *Tetrahedron Lett.* 1977, 2243. Baudoriy, R.; Crabbe, P.; Greene, A. E.; LeDrian, C.; Orr, A. F. *Tetrahedron Lett.* 1977, 2973.

(4) This compound has been fully characterized spectrally and its elemental composition determined by high-resolution mass spectroscopy and/or combustion analysis.

0276-7333/82/2301-1543$01.25/0 © 1982 American Chemical Society