We reasoned that three of the five chiral centers in **1** might be fixed enantioselectively by asymmetric cycloaddition of the known 1-(methylthio)cyclopenta-2,4-diene[14] (**4**) with an appropriate chiral acyl-nitroso compound (Scheme II).[15] Subsequent osmylation of the bicyclic adduct **6** from the less hindered endo face would complete mannostatin's oxygenation pattern.

In the event, CH_3SCl (0.8 equiv) was stirred with a suspension of thallous cyclopentadienide (CCl_4, room temperature), and after the precipitated salts were filtered, crude **4** was combined with (*R*)-mandelohydroxamic acid (**5**) in the presence of Bu_4NIO_4 (0 °C, CH_3OH, 1 h) to afford a 2.6:1 ratio of adducts (30–35% overall from CH_3SCl). Flash chromatography and recrystallization gave the major diastereomer (mp 89–90 °C), which was assigned structure **6** on the basis of steric control of addition to the internally H-bonded acyl-nitroso compound.[16]

Vicinal hydroxylation of the bicyclic adduct proved more difficult than expected. For example, attempted catalytic osmylation using *N*-methylmorpholine *N*-oxide[17] formed the corresponding sulfoxides and sulfones of **6**,[18] whereas stoichiometric amounts of OsO_4 produced α-keto amide **7**. Therefore **6** was reduced (Al-Hg, THF-H_2O) and acetylated to furnish **8** (41% yield from **6**).[19]

Completion of the synthesis relied on a remarkable syn-directive effect which has recently been noted in the osmylation of such bis-allylically substituted cyclopentenes.[20] Although solvent and chelation effects have been invoked, no clear mechanistic explanation has emerged to account for such unusual stereoselectivity.[21] In fact stoichiometric osmylation of **8** in pyridine (1.5 equiv of OsO_4, room temperature, 20 h, 74%) occurred with exceptionally high facial selectivity. Acetylation of the initial diol mixture (resulting from solvent-promoted acetyl migration) produced a 20:1 ratio of tetraacetates **9** and **10** easily separable by chromatography. Hydrolysis of **9** (HCl-CH_3OH, 60 °C, 65% yield) afforded optically active mannostatin A hydrochloride, (+)-**1**·HCl, whose physical[22] and biological[23] properties were identical in every respect with those of an authentic sample.

Acknowledgment. We thank the National Institutes of Health (GM 35712) for generous financial support. Grants to the Cornell Nuclear Magnetic Resonance Facility from the NSF (CHE 7904825; PGM 8018643) and NIH (RR02002) are also gratefully acknowledged.

Supplementary Material Available: Full experimental details, including spectral and physical data, for the synthesis of **1** (3 pages). Ordering information is given an any current masthead page.

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(22) For synthetic **1**·HCl: $[\alpha]_D = +4.5°$ ($c = 0.24$, CH_3OH). For naturally occurring **1**·HCl: $[\alpha]_D = +5.9°$ ($c = 1.08$, CH_3OH). Note: All ^1H NMR data reported for **1** in ref 10b refer to an acid salt and not the free base. Published data include a systematic error of 0.61 ppm due to use of an external standard. We thank Professor A. D. Elbein for an authentic sample of mannostatin A.

(23) Synthetic (+)-**1** exhibited the same inhibitory activity as naturally occurring mannostatin A against Golgi processing mannosidase II. Moreover, a synthetic sample of (±)-**1**, prepared as in Scheme II from racemic **5**, possessed one-half the potency of (+)-**1**, indicating that the unnatural enantiomer is devoid of activity. We are grateful to Professor A. D. Elbein for conducting these assays.

Competitive Carbonylation Pathways from a Dialkyl A-Frame Complex

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Received December 7, 1990
Revised Manuscript Received April 30, 1991

In the carbonylation of transition-metal alkyl complexes, different reaction pathways leading to the formation of aldehydes and ketones have been described.[1] Some examples involving binuclear methyl complexes have been found to yield acetone but not the doubly carbonylated product 2,3-butanedione.[2] The formation of butanedione is relatively rare and has been seen in the carbonylation of $Ni(CH_3)_2(bpy)$, the photolysis of $(\eta^5\text{-Cp})Re(CH_3)(COCH_3)(CO)_2$ under 20 atm of CO, and the carbonylation of $Pd(CH_3)_2L_2$ (L = phosphine) in low yield.[3-5] In this communication, we report the synthesis and characterization of a dimethyl A-frame complex of rhodium and its carbonylation chemistry, which leads to acetone and 2,3-butanedione by different mechanisms with a balance between the carbonylation pathways that is extraordinary.

The complex $Rh_2(\mu\text{-CO})(CH_3)_2(dppm)_2$ (**1**; dppm = bis(diphenylphosphino)methane) is synthesized by the reaction of $Rh_2(CO)_2Cl_2(dppm)_2$[6] with methylmagnesium chloride in THF at −75 °C under nitrogen. The orange, air-sensitive product is recrystallized from THF or benzene and characterized spectroscopically. The infrared spectrum of **1** shows a single ν_{CO} at 1728 cm^{-1} assignable to a bridging carbonyl. In the ^1H NMR spectrum of **1** in C_6D_6, methylene resonances occur as doublets of multiplets at δ 3.25 and 3.65 ppm, indicating an inequivalency of protons on the same dppm, while the methyl resonance appears at δ 0.35 ppm as a broad singlet due to unresolved J_{Rh-H} and J_{P-H} coupling. The $^{31}P\{^1H\}$ NMR spectrum exhibits a second-order pattern (AA'XX'X''X''') (see Figure 1a), which can be simulated with coupling constants consistent with an A-frame structure having a large trans J_{P-Rh-P} coupling of 350.0 Hz (Figure 1b).[7,8]

When **1** is labeled with ^{13}CO, the carbonyl resonance in the ^{13}C NMR spectrum is a triplet of quintets at δ 236.6 ppm, indicating coupling to equivalent Rh and P nuclei. The $^{31}P\{^1H\}$ NMR spectrum of this labeled compound (Figure 1c) possesses

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(7) ^1H NMR (δ, C_6D_6, Me_4Si): 0.35 br s (CH_3), 3.25 m (HCH), 3.65 m (HCH), 6.90 m (p,m-phenyl), 7.65 s (o-phenyl). ^{13}C NMR (δ, C_6D_6, Me_4Si): $Rh_2(\mu\text{-CO})(^{13}CH_3)_2(dppm)_2$, 3.8 (second-order pattern); $Rh_2(\mu\text{-}^{13}CO)(CH_3)_2(dppm)_2$, 236.6 t of quin ($^1J_{C-Rh}$ = 34.0 Hz, $^2J_{C-P}$ = 7.4 Hz). ^{31}P NMR (δ, C_6D_6, H_3PO_4): 32.5 (second-order pattern).

(8) Simulations were performed on a Bruker Aspect X32 using DSYMUX. ^{31}P simulation (AA'XX'X''X'''): $^2J_{P-Rh-P}$ = 350.0 Hz, $^2J_{P-C-P}$ = 95.0 Hz, $^3J_{P-P}$ = 14.5 Hz, $^1J_{Rh-P}$ = 156.5 Hz, $^2J_{Rh-P}$ = −1.2 Hz. Simulation for **1**-^{13}CO (AA'MXX'X''X'''): $^2J_{P-Rh-P}$ = 350.0 Hz, $^2J_{P-C-P}$ = 95.0 Hz, $^3J_{P-P}$ = 14.5 Hz, $^1J_{Rh-P}$ = 156.5 Hz, $^2J_{Rh-P}$ = −1.2 Hz, $^1J_{C-Rh}$ = 34.0 Hz, $^2J_{C-P}$ = 7.4 Hz.

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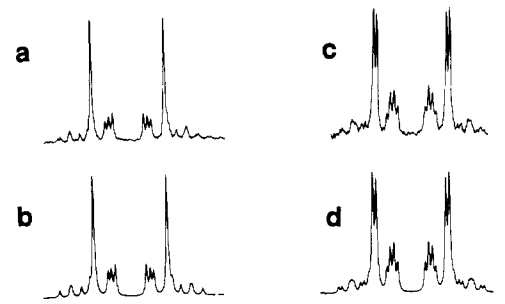
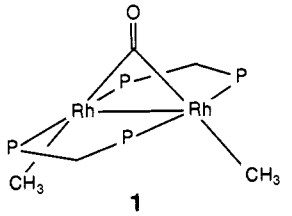


Figure 1. (a) Experimental and (b) simulated ^{31}P NMR spectra of $Rh_2(\mu\text{-}CO)(CH_3)_2dppm_2$. (c) Experimental and (d) simulated ^{31}P NMR spectra of $Rh_2(\mu\text{-}^{13}CO)(CH_3)_2dppm_2$.

additional couplings which are satisfactorily simulated with $^1J_{C\text{-}Rh}$ and $^2J_{C\text{-}P}$ obtained from the ^{13}C NMR spectrum (Figure 1d).[7] All of these data are consistent with a single bridging CO shared between two equivalent, dppm-bridged Rh atoms and lead to the structural assignment of **1** as a dimethyl A-frame complex with μ-CO at the apex.



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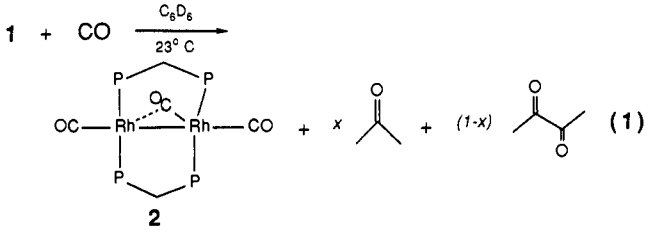
Compound **1** reacts with CO (~1500 Torr) at room temperature to form 2,3-butanedione as the major organic product with only trace amounts of acetone, as identified by ^1H and ^{13}C NMR spectroscopies, gas chromatography, and GC/mass spectrometry. At lower CO pressure (50–700 Torr), both acetone and butanedione are produced with the ratio of acetone to butanedione increasing with decreasing CO pressure (e.g., 1.6:1 at 300 Torr, 24:1 at 50 Torr). This ratio is also dependent upon sample concentration and agitation. The sole metal-containing product in these reactions is the previously reported tricarbonyl complex $Rh_2(CO)_3(dppm)_2$ (**2**).[9] By ^1H NMR spectroscopy, these reactions are quantitative in the sense of eq 1 where x depends on P_{CO}. At 760 Torr, only one intermediate, proposed as a sym-



2

metrical diacetyl species,[10] is observed whose disappearance coincides with the formation of butanedione. At 60 Torr of CO, several intermediates are observed by ^1H NMR spectroscopy corresponding to acetyl methyl species.

In order to probe the mechanism of product formation, crossover experiments using **1** and $Rh_2(\mu\text{-}CO)(CD_3)_2(dppm)_2$ (**1**-d_6) in approximate 1:1 ratios under 60, 700, and >760 Torr of CO were performed, and the organic products were analyzed by GC/mass spectrometry. For acetone, only d_0 and d_6 products were observed with little or no d_3 crossover product (0–6% of total acetone), whereas for butanedione, significant amounts of crossover occurred (23–45% d_3 product of total butanedione). The results clearly demonstrate that acetone formation is *intra*molecular, presumably via reductive elimination from a methyl acetyl species, while

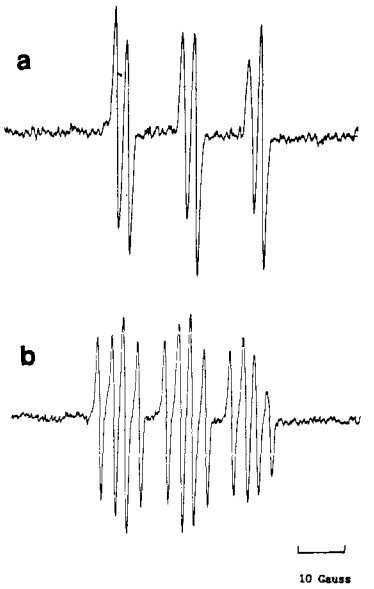
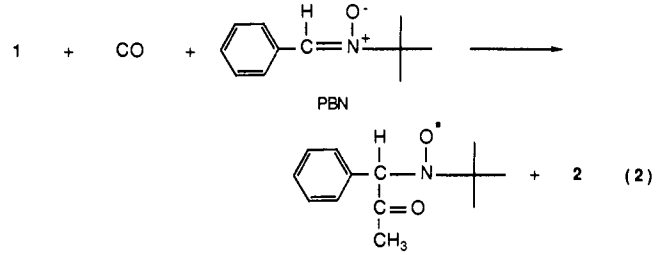


Figure 2.

butanedione forms by an *inter*molecular path, possibly involving acetyl radicals. The acetone product distribution also indicates that scrambling of methyl groups *prior* to carbonylation does not occur.

To test the notion of butanedione formation from radicals, spin-trapping experiments were performed using the spin trap phenyl-*N*-*tert*-butylnitrone (PBN). Specifically, PBN (10 mg) was added to the reaction of **1** under 760 Torr of CO, and the sample was monitored by ESR spectroscopy. The spectrum obtained is shown as Figure 2a and corresponds to a radical adduct of PBN with hyperfine splittings of a_N = 14 G and a_H = 3 G, consistent with eq 2 and previously reported hyperfine values.[11]



To establish that the radical trapped in this reaction was indeed an acetyl radical and not due to trapping of $CH_3^\bullet$ or another $R^\bullet$ generated as a consequence of reaction with PBN, eq 2 was carried out with **1**-^{13}CO under ^{13}CO. The ESR spectrum obtained from this reaction shows an additional hyperfine splitting of 5 G due to ^{13}C (see Figure 2b).

The fact that under 760 Torr of CO only a trace of acetone and no ethane are produced suggests the absence of methyl radicals in the chemistry leading to butanedione. This is further supported by carbonylation of **1** in the presence of excess tris(trimethylsilyl)silane (40 μL), which results in the formation of acetaldehyde as the major organic product, with no butanedione and only a trace amount of acetone observed.

The spin-trapping results suggest differences in the mechanism of butanedione formation from that proposed for photochemical butanedione formation from the mononuclear complex (η^5-Cp)-$Re(COCH_3)(CH_3)(CO)_2$.[4] In that case, methyl and acetyl radicals are produced by photolysis and the former carbonylated to increasing degrees under higher CO pressure. The methyl and acetyl radicals thus generated proceed to form coupled products or are trapped with CCl_4 and $CBrCl_3$ being used to generate the

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corresponding halides. The use of CCl_4 and $CBrCl_3$ as radical traps for the present study proved unfeasible as did the use of thiols and Bu_3SnH because **1** was observed to react directly with these traps in the absence of CO.

For the binuclear A-frame complex **1**, the present study, including crossover and spin-trapping results, shows that two different mechanisms are operative in carbonylation, leading to acetone and butanedione as in eq 1. The system is extraordinarily sensitive to CO pressure for product selectivity. At low CO pressure (60 Torr), an intramolecular pathway to acetone formation involving methyl acetyl intermediates predominates, whereas at only slightly higher CO pressure (760 Torr), a radical process from a symmetrical diacetyl intermediate leads to 2,3-butanedione.

Acknowledgment. We thank the National Science Foundation (CHE 89-09060) for support of this work, the Johnson Matthey Co., Inc., for a generous loan of rhodium salts, and Prof. W. D. Jones for helpful discussions. We also gratefully acknowledge support from the National Science Foundation (CHE 89-11868) in the form of funds to upgrade the NMR spectrometer.

Biosynthesis of the Benz[*a*]anthraquinone Antibiotic PD 116198: Evidence for a Rearranged Skeleton

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Received January 2, 1991

In the past 10 years the number of recognized naturally occurring benz[*a*]anthraquinones, a previously rarely encountered ring system,[1-5] has grown dramatically.[6] Three biosynthetic studies[7-10] have so far been reported, each describing a straightforward polyketide origin via derivation from a decaketide intermediate, as typified by dehydrorabelomycin, **1** (Scheme I).[9-11] We now report that the biosynthesis of the benz[*a*]anthraquinone antibiotic PD 116198, **2**, is via a decaketide polyketide derived by a novel, unexpected rearrangement of an apparent *linear* tetracyclic intermediate.

Scheme I

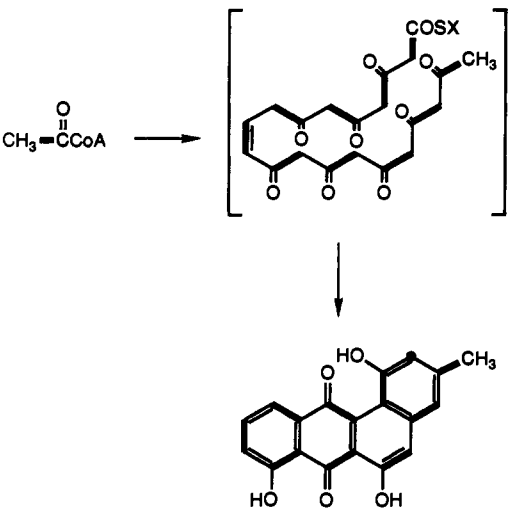

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Table I. ^{13}C NMR Spectrum of PD 116198 and Incorporation of [^{13}C]Acetates

carbon	chemical shift, ppm	2a % ^{13}C[a]	2b $^{1}J_{CC}$, Hz
1	206.3	1.10	40.4
2	82.8	7.80	40.4
3	76.1	1.01	38.9
4	44.0	8.63	
4a	76.9	1.01	37.3
5	147.3	10.40	66.5
6	117.1	1.70	66.5
6a	138.5	6.40	52.6
7	189.0	1.21	52.7
7a	115.9	6.08	64.1
8	161.9	1.10	63.5
9	124.8	11.10	57.8
10	137.1	1.70	57.8
11	119.3	8.56	61.9
11a	133.0	0.97	61.7
12	183.4	8.56	54.1
12a	139.1	1.04	54.9
12b	77.5	6.71	37.3
13	22.4	9.61	38.8

[a] Normalized to C-8 resonance.

Spores of *Streptomyces phaeochromogenes* WP 3688, known to produce PD 116198,[12] were used to innoculate a seed broth[13] (50 mL/500-mL Erlenmeyer flask), which was incubated at 28 °C/250 rpm for 48 h. A portion of this was used to innoculate (2% v/v) production broths[13] (150 mL/1-L Erlenmeyer flask), and these were similarly incubated for 40 h. Workup involved acidification to pH 2 (1 N HCl), addition of EtOAc, and filtration over Celite. The mycelial mat was washed successively with water, EtOAc, and water. The EtOAc phases were combined, and the combined aqueous phases were extracted with additional EtOAc. After drying (Na_2SO_4) and concentrating in vacuo, the crude residue (1.6 g/1800 mL fermentation) was applied to a column

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