(7) During the progress of our work, an 18% cross-linked analogue of **1** with apparent hyperentropic efficacy[2] was reported: G. Gubitosa, M. Boldt, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **99**, 5174 (1977).

(8) K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Organomet. Chem.*, **97**, 283 (1975).

(9) W. S. Lee and H. H. Brintzinger, *J. Organomet. Chem.*, **127**, 87 (1977).

(10) Complete details will be provided in a full account. In a typical run, **2** (0.53 mmol of Co) in refluxing *n*-octane converted 52% of the diyne to **3** (17%) and **4** (6%) after 99 h. Prolonged heating produced no change.

(11) Similar activity has been claimed for CpCo(CO)₂: W. J. Craven, E. Wiese, and H. K. Wiese, Esso Research and Engineering Co., U.S. Patent 3 026 344 (1958/62).

(12) Gases: 0.25 in. × 20 ft stainless steel 13X molecular sieves, ambient temperature. Higher hydrocarbons: 0.25 in. × 10 ft UCW-98, 20% on Chrom W-HP, temperature programmed. Hydroformylation products: ³/₈ in. × 10 ft 20% Carbowax on 60/80 Chrom W-AW, 25 °C, 85 °C.

(13) Precipitated cobalt on alumina and silica produces hydrocarbon mixtures of considerably different composition: M. Blanchard and R. Bonnet, *Bull. Soc. Chim. Fr.*, 7 (1977); and ref 17.

(14) For hydrocarbon formation from supported clusters, see: A. K. Smith, A. Theolier, J. M. Basset, R. Ugo, D. Commereuc, and Y. Chauvin, *J. Am. Chem. Soc.*, **100**, 2590 (1978). Although polystyrene appears to prevent irreversible aggregation of metal clusters,[15] and metal carbonyls on alumina can be reconstituted with CO after thermal or oxidative decarbonylation,[16] a mechanism that involves cobalt atoms or small clusters would necessitate extensive leaching into solution. Moreover, incomplete regeneration of the Ⓟ-Cp-Co bond from Ⓟ-CpH (derived by radical abstraction or hydrogenation) and cobalt carbonyls is to be expected owing to cyclopentadiene hydrogenation:[6] H. W. Sternberg and I. Wender, *Chem. Soc., Spec. Publ.*, **13**, 35 (1959). The possibility that *trace* amounts of cobalt crystallites are responsible for catalytic action is more difficult to discount. However, we feel that such crystallites should have formed equally well in control experiment 2, where no activity was found. Moreover, increased formation of such a species would be expected on prolonged heating of Ⓟ-CpCo-(CO)₂ or its decarbonylated derivatives, leading to increasing activity with time and frequency of catalyst recycling or widely varying degrees of catalyst strength depending on pretreatment. *No* such effects were found.

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(18) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1297 (1976); G. C. Demitras and E. L. Muetterties, *ibid.*, **99**, 2796 (1977).

(19) J. C. Huffman, J. G. Stone, W. C. Krusell, and K. G. Caulton, *J. Am. Chem. Soc.*, **99**, 5830 (1977).

(20) For the homogeneous reduction of CO to alcohols see: J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.*, **100**, 3625 (1978); J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *ibid.*, **100**, 2716 (1978); L. I. Shoer and J. Schwartz, *ibid.*, **99**, 5831 (1977); and references therein.

(21) Fellow of the Alfred P. Sloan Foundation (1976–1980) and Camille and Henry Dreyfus Teacher–Scholar (1978–1983).

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Evidence for a Possible Trans Oxidative Addition of Hydrogen to an Iridium Complex

Sir:

In all cases so far reported, oxidative addition of dihydrogen to metal complexes occurs in a cis fashion.[1] We report herein evidence for a possible case of trans addition of dihydrogen together with other observations on the stereochemistry of some iridium trihydrides.

Treatment of a solution of carbonylhydridotris(triphenylphosphine)iridium(I) (**1**) with H₂ results in formation of a equilibrium mixture of the two isomeric trihydrides **3** and **4**.[2] Kinetic evidence suggests that **3** and **4** are in equilibrium by repetitive reductive elimination and oxidative addition of H₂,
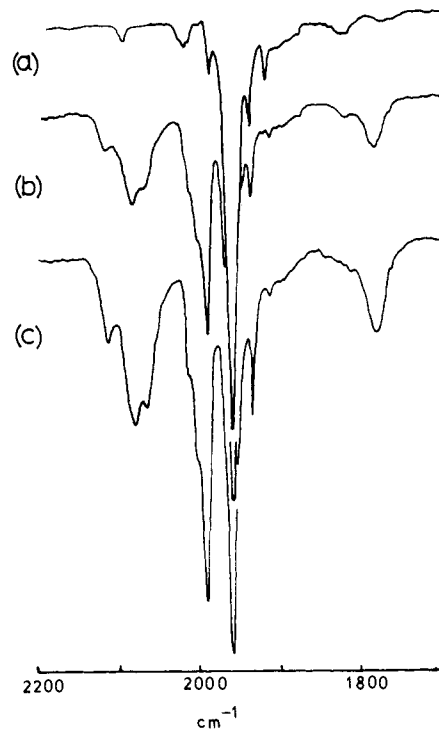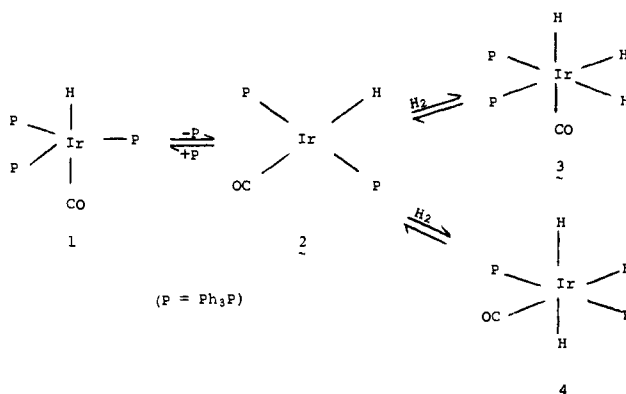

Figure 1. Infrared spectra of P₃(CO)IrD: (a) before addition of H₂, (b) after bubbling H₂ for 45 min, (c) after bubbling H₂ for 90 min. Reactions were run at 20 °C in CH₂Cl₂.

each pure isomer being converted to the equilibrium mixture at room temperature in a few hours. It is also reasonable to assume from kinetic evidence that the reaction proceeds through the square planar intermediate **2**.[2,3]

Treatment of a solution of deuterio-**1** with bubbling dihydrogen resulted in the infrared spectral changes shown in Figure 1. The most striking feature of these spectra is the appearance of rather large amounts of a product containing trans hydrogens (ν_{Ir-H} 1780 cm⁻¹)[7] in addition to the expected product, **5**, with D trans to CO ($\nu_{Ir(III)CO}$ 1985 cm⁻¹)[8] and a
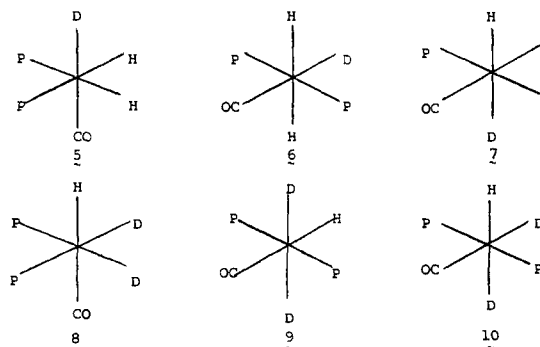
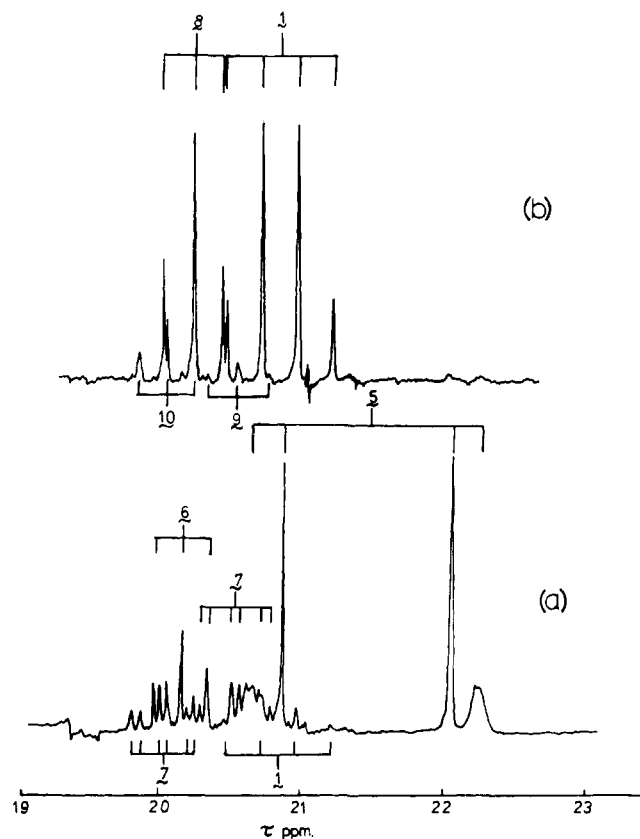**Figure 2.** ^{1}H NMR spectra of (a) solution of $P_3(CO)IrD$ treated with H_2 and (b) $P_3(CO)IrH$ treated with D_2. Reactions were run in $CDCl_2$ at 20 °C for 30 min. Spectra were measured at −20 °C.

high frequency band (ν_{Ir-H} 2112 cm^{-1}) due to H trans to P. A similar experiment in which **1** was reacted with dideuterium resulted in the appearance of new bands due to CO trans to H ($\nu_{Ir(III)CO}$ 1953 cm^{-1}) and CO trans to D ($\nu_{Ir(III)CO}$ 1998 cm^{-1}). Although additional peaks were evident in the ν_{Ir-H} region, no peak at ν >2100 cm^{-1} was observed, suggesting the absence of isomers with H trans to P.

The unexpectedly large amount of what we believed to be isomer **6** in the product of the reaction of deuterio-**1** with H_2 prompted an investigation of the solution composition by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of **3** and **4** were measured and found to conform to those expected on the basis of previous reports of the spectra of analogous trihydrides.[9]

Of particular importance to the present work is the fact that all of the resonances of both isomers are characteristically split by a proton–proton coupling of ~3 Hz. The fac isomer **3** also exhibits a typical large splitting due to H trans to P and the resonance is complex owing to the magnetic nonequivalence of the two chemically equivalent protons.[9]

A solution of deuterio-**1** treated with H_2 gave the spectrum shown in Figure 2a. It is immediately evident from this spectrum that the most important proton-containing species is **5**, its presence being unequivocally announced by the large trans-phosphorous splitting, still complex but lacking a splitting due to a chemically inequivalent proton. A second species that can be identified is **6**, since the infrared spectrum shows the presence of a compound with H trans to H and the proton spectrum exhibits a simple triplet at virtually the same chemical shift as the analogous protons in **4**. The remaining lines in the spectrum are due to the species **7** and consist of two triplets of doublets, the lower field triplet exhibiting an interestingly large downfield isotope shift induced by the trans deuterium.[10] It is particularly noteworthy that no **1** is evident in the reaction mixture when the NMR spectrum is recorded at −20 °C thus confirming the absence of H/D exchange. In

similar experiments at room temperature a considerable amount of **1** was evident in the solution owing to exchange occurring between metal complexes and dissolved hydrogen over the rather long time required to obtain good spectra. In addition, at room temperature the proton–proton coupling of the low field triplet was not evident owing to the presence of large amounts of species **10** produced by exchange processes.

The ^{1}H NMR spectrum of a solution of **1** treated with D_2 was surprisingly simple. Apart from **1**, the major species present was **8** (strong triplet at τ 20.19). In addition, the presence of **10** and **9** was signalled by simple triplets at τ 19.99 and 20.55, respectively. The species **10** was therefore responsible for the $\nu_{Ir(III)CO}$ band observed at 1998 cm^{-1} in the IR spectrum.

All of the above results can be accommodated by the assumption of three stereochemical pathways for the addition of hydrogen to **2**. These three pathways are illustrated for the
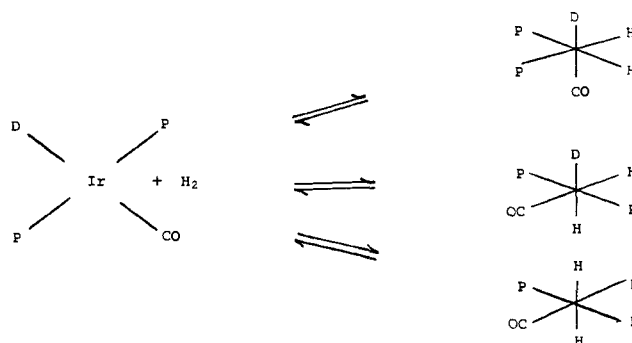
case of H_2 addition to deuterio-**2** in the scheme shown. The first pathway, a cis addition leading uniquely to the fac isomer, exhibits the same stereochemistry as previously observed for reactions of **2** with group 4 hydrides.[11] The second pathway, also a cis addition, corresponds to the stereochemistry normally observed for cis additions to Vaska's complex and its analogues.[1,13] The third pathway corresponds to a trans addition of molecular H_2, and, if the species **6** and **9** do indeed result from trans additions, this represents the first observation of such a reaction.[12]

The most serious alternative explanation for the appearance of species **6** and **9** is the intramolecular interchange of the central hydride/deuteride in species **7** or **10** with its hydride/deuteride neighbors. That such intramolecular interchange occurs is strongly suggested by the fact that **9** and **10** (or their isotopic conjugates) appear in roughly a 1:2 ratio, as one would expect if they were in equilibrium. The problem is that we cannot distinguish between the extreme alternatives of cis or trans addition since the intramolecular interchange would give the same products from either. The interchange, if it occurs, is slow on the NMR time scale up to 0 °C. Above that temperature intermolecular H/D exchange becomes fast enough to render interpretation of spectra impossible.

The fact that intramolecular interchange could occur in the mer isomer, but not the fac isomer is likely due to the large trans effect of the hydride ligand. A cis interchange such as that presently suggested is uniquely simple in the area of molecular dynamics of transition complexes,[14] and we are presently attempting to confirm its occurrence by alternative stereospecific synthesis of either of the isotopomers **9** or **10**.

References and Notes

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(2) These isomers may be prepared in a pure state by an alternative method. Their interconversion has been studied in detail, and the results will be published elsewhere. In addition to rate law evidence, the close similarity of the rates of reaction of **3** and **4** with Ph₃P (to produce **1**) to their rates of isomerization strongly supports the suggested mechanism.
(3) The synthesis of this intermediate has been claimed[4] and its existence has frequently been cited in the literature.[5] These claims are all erroneous and we have established that the putative **2** is in fact P₂(CO)₂IrH, as previously suspected by Yagupsky and Wilkinson.[6] Since the compound **2** has not been isolated, its stereochemistry is unknown, a fact which contributes some uncertainty to the interpretation placed on the results reported herein.
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(10) The isotopic effect of D cis to H on chemical shift in no case exceeds 0.02 ppm, while the measured value for D trans to H is 0.1 ppm in both **7** and **10**.
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(12) R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970).
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Benzocyclobutenedione Monoketal. A 1,4-Dipole Equivalent for Anthracyclinone Synthesis. Synthesis of (±)-4-Demethoxydaunomycinone

Sir:

The clinical activity[1] of the anthracyclinone antibiotics daunomycin, adriamycin, and carminomycin has inspired much synthetic work on the aglycones of these molecules, **1a–c,**

1a, R¹ = CH₃, R² = H
b, R¹ = CH₃, R² = OH
c, R¹ = R² = H
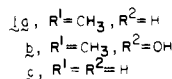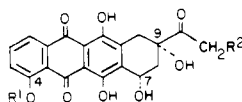
and their analogues. The 4-demethoxy system, first prepared by Wong,[2] has also proven especially promising in clinical trials,[3] and several publications regarding the synthesis of this tetracyclinone have resulted.[4]

Our anionic approach to anthracyclinones via coupling of an AB ring to a D-ring precursor would be equally applicable to the synthesis of the 4-demethoxy system.[5] However, the synthesis of a 7- or a 7,9-deoxy analogue, followed by subsequent introduction of the remaining A-ring oxygen substituent(s), affords only an alternative to Wong's[2,6] original and quite acceptable synthesis of these deoxygenated species. In fact, current work on both the 4-demethoxy and naturally occurring systems has involved introduction of the 7- or 7,9-hydroxyl group(s) after formation of the tetracyclic ring by methods that proceed in modest yields at best,[2,3a,6] two exceptions being the elegant use of a trimethylsilyl group as a latent 7-oxygen function[4d] and the Diels–Alder route of Krohn.[4f] As outlined earlier, we conceived of quinone bisketals

## Scheme I. General Outline for One-Step Construction of Anthracyclinone Systems
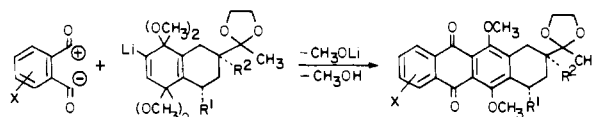
serving as key moieties in mild procedures for one-step formation of anthracyclinones in which a completely functionalized, optically active AB-ring system is linked with a D-ring precursor.[5,8] We report studies which utilize benzocyclobutenedione monoketal as a 1,4-dipole equivalent[9,12] (Scheme I) culminating in the synthesis of (±)-4-demethoxydaunomycinone.

The reaction of **2**[13] with **3** at −65 °C for 30 min, followed by warming to room temperature and then heating at reflux for 3 h, afforded after standard workup a yellow solid, which was crystallized from methylene chloride–ether to afford yellow needles (70%, mp 198.5–199.5 °C). Hydrolysis of a

2   **3**   **4**   **5**
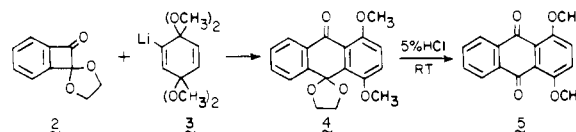
heterogeneous mixture of **4** and 5% hydrochloric acid at room temperature for 15 h afforded a quantitative yield of **5**, which was identical with the methylation product of quinizarin. Likewise, coupling of **2** with **6** (prepared from the requisite bromo alcohol by treatment with 2 equiv of butyllithium) afforded **7** (47%, mp 245–247 °C from CH₂Cl₂–ether), which was quantitatively hydrolyzed (THF–3 M HCl, 15:8, 20 h, room temperature) to **8**, mp 183.5–186 °C (lit.[4c] mp 184–186 °C).

6   **7**   **8**
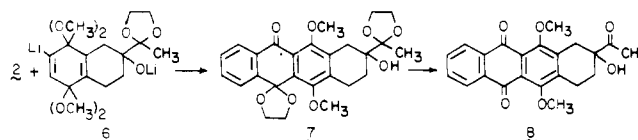
There now remained the application of this mild ring formation method to the fully oxygenated AB-ring precursor. The appropriately functionalized AB-ring system **12** was readily available as outlined in Scheme II;[14] only the salient points will

Scheme II. Synthesis and Coupling Reactions of the AB-Ring System

9

10a, R¹ = OH, R² = H
b, R¹ = OCH₃, R² = H
c, R¹ = OCH₃, R² = CH₃

11a, R¹ = OCH₃, R² = H
b, R¹ = H, R² = OCH₃

12a, R¹ = OCH₃, R² = H
b, R¹ = H, R² = OCH₃

13

14   **15**