(n = 1) obtained from 3-buten-1-ol furnished the corresponding lactone 8 in excellent yield (84%). This time, the 5-exo cyclization of the intermediate (3-butenyloxy)carbonyl radical is faster than decarboxylation. Heating 8 with copper powder under vacuum caused the elimination of the xanthate group[2a] and provided the known exo-methylene lactone 9 (also called tulipalin A) in 45% yield.

Apart from providing incontrovertible evidence as to the radical nature of the intermediates, the last two experiments underscore the flexibility and synthetic potential of this novel reaction as a mild generator of carbon-centered radicals from alcohols.

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Unprecedented Bonding Mode in (OC)₃[MeC(CH₂O)₃P]₂OsOs(CO)₄W(CO)₅

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We have recently described the preparation of complexes of the type $(R_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W) in which the 18-electron compound $Os(CO)_4(PR_3)$ acts as a ligand to the group 6 metal atom via an unbridged, donor–acceptor metal–metal bond.[1] In the preparation of one of these derivatives, namely, $(L)(OC)_4OsW(CO)_5$ (L = $P(OCH_2)_3CMe$), low yields of a second compound were obtained, the ¹³C NMR spectrum of which indicated it to be $(L)(OC)_4OsOs(CO)_3(L)W(CO)_5$ (2) with two unbridged, dative metal–metal bonds.[2] This prompted an investigation into the rational synthesis of such compounds, and here we report the synthesis and structure of $(OC)_3(L)_2OsOs(CO)_4$-$W(CO)_5$ (1), an isomer of 2. The crystal structure confirms the presence of unbridged, dative metal–metal bonds in tandem in 1. Such a bonding mode has, to our knowledge, not been previously observed.

A hexane/THF solution of $(L)(OC)_4OsW(CO)_5$ and $Os(C-O)_4(L)$ (in a molar ratio of 0.67:1) was heated under vacuum at 90 °C for 6.4 days, during which time a yellow solid precipitated. The yellow solid was chromatographed (alumina, CH_2Cl_2/hexane, 1/2, as eluant) and gave a yellow band from which 1 was obtained (22% yield) upon recrystallization as yellow, air-stable crystals.[3] The structure[4] of 1 (Figure 1) reveals an approximately linear
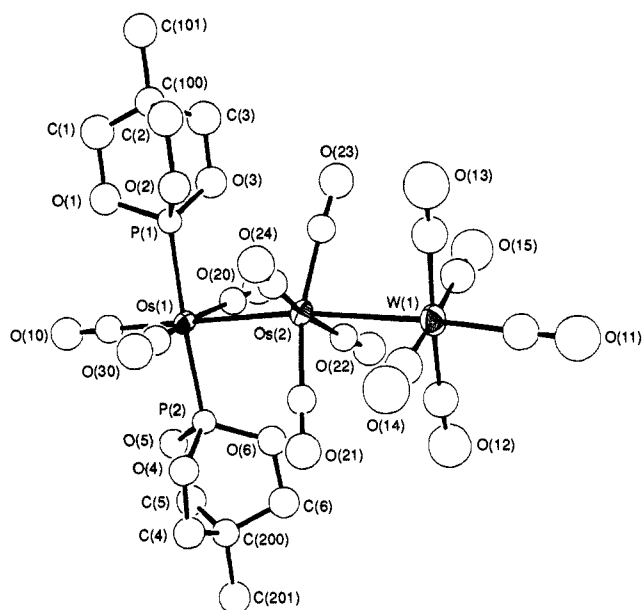
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(2) Isolated yield: 13% (after chromatography). IR: ν(CO) (CH₂Cl₂) 2126 (w), 2114 (w), 2051 (s), 2041 (s), 2008 (m, sh), 1973 (m, sh), 1957 (s), 1904 (s), 1844 (m) cm⁻¹. ¹³C NMR (CD₂Cl₂/CH₂Cl₂, 1/4): major isomer (L trans to the Os–Os bond), δ 206.4 (1), 203.8 (4, J_{183W-C} = 123.9 Hz), 195.8 (2, d, J_{P-C} = 19.2 Hz), 192.4 (1, d, J_{P-C} = 121.4 Hz), 179.9 (4, d, J_{P-C} = 6.7 Hz); minor isomer (L cis to Os–Os bond), δ 203.9 (4), 195.4 (2, d, J_{P-C} = 20.2 Hz), 180.2 (2, d, J_{P-C} = 18.4 Hz), signals of intensity 1 of the minor isomer were not observed. Anal. Calcd for C₂₂H₁₈Os₂WO₁₈P₂: C, 22.08; H, 1.52. Found: C, 21.86; H, 1.53.

(3) IR: ν(CO) (CH₂Cl₂) 2101 (w), 2059 (s), 2022 (vs), 1977 (vs), 1902 (s), 1856 (m) cm⁻¹. ¹³C NMR (CH₂Cl₂/CD₂Cl₂, 4/1): δ 206.4 (1, J_{183W-C} = 177 Hz), 204.1 (4, J_{183W-C} = 125.1 Hz), 193.3 (4), 183.2 (2, t, J_{P-C} = 16.1 Hz), 165.6 (1, t, J_{P-C} = 11.1 Hz). ³¹P NMR (CH₂Cl₂/CD₂Cl₂,4/1): δ 78.1. Anal. Calcd for C₂₂H₁₈Os₂WO₁₈P₂: C, 22.08; H, 1.52. Found: C, 22.33; H, 1.54.

(4) X-ray diffraction data for (OC)₃[MeC(CH₂O)₃P]₂OsOs(CO)₄W-(CO)₅: M_r = 1196.6; monoclinic; space group P2₁/c; a = 16.291 (3) Å, b = 11.415 (3) Å, c = 17.371 (3) Å, β = 91.40 (2)°; V = 3229.4 Å³; Z = 4; D_{calcd} = 2.461 g cm⁻³; μ = 116.6 cm⁻¹ (an absorption correction based on ψ scans was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator (λ(Kα_1) = 0.709 30 Å); 4° ≤ 2θ ≤ 48°; reflections = 2700 with I_0 > 2.5σ(I_0); (number of variables = 176) R_F = 0.043, R_{wF} = 0.048. Residual peaks of up to 2.0 (1) e/Å³ occur 0.9–1.0 Å from Os and W atoms. Attempts to develop an improved model for the structure are in progress.

Figure 1. Molecular structure of (OC)₃[MeC(CH₂O)₃P]₂OsOs(CO)₄W-(CO)₅ (1).

arrangement of the Os₂W atoms; each of the metal–metal bonds is unbridged. An electron count for each metal atom indicates that both metal–metal bonds should be regarded as dative bonds in order for each metal atom to achieve an 18-electron configuration. This is shown below (the eclipsed form is drawn for convenience).

I
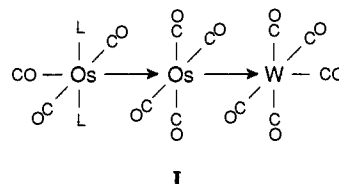
The complex is remarkably stable (note that it was prepared in a reaction at 90 °C that took several days to go to completion). It appears more thermally stable than any of the (R_3P)-$(OC)_4OsW(CO)_5$ complexes[1] that have a single dative metal–metal bond. This extra stability may be the result of greater charge separation when two dative metal–metal bonds are linked as in 1 (i.e., $(\delta+)Os \rightarrow Os \rightarrow W(\delta-)$). The Os–W bond length in 1 at 3.039 (1) Å is somewhat shorter than that in (Me_3P)-$(OC)_4OsW(CO)_5$ (3.0756 (5) Å)[1] and in $(OC)_3(Me_3P)_2OsW$-$(CO)_5$ (3.1417 (6) Å).[5] The Os–Os distance in 1 (2.940 (1) Å) is comparable to the dative Os–Os bond distances found in the three independent molecules in the unit cell of $(OC)_5OsOs(C-O)_3(GeCl_3)(Cl)$ (2.916 (2), 2.927 (2), 2.931 (2) Å)[6] and the covalent Os–Os bond lengths in $Os_3(CO)_{12}(SiCl_3)_2$ (2.9120 (1) Å)[7] and $Os_3(CO)_{12}(I)_2$ (2.935 (2) Å).[8] The Os(1)–Os(2)–W angle (172.07 (4)°) in 1 is virtually identical with the P-Os-W angle in $(Me_3P)(OC)_4OsW(CO)_5$ (171.31 (4)°).[1]

The ¹³C NMR spectrum of 1 in CH_2Cl_2/CD_2Cl_2 clearly shows that the solid-state structure is maintained in solution.[3] The spectrum also indicates that 1 should be formulated as shown and not $(OC)_3(L)_2Os \rightarrow W(CO)_4 \leftarrow Os(CO)_5$. In contrast to 2,[2] $(L)(OC)_4OsW(CO)_5$,[1] and $(OC)_3(Me_3P)_2OsW(CO)_5$,[5] there is no evidence for a second isomer in solution. The resonance at δ 165.6 in the spectrum of 1 is attributed to C(10) (Figure 1).

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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-(BuᵗNC)OsOs(CO)₃(CNBuᵗ)W(CO)₅ is a minor product in the reaction of Os(CO)₄(CNBuᵗ) and W(CO)₅ (THF) in hexane. Like P(OCH₂)₃CMe, CNBuᵗ 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.

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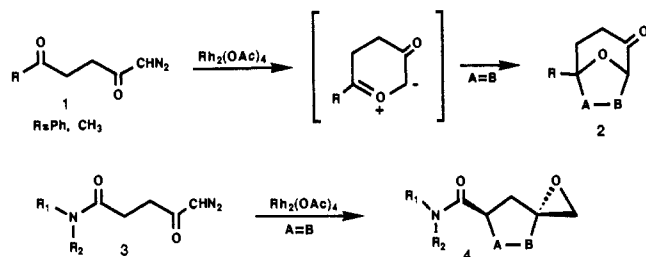
Novel Rhodium(II)-Catalyzed Cycloaddition Reaction of α-Diazo Keto Amides

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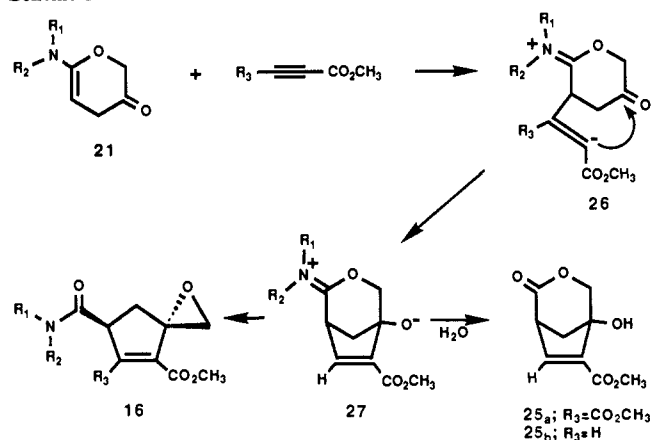Atlanta, Georgia 30322*

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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
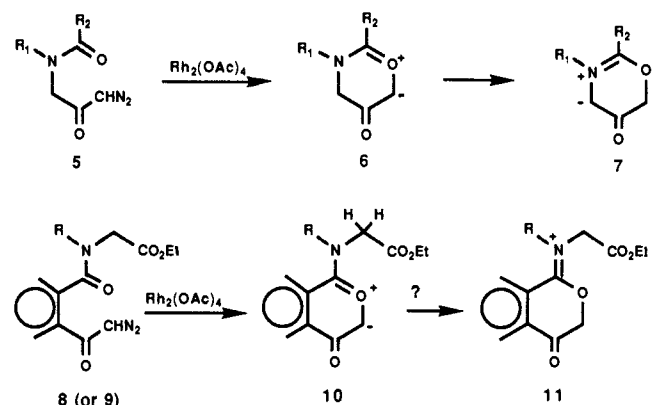

methodology to other carbonyl-containing compounds, we examined the rhodium(II)-catalyzed behavior of several diazo keto amides of genus 3. In this communication we report a new and novel type of cycloaddition of these substrates with both olefinic

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Scheme I

and acetylenic dipolarophiles to give amido cyclopentyl epoxides of general structure 4.

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 cal-

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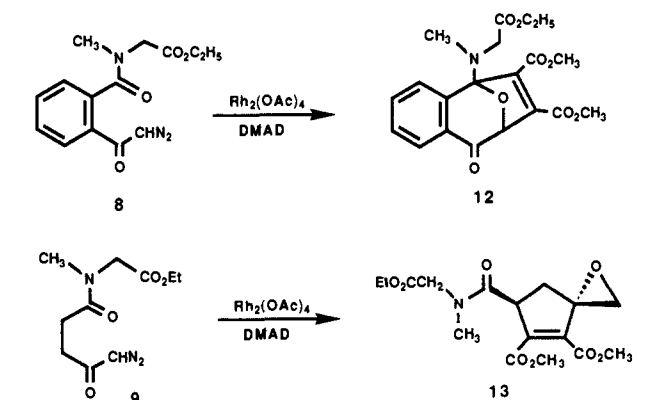
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(13) Ampac calculations (QCPE No. 506 using the AM1 Hamiltonian) indicate that the carbonyl ylide dipole derived from 8 (i.e., 10a) has a heat of formation (−69.6 kcal/mol) that is 7.5 kcal less than that of the corresponding azomethine ylide 11a (−62.1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