as large or larger than the apparent transition-state stabilizations. The agostic bonding in the transition states for Mo and W may be greater than for Cr because the latter are more hindered sterically.[17b] If the transition state for CO substitution by alkane on $Mo(CO)_6$ and $W(CO)_6$ involves coordination of the alkane, it is unlikely that naked $M(CO)_5$ is formed to a significant extent in these reactions. We therefore conclude that these substitutions occur via an associative process; however, some of the substitution occurring by a dissociative process cannot be ruled out. In support of an associative process, it is known that $Mo(CO)_6$ and $W(CO)_6$ have a much greater tendency to undergo associative ligand exchange than $Cr(CO)_6$.[17b] Consistent with this conclusion is the interpretation of a recent femtosecond flash photolysis study of the photodissociation of CO from these complexes.[2a] Apparently naked $M(CO)_5$ is only observed in an excited state and reacts with a solvent molecule before returning to the ground state.

Our results and conclusion that naked $W(CO)_5$ is not formed upon CO dissociation in solution appear to be inconsistent with those of a flash photolysis study of $W(CO)_6$ in methylcyclohexane.[18] It was asserted that $W(CO)_5$(methylcyclohexane) was 0.9 kcal/mol more stable than $W(CO)_5$ (plus free methylcyclohexane) and that both species are important intermediates. Our measurement of $\Delta H_{W\text{-heptane}}$ (as well as the gas-phase $W(CO)_5$(ethane) value)[5b] does not agree with this result. Our results in Table I indicate the order of magnitude difference between $\Delta H_{W\text{-heptane}}$ and the above value is not likely to be due to the difference in agostic bonding to heptane and methylcyclohexane.

It is clear that agostic bonds are relatively large and agostic bonded complexes are important intermediates. It will be of great interest to determine the upper limit of agostic bond strengths. Presumably this limit is ultimately determined by the insertion into a C-H bond.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; CO, 630-08-0; pentane, 109-66-0; heptane, 142-82-5; isooctane, 540-84-1; cyclohexane, 110-82-7.

(18) Lees, A.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381-4384.

Deprotonation of the Adducts of β-Dicarbonyl Anions and $[(\eta^4\text{-Diene})Co(CO)_3]BF_4$

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The adducts of stabilized enolates and $[(\eta^4\text{-1,3-butadiene})Co(CO)_3]BF_4$ (**1**) and $[(\eta^4\text{-1,3-cyclohexadiene})Co(CO)_3]BF_4$ (**2**) undergo deprotonation and subsequent reactions to form either hydrofurans, cyclopropanes, or α,β,γ,δ-diunsaturated dicarbonyl derivatives depending upon the reacting complex and the β-dicarbonyl component. All of the observed reactions are strongly promoted by HMPA.

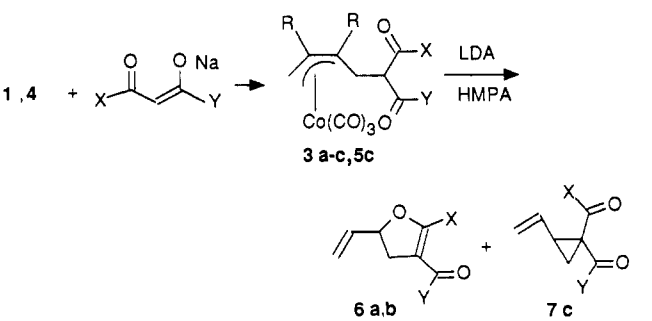
Introduction

Recently we discovered the unexpected, yet synthetically versatile, conversion of $[(\eta^4\text{-diene})Co(CO)_3]BF_4$ complexes to dihydrofurans and tetrahydrobenzofurans via their reactions with dianions of β-dicarbonyl compounds and the related 2,4-bis(trimethylsiloxy) dienes.[1] In order to explore the scope and to probe the mechanism of these transformations we have examined the stepwise addition/deprotonation of a set of β-dicarbonyl derivatives to $[(\eta^4\text{-1,3-butadiene})Co(CO)_3]BF_4$ (**1**) and $[(\eta^4\text{-1,3-cyclohexadiene})Co(CO)_3]BF_4$ (**2**). Herein we report the remarkably variable course of this reaction depending upon the nature of both the complex and the β-dicarbonyl derivative as well as a dramatic accelerating effect of added HMPA.

Results and Discussion

When $[(\eta^4\text{-1,3-butadiene})Co(CO)_3]BF_4$ (**1**) is treated with 1 equiv of the sodium enolate of either benzoylacetone, methyl acetoacetate, or dimethyl malonate in THF at −78 °C, the corresponding C-alkylated adducts **3a–c** are produced (Scheme I) as determined by IR monitoring (typically ν(MC≡O) ca. 2060 and 1980 and ν(C=O) ca. 1720–1755 cm^{-1}) and acidic hydrolysis of the malonate adduct **3c** to a mixture of C-butenylated derivatives. Adducts **3a–c** were not completely characterized, however, due to their thermal instability. On the other hand, the product of malonate addition to $[(\eta^4\text{-2,3-dimethyl-1,3-butadiene})Co(CO)_3]BF_4$ (**4**) was sufficiently stable to allow its complete spectroscopic characterization and identification as **5c**, the result of C-alkylation of the malonate nucleophile. Subsequent treatment at −78 °C of adducts **3a,b** with an equivalent of LDA or NaH in THF/HMPA

Scheme I



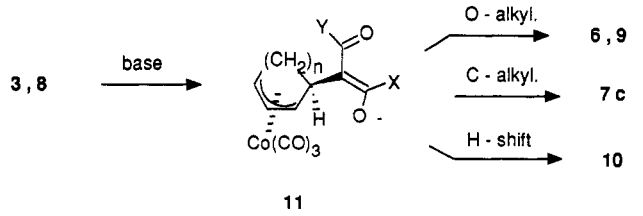
1: $[(\eta^4\text{-1,3-butadiene})Co(CO)_3]BF_4$; **4**: $[(\eta^4\text{-2,3-dimethyl-1,3-butadiene})Co(CO)_3]BF_4$

a: X=CH_3, Y=C_6H_5; **b**: X=CH_3; Y=OCH_3; **c**: X=Y=OCH_3; R=H or CH_3

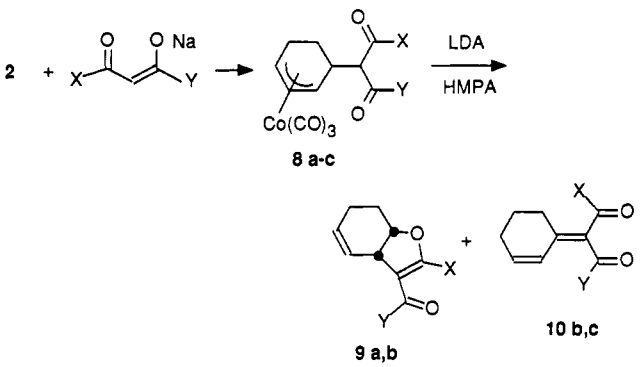
(1) Barinelli, L. S.; Nicholas, K. M. *J. Org. Chem.* **1988**, *53*, 2114.

0276-7333/89/2308-2474$01.50/0

Scheme II



Scheme III



2: [(η^4-1,3-cyclohexadiene)Co(CO)$_3$]BF$_4$;
a: X=CH$_3$, Y=C$_6$H$_5$; **b**: X=CH$_3$; Y=OCH$_3$; **c**: X=Y=OCH$_3$

(20:1) followed by warming to room temperature gave the expected *dihydrofuran* derivatives **6a** and **6b** in good yield following aqueous (dilute HCl) workup in accord with our earlier observations.[1] These results support (but do not prove) our belief that the corresponding reactions of **1** with β-dicarbonyl *dianions* and bis(trimethylsiloxy) dienes follow a similar reaction pathway involving unusual initial attack on the diene complex by C3 of the nucleophile. The selective attack by the acetyl (rather than the benzoyl) oxygen in the precursor **11** leading to **6a** and the ketonic (rather than the carboxyl) oxygen of intermediate **11** (Scheme II) leading to **6b** probably reflect the greater electron density at these centers and parallels the general behavior of unsymmetrical β-diketone and -ketoester enolates toward O-centered electrophilic attack.[2] However, parallel LDA treatment of malonate adduct **3c** produced instead the *vinylcyclopropane* diester **7c** (X = Y = OMe) as the sole product (75%). Cyclopropane **7c** may be viewed as the product of intramolecular C-alkylation of the intermediate anionic complex from **3c** and although such C-alkylation is expected to be favored with β-diester (relative to β-diketone) enolates,[2] the total reversal of regioselectivity upon deprotonation of **3a,b** compared to **3c** is striking. A similar, albeit unexplained, effect has been noted in the Pd-catalyzed coupling of stabilized enolates with 2-butenylene dicarbamate.[3]

[(η^4-1,3-Cyclohexadiene)Co(CO)$_3$]BF$_4$ (**2**) likewise formed C-alkylated adducts when treated with the respective enolates from benzoylacetone, methyl acetoacetate, or dimethyl malonate (Scheme III). Additional surprises were encountered, however, when the parallel set of deprotonation reactions of these adducts **8** was examined. Treatment of diketone enolate adduct **8a** with LDA/HMPA in THF, as anticipated, afforded the previously observed[1] *tetrahydrobenzofuran* derivative **9a** exclusively (80%). Similarly, deprotonation of ketoester adduct **8b** produced the corresponding benzofuran derivative **9b** primarily, accompanied by a small amount of an unexpected product identified as the previously unknown diene *ketoester* **10b** (10:1, 65%). An analogous compound, *diene diester* **10c**, became the *exclusive* product (73%) when adduct **8c** reacted with LDA/THF/HMPA under identical conditions.

The diene esters **10b** and **10c** are the products of a formal 1,4-dihydride shift in anionic intermediate **11** (Scheme II), a process which appears to have little precedent in organometallic chemistry. Although we have minimal experimental data regarding the mechanism of this novel process, we do note that the formation of diene derivative **10c** (and presumably **10b**) is strongly dependent on the presence of HMPA for when **8c** was deprotonated by LDA/THF alone followed by warming to room temperature and hydrolysis (dilute HCl), the major products were the 2- and 3-cyclohexenylmalonates (10:1 vs **10c**, 80% combined yield); i.e., virtually no H-shift had occurred. It is tempting to suggest that the $-Co(CO)_{2,3}$ group serves as a conduit for this anionically driven hydride transfer. This process could be mechanistically related to the equilibration of agostic *neutral* (η^3-allyl)Mn(CO)$_3$ complexes recently reported by Brookhart and co-workers.[4] Firmer conclusions must await the results of planned labeling experiments. The origin of the selectivity reversal upon deprotonation of the malonate adducts **3c** (from **1**) and **8c** (from **2**) is an intriguing issue. The exclusive H transfer (vs C-alkylation) pathway observed in the latter case may reflect the conformationally favorable disposition of a hydrogen syn to the metal in intermediate **11** resulting from exo attack by malonate on **2**.

Finally we point out that the anionic complexes **11** produced by deprotonation (LDA/THF) of adducts **3** and **8** are in general stable at room temperature for several hours *in the absence of HMPA*; i.e., none of the above organic products, **6**, **7**, **9**, and **10**, are produced. Strong solvation of the lithium (sodium) counterion of **11** by HMPA apparently renders the enolate fragment sufficiently reactive to facilitate the various observed processes including intramolecular O- and C-alkylation and the novel hydride migration.

Experimental Section

General Data. All reactions and manipulations were conducted under a nitrogen atmosphere utilizing standard Schlenk line techniques. Solvents and common reagents were obtained commercially and used as received or purified as follows: tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium/benzophenone; methylene chloride and pentane were distilled under nitrogen from calcium hydride; HMPA was distilled from BaO or CaH$_2$. [(η^4-1,3-Butadiene)Co(CO)$_3$]BF$_4$ and [(η^4-1,3-cyclohexadiene)Co(CO)$_3$]BF$_4$ were prepared as previously described.[5] Thin-layer chromatography was carried out on 0.2-mm silica gel coated plastic sheets with F-254 indicator (EM). Column chromatography was carried out by using flash silica gel (230–400 mesh). Gas chromatography was carried out on a Hewlett-Packard 5790 instrument using a $^1/_8$ in. × 6 ft column packed with OV 101. IR spectra were recorded on a Perkin-Elmer Model 1420 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on either a IBM NR-80 or a Varian XL-300 NMR spectrometer; resonances are reported relative to Me$_4$Si standard. Low- and medium-resolution mass spectra were obtained on a Hewlett-Packard 5985 or on a Kratos MS 25 RF instrument at 12 or 70 eV. High accuracy mass spectra were obtained on a VG Instruments Zab E spectrometer.

Preparation of [(η^4-2,3-Dimethyl-1,3-butadiene)Co(CO)$_3$]BF$_4$ (4). Following our previously described procedure[5]

(2) Bates, R. B.; Ogle, C. A. *Carbanion Chemistry*; Springer-Verlag: Berlin, 1979; pp 40–55, 58–60. Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley: New York, 1979; pp 191–216.
(3) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 669.
(4) Brookhart, M.; Noh, S. K.; Timmers, F. J. *Organometallics* **1987**, *6*, 1829.

complex **4** was prepared from [(η^4-2,3-dimethyl-1,3-butadiene)$_2$Co$_2$(CO)$_6$][6] and obtained as a yellow solid in 52% yield: IR (KBr, cm^{-1}) 2150, 2110, 1050; ^{1}H NMR (acetone-d_6) δ 3.66 (d, J = 1.5 Hz, 2 H), 2.60 (s, 6 H), 2.53 (d, J = 1.5 Hz, 2 H); MS (FAB, m/e) 225 ([$C_6H_{10}Co(CO)_3^+$], 100). Anal. Calcd for $C_9H_{10}BCoF_4O_3$: C, 34.65; H, 3.23. Found: C, 34.31; H, 3.31.

Addition of Enolates to Complexes 1, 2, and 4. A 100-mL round-bottom flask was equipped with a magnetic stir bar and a nitrogen inlet tube and was charged with 0.64 mmol of complex **1**, **2**, or **4** and 10 mL of THF. The flask was cooled to −78 °C, and to it was added a freshly prepared THF solution (10 mL) containing 0.64 mmol of sodium dimethyl malonate [from 170 mg of dimethyl malonate and 61.6 mg of sodium hydride (50% oil dispersion)], sodium benzoyl acetonate, or sodium acetoacetate. After 1 h IR monitoring of the reactions indicated consumption of the starting complex and formation of the respective η^3-allyl adducts [ν(MC≡O) ca. 2060, 1980 cm^{-1}; ν(C=O) for **8c** 1740, 1755 cm^{-1}].

Hydrolysis of 3a and 8c. The above reaction mixture was poured into 50 mL of 1.5 M HCl, stirred for 30 min at room temperature, and then extracted thrice with 50-mL portions of ether. The combined ether extracts were washed with saturated sodium chloride and dried over $MgSO_4$. Removal of the solvent and subsequent chromatography of the resulting residue (silica gel; 30% Et_2O/petroleum ether) afforded the organic products.

3a: obtained 70% of primarily 2-(2-butenyl)-1-phenyl-butane-1,3-dione as a mixture of keto and enol tautomers; ^{1}H NMR ($CDCl_3$) δ 7.9–7.4 (m, Ph), 5.9–5.7 (m, CH_2=C*H*), 5.4–5.2 (m, C*H*$_2$=CH), 5.1–4.9 (m, C*H*$_2$=CH), 4.49 (apparent t, J = 7 Hz, C(O)C*H*, keto), 3.0 (dd, J = 6, 7 Hz, C$_1$*H*$_2$, enol), 2.2–2.0 (m, C*H*$_2$), 2.15 (s, C*H*$_3$), 2.0 (s, C*H*$_3$); IR (neat) 3070, 2940, 2760, 1720, 1680, 1645 (w) cm^{-1}; MS (70 eV) 216 (M$^+$, 0.9), 162 (M$^+$ − CH_2=CH-CH=CH_2, 35), 161 (M$^+$ − CH_2CHCH_2, 15.1), 105 ($C_6H_5CO^+$, 100), 77 ($C_6H_5^+$, 36.1).

8c: produced a mixture (ca. 2:1) of dimethyl 2-cyclohexenyl- and 3-cyclohexenylmalonates (75%); ^{1}H NMR ($CDCl_3$) δ 5.80–5.50 (4 H, m, C*H*=CH), 3.74 (12 H, s, CO_2CH_3), 3.30 (2 H, d, J = 9.5 Hz, C*H*(CO_2CH_3)), 2.90 (1 H, m, CH=CHC*H*), 2.10–1.90 (6 H, m, CH=CHC*H*$_2$), 1.8–1.25 (7 H, m, C*H*$_2$); MS (70 eV) 212 (M$^+$, 4.1), 181 (M$^+$ − OCH_3, 8.2), 152 (73.0), 133 (M$^+$ − C_6H_9, 100). The NMR of the 2-cyclohexenyl isomer is virtually identical with diethyl 2-cyclohexenylmalonate[7] except for the alkoxy resonances.

Isolation of Adduct 5c. The THF solvent was removed under reduced pressure from the solution of adduct **5c** (from **4** and sodium dimethyl malonate) and the resulting residue was extracted with pentane (3 × 15 mL). Evaporation of the pentane afforded **5c** as an orange oily solid in 89% yield (dec 53–55 °C): IR (pentane) 2060, 1990, 1760, 1745 cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.47 (dd, J = 4.1, 11.4 Hz, 1 H), 3.28 (s, 3 H), 3.27 (s, 3 H), 2.82 (d, J = 1.3 Hz, 1 H), 2.49 (dd, J = 4.1, 14 Hz, 1 H), 2.40 (d, J = 1.3 Hz, 1 H), 1.97 (dd, J = 11.4, 14 Hz, 1 H), 1.63 (s, 3 H), 1.56 (s, 3 H); MS (FAB, m/e) 300.1 (M$^+$ − 2CO, 55), 272.1 (M$^+$ − 3CO, 100). Anal. Calcd for $C_{14}H_{17}CoO_7$: C, 47.20; H, 4.81. Found: C, 47.17; H, 4.78.

Deprotonation of Enolate Adducts 3 and 8. A freshly prepared THF/HMPA (20:1) solution (10 mL) containing 1 molar equiv of lithium diisopropylamide (from butyllithium and diisopropylamine) was added dropwise to a solution of the enolate adducts **3** and **8** (described above) at −78 °C. After the reaction mixture was allowed to warm to room temperature, it was stirred for 12 h and then poured into 50 mL of 1.5 M HCl. The mixture was extracted thrice with 50-mL portions of diethyl ether; the combined ether extracts were washed with three 50-mL portions of water, followed by saturated NaCl, and dried over $MgSO_4$. Evaporation of the solvent and subsequent chromatography of the residue on silica gel (elution with 20% ethyl acetate/pentane) afforded the organic products **6**, **7**, **9**, and **10**.

2-Vinyl-4-benzoyl-5-methyl-2,3-dihydrofuran (**6a**; 75%) had spectral properties identical with those reported previously.[1]

2-Vinyl-4-carbomethoxy-5-methyl-2,3-dihydrofuran (**6b**; 65%) had spectral properties identical with those reported previously.[1]

Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**7c**; 75%): IR, ^{1}H NMR, and mass spectra were identical with those reported previously.[8]

2-Methyl-3-benzoyl-4,5,8,9-tetrahydrobenzofuran (**9a**; 80%) had spectral properties identical with those reported previously.[1]

2-Methyl-3-carbomethoxy-4,5,8,9-tetrahydrobenzofuran (**9b**; 60%) had spectral properties identical with those reported previously.[9]

Methyl 2-cyclohexene-1-ylidene acetoacetate (**10b**, *E,Z*; 6%): ^{1}H NMR ($CDCl_3$) δ 6.91 (1 H, dt, J = 10, 2 Hz, H$_2$ *Z* isomer), 6.22 (1 H, dt, J = 10, 2 Hz, H$_2$ *E* isomer), 3.37 (2 H, overlapping dt, J = 10, 5 Hz, H$_1$ *E*+*Z* isomers), 3.79 (3 H, s, CO_2CH_3), 3.77 (3 H, s, CO_2CH_3), 2.78 (1 H, t, J = 5 Hz, H$_4$ *E* isomer), 2.57 (1 H, t, J = 5 Hz, H$_4$ *Z* isomer), 2.28 (4 H, m, H$_6$ *E*+*Z* isomers), 1.74 (4 H, q, J = 5 Hz, H$_5$ *E*+*Z* isomers); MS (12 eV) 194 (M$^+$), 163 (M$^+$ − OCH_3), 135 (M$^+$ − CO_2CH_3), 134 (M$^+$ − CH_3CO_2H).

Dimethyl 2-cyclohexen-1-ylidenemalonate (**10c**; 73%): ^{1}H NMR ($CDCl_3$) δ 6.76 (1 H, dt, J = 10, 2 Hz, H$_2$), 6.37 (1 H, dt, J = 10, 5 Hz, H$_1$), 3.77 (3 H, s, CO_2CH_3), 3.76 (3 H, s, CO_2CH_3), 2.68 (2 H, tt, J = 7, 1 Hz, H$_4$), 2.20 (2 H, ddt, J = 2, 5, 6 Hz, H$_6$), 1.76 (2 H, tt, J = 7, 6 Hz, H$_5$); partial decoupling, irradiation of the signal at δ 6.37 caused collapse of the δ 2.20 signal to a dt, J = 6, 2 Hz; irradiation of the δ 2.68 signal caused collapse of the δ 1.76 absorption to a triplet, J = 6 Hz; ^{13}C NMR ($CDCl_3$) δ 166.2 (*C*O_2CH_3), 166.1 (*C*O_2CH_3), 151.6 (CH_2CH=CH), 141.0 (*C*=C(CO_2CH_3)$_2$), 125.5 (CH_2CH=*C*H), 120.4 (C=*C*(CO_2CH_3), 57.2 (CO_2CH_3), 52.1 (CO_2CH_3), 27.9 (CH_2CH_2), 25.7 (*C*H_2CH=CH), 21.8 ($CH_2CH_2CH_2$); IR (neat) 1740, 1720, 1620, 1580 cm^{-1}; HRMS for $C_{11}H_{14}O_4$ calcd 210.0892, found 210.0883.

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Registry No. **1**, 90502-48-0; **2**, 113949-35-2; **3a**, 122471-23-2; **3b**, 122471-24-3; **3c**, 122471-25-4; **4**, 122471-22-1; **5c**, 122471-26-5; **6a**, 113949-31-8; **6b**, 88326-56-1; **7c**, 17447-60-8; **8a**, 122471-27-6; **8b**, 122471-28-7; **8c**, 122471-29-8; **9a**, 122471-16-3; **9b**, 122471-17-4; (*E*)-**10b**, 122471-18-5; (*Z*)-**10b**, 122471-19-6; **10c**, 122471-20-9; HMPA, 680-31-9; [(η^4-2,3-dimethyl-1,3-butadiene)$_2$Co$_2$(CO)$_4$], 33009-59-5; 2-(2-butenyl)-1-phenylbutane-1,3-dione, 122471-14-1; 3-(hydroxyphenylmethylene)-5-hepten-2-one, 122471-15-2; dimethyl 2-cyclohexenylmalonate, 34939-28-1; dimethyl 3-cyclohexenylmalonate, 115740-69-7; sodium dimethyl malonate, 18424-76-5; sodium benzoylacetonate, 17664-05-0; sodium methylacetoacetate, 623-58-5.

(5) Barinelli, L. S.; Ke, T.; Nicholas, K. M. *Organometallics* **1986**, *5*, 588.
(6) Winkhaus, G.; Wilkinson, G. *J. Chem. Soc.* **1961**, 602.
(7) Andell, O. S.; Backvall, J. E.; Moberg, C. *Acta Chem. Scand.* **1986**, *B40*, 184.
(8) Jones, W.; Ando, W.; Hendrick, M. E.; Kulczycki, A.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469.
(9) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Chun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.