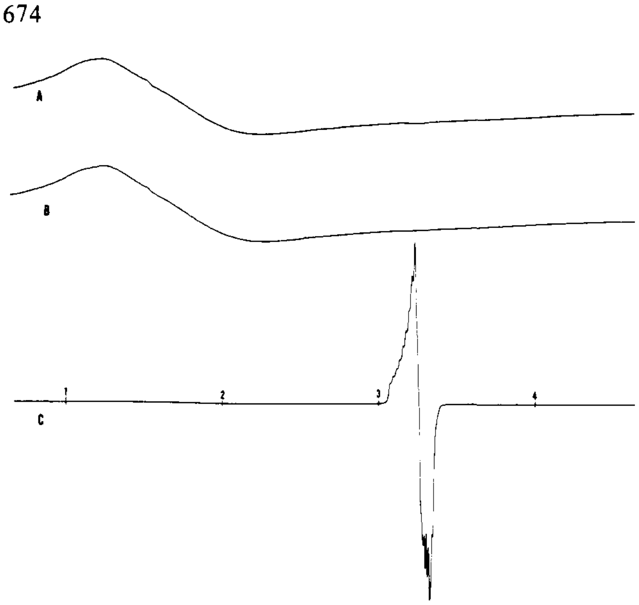

Figure 1. Epr spectrum of Co(Me) in 1/1 (v/v) CH_2Cl_2-toluene at 77°K: (A) degassed; (B) equilibrated with 960 Torr of CO; (C) with CO removed and 960 Torr O_2 added. Intensity in (C) is times 1/10. Field calibration, in kG, indicated in (C).

(−93°), (b) Dry Ice–ethanol slush (−78°), or (c) at room temperature. After 15 min, a spectrum was taken at room temperature and 77°K. The sample was then thawed and shaken in the sealed epr tube in order to promote dissolution of CO, reequilibrated at one of the three temperatures, frozen, and reexamined. Samples were then left under 960 Torr of CO for up to 1 week, and examined as above. No sample of Co(H) or Co(Me), in any solvent or solvent combination, using any equilibration techniques, showed *any* evidence of forming a CO adduct (Figure 1B). *No* sign of an epr spectra similar to those exhibited by a Co–O_2 adduct, either at 77°K or at room temperature, was produced by addition of CO. As verification of the procedures used, Co(TPP)-CO was prepared, and found to give an epr spectrum identical with that reported by Wayland.[11]

In contrast, removal of CO and addition of O_2 gave very intense spectra of Co(H)O_2 and Co(Me)O_2 (Figure 1C), as observed, respectively, in ref 7a and 1. In addition some diamagnetic μ-peroxo bridged species is formed.[13b]

We have also examined the ^1H nmr of Co(H) and Co(Me) in $CDCl_3$; the former was originally reported in an unpublished thesis.[13b] Although ref 1 discusses resonances less than 50 ppm from TMS, these high-spin compounds in fact exhibit resonances spread over ca. 900 ppm (−64°). *No* change is observed, even at −64°, upon addition of CO. Addition of O_2 causes the slow appearance of a new species with a much smaller span of resonances (<10 ppm). These studies, to be published later,[16] confirm the absence of any adduct formation with CO by these high-spin Co(II) Schiff bases; the new species is not the paramagnetic 1:1 dioxygen adduct, as claimed in ref 1, but appears to be the diamagnetic μ-peroxo-bridged complex.[13,16] The nmr spectrum of the 1:1 adduct appears to be unobservable.

An experiment was also performed using C_2H_5NC.[17] With 20% (v/v) of ligand added to a CH_2Cl_2 toluene solution of Co(Me), a new signal with low intensity appears, with superhyperfine splittings from a single ^{14}N and the spin-Hamiltonian parameters (g_z = 2.02, $g_x \sim g_y$ = 2.20; $A_\perp^{Co} \approx 40$, $A_\parallel^{Co} = 64$, $A_\parallel^{N} = 12.5$ G). The spectrum, corresponding to a low-spin Co(II) complex, is similar to those for six-coordinate Co(II) porphyrins[7c,d] and is probably Co(Me)(C_2H_5NC), with splitting from the apical nitrogen. The spectrum is wholly distinguishable and different from those of oxygen adducts.[4,7,1d]

In summary, there is no evidence for any coordination of CO by Co(Me) and Co(H); the adduct formed upon addition of RNC is typical of low-spin cobalt(II) complexes, not Co–O_2 adducts. It must be concluded that the observations of ref 1 are artifacts caused by the presence of O_2, and therefore their conclusions must be dismissed. Thus, the evidence for spin transfer to O_2 and for the formal description of Co–O_2 adducts as Co(III)–O_2^- adducts remains secure.

Acknowledgment. We thank Professor T. J. Marks for performing and discussing the nmr studies. This research was supported by National Institutes of Health Grant HL-13412 and by the donors to the Petroleum Research Fund, administered by the American Chemical Society. B.M.H. is the recipient of a National Institutes of Health Career Development Award.

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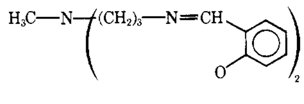
(12) Abbreviations: salMeDPT^{2-} =



salHDPT^{2-} = above with H in place of CH_3, Co(salMeDPT) = Co(Me), Co(salHDPT) = Co(H).
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(16) T. J. Marks, T. Szymanski, B. M. Hoffman, and F. Basolo, to be submitted for publication.
(17) The C_2H_5NC was a generous gift of Dr. B. L. Haymore.

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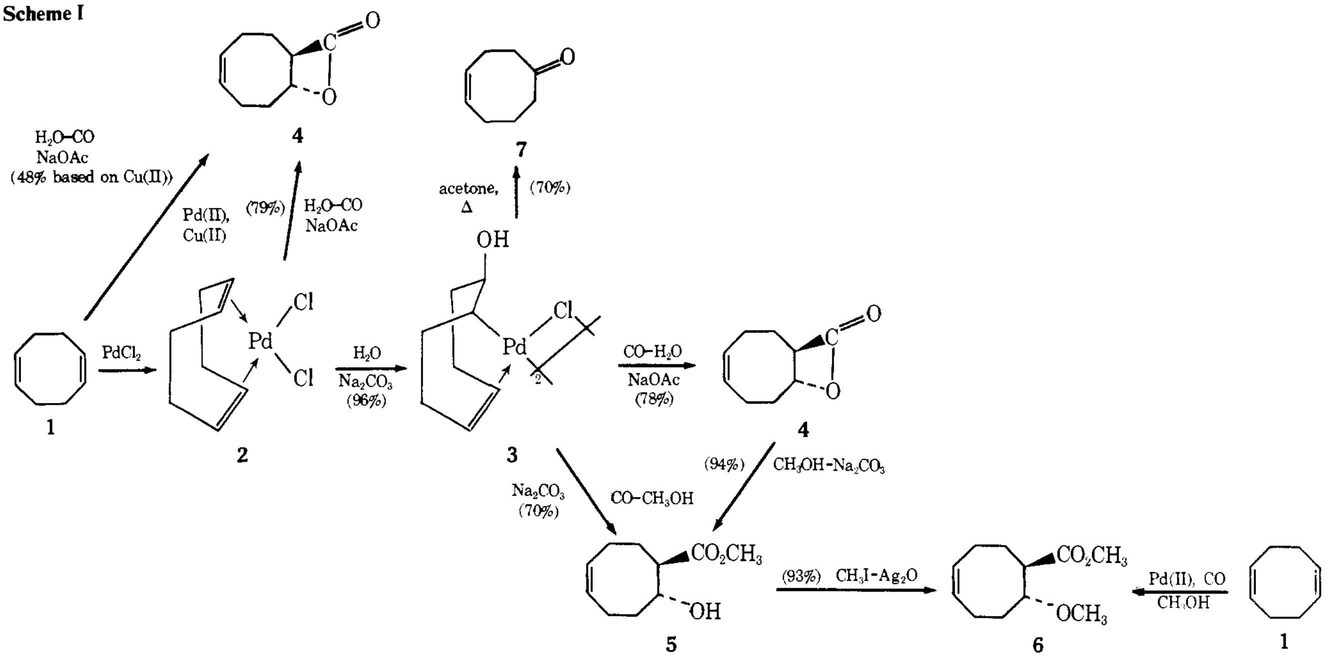
Received November 18, 1974

Stereochemistry of the Hydroxypalladation of Cyclooctadiene

Sir:

The stereochemical course of the reaction of olefin–transition metal complexes may be considered the result of two distinct mechanistic processes.[1] Reactions in which the addend or nucleophile is coordinated to the metal and transfers directly from the metal to an olefinic carbon proceed by cis addition in an anti-Markovnikov direction. Those reactions in which the nucleophile is solvated but not coordinated and forms a bond with an olefinic carbon by external nu-

Scheme I



cleophilic attack proceed by trans addition in a Markovnikov direction.

Since the mechanism for the Wacker oxidation[2] of monoolefins was proposed,[3] on the basis of kinetic results, to be consistent with cis hydroxypalladation in the rate determining step, the stereochemistry of the methoxypalladation of chelating diolefins, which was demonstrated[4,5] to proceed in all cases by direct attack of methanol exo on the coordinated double bond of the ligand, was regarded as anomalous.[6-10] However, the analogous trans stereochemistry for the methoxypalladation of the monoolefins, *cis-* and *trans-*2-butene, has been established.[11]

Clearly, the stereochemistry of the reactions of chelating diolefins can no longer be considered anomalous.[12] Trans addition of nucleophiles occurs in the methoxypalladation of both mono- and diolefins as well as in the addition of acetate (monoolefin,[13] diolefin[14]) and chloride (monoolefin,[15] diolefin[16]). Cis phenylpalladation has been demonstrated for both monoolefin[17] and diolefin.[18] Therefore, because of the apparent mechanistic conflict between the course of the oxypalladation reactions of methanol and water, we have investigated the nucleophilic attack by water on coordinated 1,5-cyclooctadiene.[19]

The σ-bonded hydroxy enyl complex **3**[20] was easily prepared by the reaction of water with dichloro(1,5-cyclooctadiene)palladium(II) in the presence of sodium carbonate (Scheme I). The stereochemistry of the hydroxypalladation reaction was determined by carbon monoxide insertion which has been demonstrated to proceed with 100% retention at the carbon bearing the palladium.[14] Carbonylation of **3** in water in the presence of sodium acetate afforded metallic palladium and a single organic product, 2-hydroxycyclooct-5-enecarboxylic acid β-lactone (**4**), whose structure was assigned from the following evidence. Methanolysis of the lactone in the presence of base yielded exclusively *trans*-methyl 2-hydroxycyclooct-5-enecarboxylate (**5**).[21] Methylation of 5 gave the trans methoxy ester **6** as shown by comparison to an authentic sample.[14] Carbonylation of **3** in methanolic sodium carbonate produced **5** as the only organic product. β-Lactone **4** also can be prepared directly from the diene complex **2** by carbonylation in aqueous sodium acetate.

In addition, the carbonylation of 1,5-cyclooctadiene (**1**) employing a catalytic amount of palladium(II) and copper(II) as reoxidant was investigated. A mixture of **1**, palladium chloride, cupric chloride, and sodium acetate in a water-acetone solution was allowed to react with carbon monoxide (3 atm) at room temperature to afford a 48% yield (based on Cu(II)) of **4**. In this reaction, 1.7 mmol of palladium(II) gave 11.8 mmol of lactone for a catalytic turnover of 6.9 times.

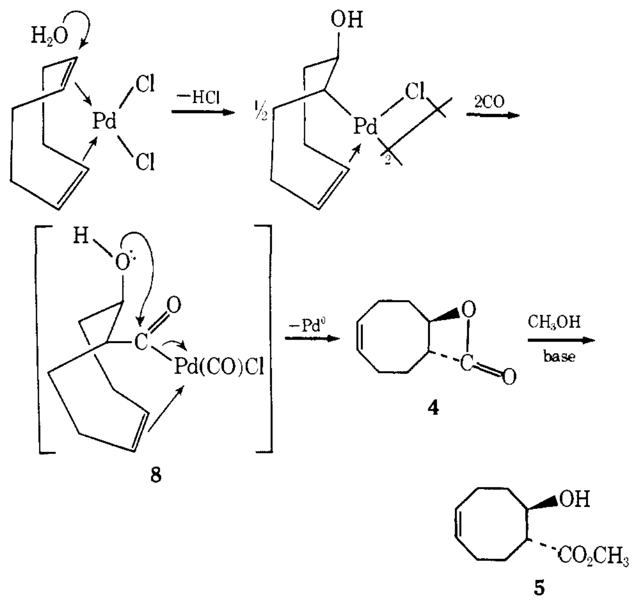
Thermolysis of **3** in acetone provided a 70% yield of the γ,δ-unsaturated ketone **7**. This is the product expected from the Wacker oxidation of 1,5-cyclooctadiene, a reaction which has been demonstrated to proceed *via* a σ-bonded β-hydroxyalkylpalladium intermediate.[22]

The trans stereochemistry of the lactone **4** cannot be the result of a base-catalyzed epimerization process. Because of the high reactivity of the strained β-lactone four-membered ring system, any base-catalyzed solvolysis will result in an irreversible ring-opening reaction.[21] Alcoholysis of β-lactones in the presence of a strong base such as alkoxide ion (necessary to cause epimerization at the carbon α to the carbonyl) affords unsaturated esters. Interestingly, treatment of the more stable methoxy ester **6** with sodium methoxide in methanol yields predominantly unsaturated ester (70%).[14] The remainder of the product (30%) is an equimolar mixture of the epimerized *trans-* and *cis-β*-methoxy esters.

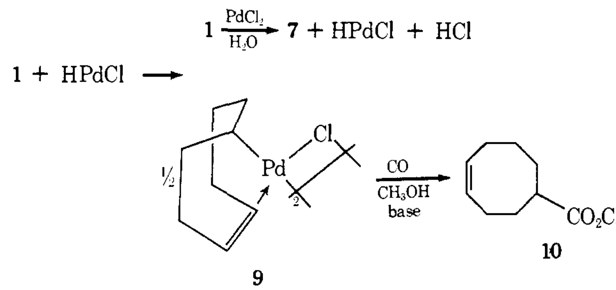
The trans stereochemistry of the lactone **4**, therefore, indicates that as with methanol, oxypalladation proceeds exclusively with attack by the nucleophile (water) from outside the coordination sphere of palladium. The carbonylation reaction mechanism (Scheme II) probably involves carbon monoxide insertion into the palladium-carbon bond followed by intramolecular alcoholysis of the acylpalladium bond of **8** to give **4**. The hydroxy ester **5** can be formed by base catalyzed methanolysis of **4** and/or **8**.

In an attempt to prepare **3** directly from 1,5-cyclooctadiene,[23] a slightly greater than twofold excess of **1** was stirred with palladium chloride in water-acetone solution. The reaction resulted in isolation of equimolar amounts of two products, the Wacker oxidation product **7** and the dimeric σ-bonded enyl complex **9** (Scheme III). The Wacker oxidation of the diolefin generates Pd(0) and hydrogen chloride (effectively HPdCl) which reacts with another

Scheme II



Scheme III



molecule of cyclooctadiene to form the hydride addition complex **9**. Carbonylation of **9** yields methyl 4-cyclooctenecarboxylate (**10**).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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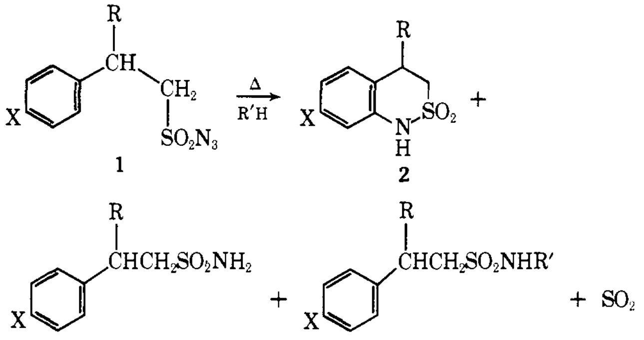
Flash Vacuum Pyrolysis of β-Arylethylsulfonyl Azides. Dihydropyrindine Formation

Sir:

Intramolecular cyclization of sulfonyl azides has been shown to be a useful approach to interesting cyclic sulfonamides.[1] In contrast, decomposition of α-toluenesulfonyl azide in solution gave none of the desired cyclization product and this was attributed[1] to strain in the required fused benzaziridine intermediate. Support for this comes from the fact that thermolysis of β-phenethylsulfonyl azide (**1a**) in diglyme at 149° gave 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**2a**) (6%), β-phenethylsulfonamide (**3**) (30.6%), and SO_2 (10%), while in *n*-tetradecane at 149°, **2a** (6–8%), **3** (6–7%), and a mixture of isomeric *N*-tetradecyl-β-phenethylsulfonamides (**4a**) (47%) were isolated. In cyclohexane, similar results were obtained, and the main product was (**4a**, R′ = C_6H_{11}) (44.5%).[2]



In the hope of improving the yield of **2** by decreasing or eliminating the opportunity for intermolecular reactions of the nitrene the flash vacuum pyrolysis (FVP) of **1a** was studied. The highest yield of **2a** (12.8%) was obtained at 300° (3 mm). In addition, however, there was obtained a 6.9% yield of dihydropyrindine (**5a**). At 400°, the yield of **2a** dropped slightly (11.3%) but that of **5a** rose to 32.7%, and traces of indole, indoline, and styrene were detected by GLC/mass spectrometry. FVP of **1a** at 650° (3 mm) (N_2 carrier gas) gave **5a** (64.8%), indoline (11.2%), indole (1.5%), and styrene (8.2%), but no **2a**.

Dihydropyrindine (**5**) and styrene are not formed from **2** on FVP, and indeed the latter is stable at 300°. The possibility was considered that indoline arose from phenethylnitrene formed in the gas phase by a Wolff-type rearrangement of the sulfonylnitrene followed by loss of SO_2. This was shown not to be the case by FVP of β-phenethyl azide when, as expected,[3] no intramolecular substitution occurred and only tars were formed. The indole and indoline arise from the FVP of **2a**: at 650° (N_2 carrier gas) the latter gave