This is at an unusually high field for an osmium-carbonyl resonance and appears to be characteristic for a carbonyl ligand that is trans to a donor-acceptor metal-metal bond.[1]

The mechanism of formation of **1** (and **2**) is currently under investigation. It has, however, been established that **2** does not isomerize to **1** when heated in solution at 90 °C. We are also investigating the synthesis of other complexes with chains of dative metal-metal bonds. Preliminary results indicate that $(OC)_4(Bu^tNC)OsOs(CO)_3(CNBu^t)W(CO)_5$ is a minor product in the reaction of $Os(CO)_4(CNBu^t)$ and $W(CO)_5$ (THF) in hexane. Like $P(OCH_2)_3CMe$, $CNBu^t$ is a better donor ligand than CO and can occupy a coordination site cis to the dative metal-metal bond without causing too much steric interaction with the equatorial carbonyls on the neighboring metal atoms.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles for **1** (7 pages). Ordering information is given on any current masthead page.

Novel Rhodium(II)-Catalyzed Cycloaddition Reaction of α-Diazo Keto Amides

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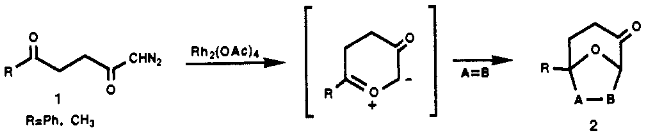
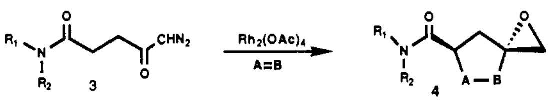
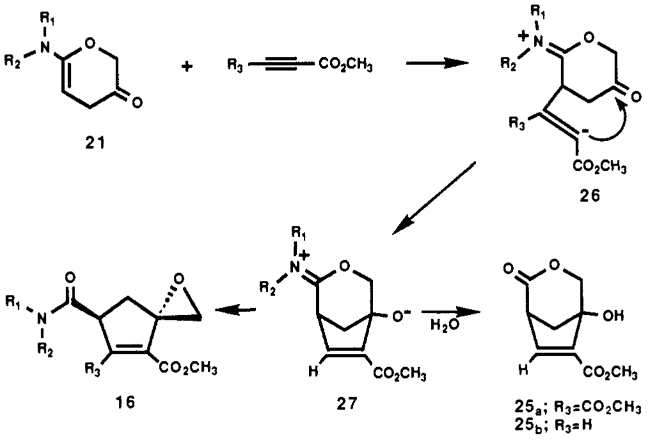
The role of α-diazo carbonyl compounds in organic synthesis is well established,[1-10] and much effort has been devoted to the study of the transition-metal-catalyzed behavior of these substrates.[2] Recent papers from these laboratories have described a route to oxapolycyclic ring systems which involves the tandem cyclization-cycloaddition reaction of a transient rhodium carbenoid.[11] As indicated in the illustration, a cyclic carbonyl ylide intermediate was generated by treatment of a diazoalkanedione (**1**) with rhodium(II) carboxylates. In an effort to extend this methodology to other carbonyl-containing compounds, we examined the rhodium(II)-catalyzed behavior of several diazo keto amides of genus **3**. In this communication we report a new and novel type of cycloaddition of these substrates with both olefinic and acetylenic dipolarophiles to give amido cyclopentyl epoxides of general structure **4**.

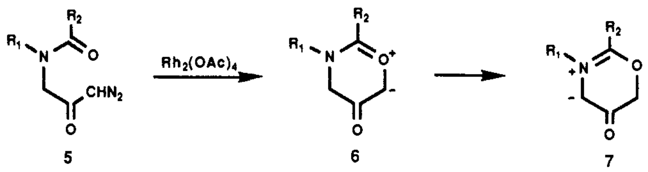


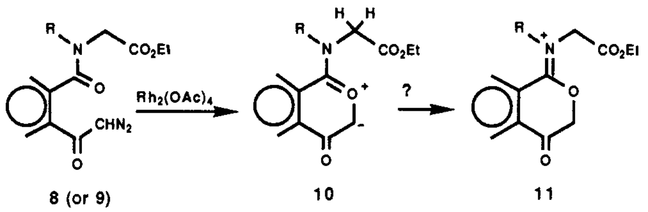


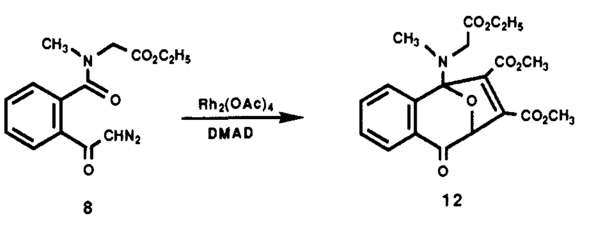
Scheme I

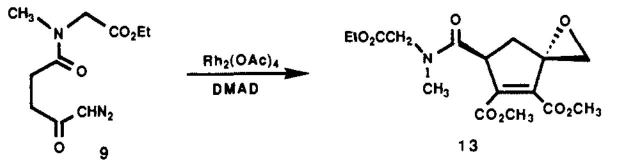


Our recent discovery of a *dipole cascade*[12] which interconverts α-diazo ketones **5** to azomethine ylides **7** via the intermediacy of carbonyl ylides **6** prompted us to explore the generality of this process using α-diazo keto amides (**8** and/or **9**). Ampac calculations show that cyclic azomethine ylides of type **7** are ca. 15 kcal/mol lower in their heat of formation than the corresponding carbonyl ylides **6**. Some of this energy difference is presumably responsible for the facility with which the dipole reorganization occurs. Within this context, we studied the rhodium(II)-catalyzed behavior of α-diazo keto amide **8**. In this case, the carbonyl ylide dipole **10a** is sufficiently stabilized via resonance[13] to be trapped by dimethyl acetylenedicarboxylate (DMAD) to give cycloadduct **12** in 90% yield. No signs of any material derived from azo-









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(13) Ampac calculations (QCPE No. 506 using the AM1 Hamiltonian) indicate that the carbonyl ylide dipole derived from **8** (i.e., **10a**) has a heat of formation (−69.6 kcal/mol) that is 7.5 kcal less than that of the corresponding azomethine ylide **11a** (−62.1 kcal). In contrast, carbonyl ylide **10b** (−94.93 kcal) derived from **9** is 19 kcal less stable than azomethine ylide **11b** (−113.95 kcal).

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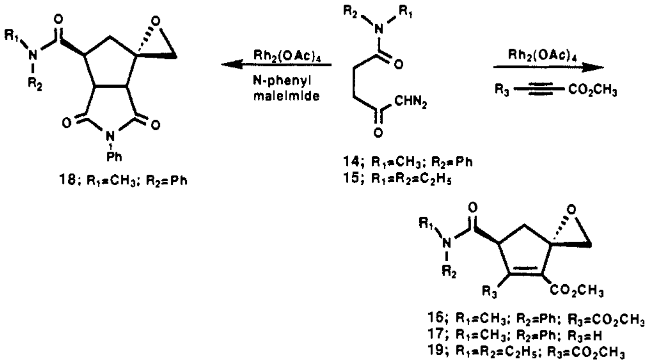
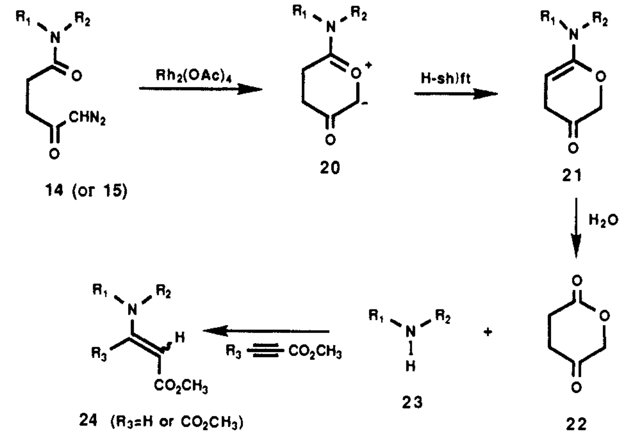
methine ylide **11a** could be detected in the crude reaction mixture. We also examined the rhodium(II) acetate catalyzed behavior of the closely related diazo keto amide **9**. Our first expectation was that the initially formed carbonyl ylide intermediate **10b** would undergo proton transfer to give the thermodynamically more stable azomethine ylide dipole.[13] We found, however, that treatment of **9** with DMAD and a catalytic amount of rhodium(II) acetate resulted in the isolation of the unexpected cycloadduct **13** in 60% yield. Similar results were obtained when diazo keto *N*-phenyl-*N*-methylamide **14** was used. Treatment of this material with rhodium(II) acetate in the presence of DMAD, methyl propiolate, or *N*-phenylmaleimide afforded cycloadducts **16** (60%), **17** (55%), and **18** (70%). Analogous products were also obtained when diazo keto *N*,*N*-diethylamide **15** was used.[14]



A variety of reaction conditions were examined in order to maximize the yields of the cycloadducts. We found that the highest yields were obtained when the solvent (benzene or methylene chloride) was rigorously dried. Use of ordinary solvents routinely led to lower yields of cycloadducts as well as to the formation of variable amounts of enamide **24** and lactones **22** and **25** (vide infra). The reaction was also carried out in the absence of a trapping agent, and the cyclic ketene *N*,*O*-acetal **21** could be isolated in 70% yield. This material was unstable and upon standing was readily hydrolyzed to lactone **22** and amide **23**. In fact, treating a sample of **21** with "wet" benzene in the presence of DMAD (or methyl propiolate) afforded high yields of lactone **22** and enamide **24** derived from conjugate addition of the amine to the activated acetylenic π-bond.[15]



A mechanism that rationalizes the formation of the cycloadducts and that is consistent with all the data is outlined in Scheme I. The initial reaction involves generation of the expected carbonyl ylide dipole **20** by intramolecular cyclization of the keto carbenoid onto the oxygen atom of the amide group. This highly stabilized dipole does not readily undergo 1,3-dipolar cycloaddition but rather loses a proton to produce the cyclic ketene *N*,*O*-acetal **21**. In the absence of any significant amount of water, this material reacts with the activated π-bond of the dipolarophile to produce zwitterion **26**. The anionic portion of **26** adds to the adjacent carbonyl group, affording a new zwitterionic intermediate **27**. If there is some water present, this species is converted to lactone **25**. Under anhydrous conditions, however, epoxide formation occurs with charge dissipation to produce the observed cycloadduct(s) **16**.[16]

We are continuing to explore the scope and mechanistic details of these rhodium-catalyzed reactions of diazo keto amides and will report additional findings at a later date.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. Use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

Supplementary Material Available: Experimental details of the rhodium-catalyzed reactions of **14**, of **8**, **14**, and **15** in the presence of DMAD, of **14** in the presence of methyl propiolate, and of **14** in the presence of *N*-phenylmaleimide (3 pages). Ordering information is given on any current masthead page.

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Porphyrin Synthesis from a,c-Biladienes. Evidence for a Common Mechanistic Pathway in the Electrochemical and Chemical Routes: Formation of Novel Macrocycles Possessing the Homoporphyrin Carbon Skeleton

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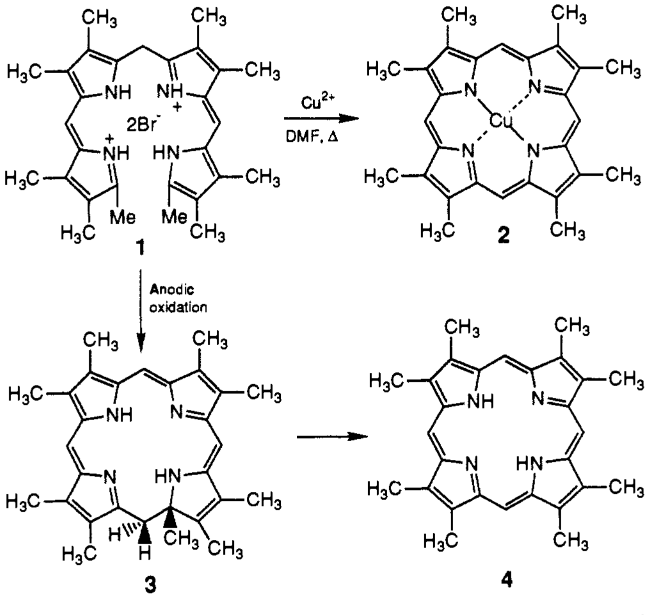
The most general synthesis of unsymmetrical porphyrins employs the copper(II)-catalyzed cyclization of 1′,8′-dimethyl-a,c-biladiene salts **1** to give copper(II) porphyrins **2**. The methodology was discovered in 1961 for symmetrical cases by Johnson and Kay[1] and has since been generalized[2-6] for preparation of completely



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