all cases examined to date, PEG-Su has been linked to the acceptor. Glycosylating agents have been added several times, if required, for completion of the glycosylation (unoptimized yields of isolated products were 85–95%, or greater; small losses occurred during crystallization). The progress of glycosylation was monitored by NMR spectroscopy (cf. above). After the reaction is completed, the PEG-bound product is precipitated from solution with diethyl ether or *tert*-butyl methyl ether, is recrystallized from ethanol, and after drying is ready for the next step of the synthetic sequence. PEG-Su is eventually easily cleaved from the saccharide by DBU-catalyzed methanolysis in dichloromethane or by hydrazinolysis[21] if a phthalimido group is to be removed as in VI. Peracetylated oligosaccharides for final purification[22] are obtained from dried residues after methanolysis by acetylation with acetic anhydride in pyridine. The expected anomer[3,4] was formed in each glycosylation; the other anomer was not detected. The silyl group used for protection of hydroxyl groups was found to be compatible with this design. Regioselectivity of the glycosylation is exemplified by the formation of IIIa and IIIb.

Supplementary Material Available: Experimental details including procedures for the preparation of IIIa,b, IV, and VI and the cleavage of IIIa,b (6 pages). Ordering information is given on any current masthead page.

(20) The structures of all compounds were confirmed by NMR (500 MHz) spectroscopy and FAB mass spectrometry. Presaturation of PEG at δ 3.640 (CH_2O signals) was carried out to ensure no dynamic range overflow. We are indebted to Dr. H. Pang, Carbohydrate Research Centre, for measuring the mass spectra with a ZAB SE mass spectrometer.

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(22) Peracetylated oligosaccharides are usually more suitable for final purification by chromatography than deprotected compounds; after deacetylation pure oligosaccharides are obtained.[21]

Reactivity of a Binuclear Ruthenium(0) Complex with an Electron-Poor Alkyne. An Unusual Double Insertion of Carbon Monoxide

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Received February 19, 1991

Many examples of metal-catalyzed double-carbonylation reactions (eq 1) have been reported.[1] Mechanistic studies of the

$$RX + 2CO + NuH \rightarrow RC(O)C(O)Nu + HX \quad (1)$$

$$(NuH = R'NH_2, R'OH, H_2O)$$

most common palladium-catalyzed system have shown that the critical C–C bond forming step occurs via reductive elimination from a bis(acyl) complex.[2-8] Except for alkyls of lutetium[9] and thorium,[10] the alternative C–C coupling pathway involving the consecutive insertion of two carbon monoxides into a metal–carbon bond has not been observed. Only one example of a migratory insertion of CO into a d-block metal–acyl bond has been reported.[11] In this paper we describe a facile, high-yield reaction between a metal carbonyl and an alkyne that results in the net double insertion of CO into a putative metal–alkyne bond.

As shown in Scheme I, the reaction of $Ru_2(dmpm)_2(CO)_5$ (**1**)[12] with dimethyl acetylenedicarboxylate (DMAD) resulted in the formation of three isolable products. In concentrated solutions of toluene (15–20 mmol/L), at room temperature, a red product was formed and crystallized from solution 10–15 min after mixing (isolated yield = 81%). The analytical and mass spectral data established the molecular formula as $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Me)_2]_2$ (**2**).[13] Spectroscopic data alone did not allow assignment of the structure, which was established via single-crystal X-ray crystallography.[14]

The $Ru_2(dmpm)_2$ framework is nearly planar, exhibiting a twist angle (defined as the angle between planes Ru1–P12–P11–Ru2 and Ru2–P21–P22–Ru1) of 4.16°. This portion of the structure is similar to related bis(diphosphine) diruthenium compounds with the exception of the long Ru1–Ru2 distance of 3.153 (1) Å.[15-20] The surprising feature in the structure of **2** was a five-membered metallocyclic ring that appears to have resulted from the double insertion of two CO ligands into a metal–alkyne bond. This ring was found to be distinctly nonplanar, exhibiting a dihedral angle of 18° between the planes comprising Ru2–C20–C16 and C16–C13–C19–C20. Identification of C19, C20, O5, and O6 as carbons and oxygens was based on their temperature factors, bond distances, and knowledge of the overall formula of **2**. The bond distances within the α-ketoacyl portion of **2** are similar to those in the previously characterized examples of this type of ligand.[6,11,21,22] The second alkyne bridges the two Ru atoms and is bound as a cis-dimetalated alkene. Consistent with the infrared spectral data, the structure contains a semibridging carbonyl ligand. The long Ru–Ru distance suggests that there is no direct metal–metal bond, and we propose that both metals exist in the 2+ oxidation state. This implies that Ru1 would be a 16-electron

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(13) Spectroscopic data for **2**: IR (cm^{-1}, CH_2Cl_2) 2042 (s), 1986 (s), 1835 (m), 1693 (m, br), 1642 (m), 1501 (w), 1427 (w); ^1H NMR (ppm, CD_2Cl_2) 1.22 (t, J_{HP} = 3.5 Hz, 6 H, Me), 1.38 (t, J_{HP} = 3.3 Hz, 6 H, Me), 1.66 (t, J_{HP} = 3.5 Hz, 6 H, Me), 1.78 (t, J_{HP} = 3.1 Hz, 6 H, Me), 1.87 (m, 2 H, CH_2), 2.85 (m, 2 H, CH_2), 3.63 (s, 3 H, OMe), 3.71 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 3.78 (s, 3 H, OMe); ^{13}C NMR (ppm, $CDCl_3$) 15.4 (t, J_{CP} = 15 Hz, 2 Me), 17.4 (m, 4 Me), 20.0 (t, J_{CP} = 15 Hz, 2 Me), 34.7 (t, J_{CP} = 12 Hz, CH_2), 50.95 (s, OCH_3), 51.38 (s, OCH_3), 51.43 (s, OCH_3), 51.63 (s, OCH_3), 127.5 (m), 135.6 (s), 151.3 (m), 163.7 (s), 172.1 (s), 178.27 (s), 178.34 (s), 189.5 (t, J_{CP} = 8.3 Hz), 196.2 (t, J_{CP} = 12 Hz), 198.8 (s), 218.7 (m), 222 (t, J_{CP} = 8.2), 254.6 (t, J_{CP} = 11 Hz); ^{31}P NMR (ppm, $CDCl_3$, relative to H_3PO_4) 0.44 (t, J_{PP} = 16 Hz), −2.98 (t, J_{PP} = 16 Hz).

(14) X-ray diffraction data for **2**: FW 898.64; ρ_{calcd} = 1.671 g cm^{-1}; crystal system = orthorhombic; space group = $P2_12_12_1$ (No. 19); T = −101 °C; a = 13.932 (5) Å; b = 14.360 (3) Å; c = 17.854 (3) Å; V = 3572 (3) $Å^3$; Z = 4; μ = 10.62 cm^{-1} (empirical correction applied); radiation = Mo Kα; scan range = $0 < 2\theta < 49.9°$; unique reflections collected = 6299; reflections used ($I > 2.0\sigma(I)$) = 5179; R = 0.050; R_w = 0.055. Thermal ellipsoids in Scheme I were drawn at the 50% probability level. Selected distances (Å): Ru1–C23, 2.115 (9); Ru1–C22, 2.510 (8); Ru2–C22, 1.907 (8); Ru2–C26, 2.138 (8); Ru2–C20, 2.097 (8); Ru2–C16, 2.153 (8); C23–C26, 1.33 (1); C20–C19, 1.57 (1); C20–O6, 1.197 (9); C19–C13, 1.44 (1); C19–O5, 1.21 (1); C13–C16, 1.35 (1).

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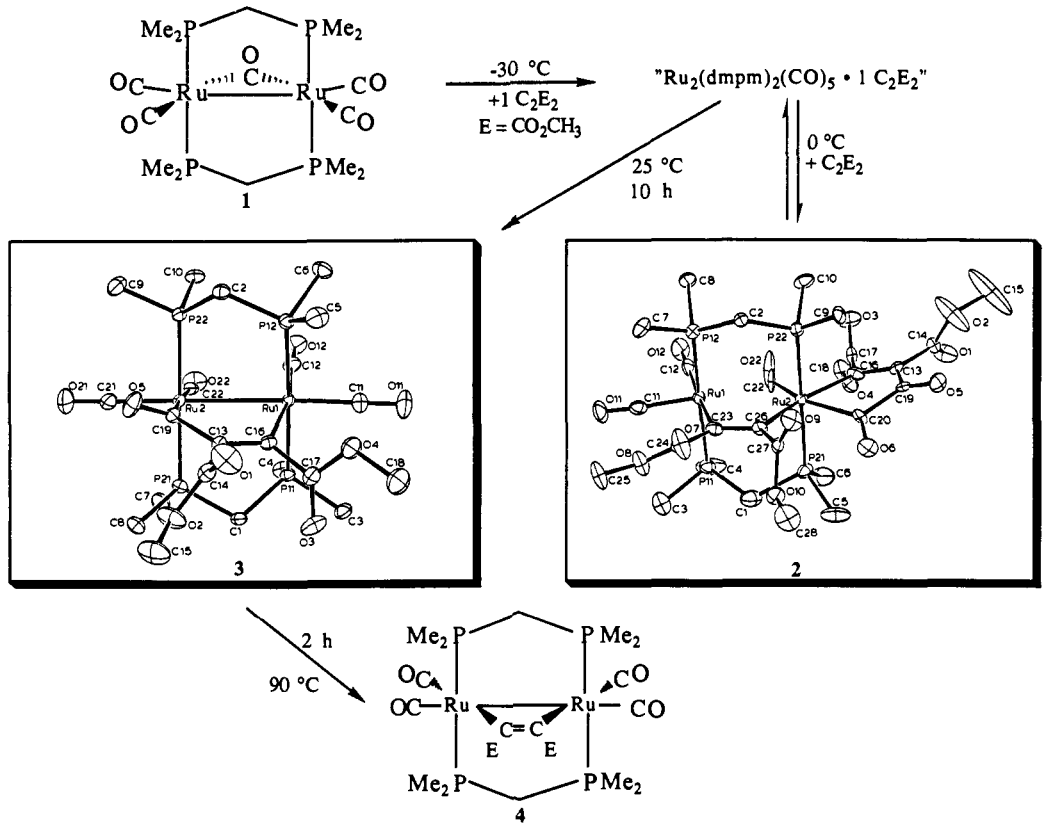
Scheme I

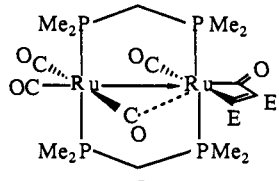


center with a formal charge of 1+, while Ru2 would be considered an 18-electron center having a formal charge of 1−. The semi-bridging carbonyl would serve to shift some electron density from the electron-rich Ru2 to the unsaturated Ru1.

Stirring a solution (CH_2Cl_2) of **2** at room temperature for 10–12 h resulted in quantitative loss of 1 equiv of DMAD and formation of a new orange compound, **3**. The mass spectrum and elemental analysis established the formula of **3** as $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Me)_2]$.[23] Solution spectroscopic data were consistent with the single-crystal X-ray crystallographic study establishing the structure as a diruthenacyclopentenone.[24] Two previous examples of this structural feature have been reported.[25,26] High yields (78%) of **3** result from the direct reaction between **1** and DMAD in toluene upon lowering the concentrations to 4 mmol/L and stirring for 8–12 h.

Deinsertion and loss of carbon monoxide occurs quantitatively upon heating a toluene solution of **3** to 90 °C for 2 h to yield the previously characterized yellow compound $Ru_2(dmpm)_2(CO)_4[C_2(CO_2Me)_2]$ (**4**).[12] The direct reaction of **1** with DMAD in toluene at 70 °C produces **4** in 84% yield. Attempted carbonylation of **4** into **3** at high CO pressure (75 atm) was unsuccessful.

^1H and ^{31}P NMR spectroscopy of a yellow solution (C_6D_6) containing 1 equiv of DMAD and 1 equiv of **1** established that an intermediate complex having this ratio of reagents precedes the formation of **2** at −30 °C.[27] While the structure of the intermediate could not be determined uniquely, these data establish that both ends of the alkyne are different, as are the two metals. The only symmetry element retained in the intermediate is the equatorial mirror plane. A possible structure, **5**, would be isomeric with **3** and consistent with, but not uniquely defined by, all available spectroscopic data. We propose that, in the presence



5

of a second equivalent of DMAD, **5** is trapped, giving compound **2**, which can be isolated in high yield because of its limited solubility in toluene. The observation that **2** converts to **3** suggests that the second DMAD addition is reversible. Upon standing at room temperature, the intermediate prepared from the solution that contained a 1:1 ratio of **1**:DMAD slowly converted to **3**.

The initial reaction between **1** and DMAD occurs at an unusually low temperature for the reaction of a saturated metal carbonyl with an alkyne, and it contrasts sharply with the higher temperature required (95 °C) to induce the reaction between **1** and diphenylacetylene to give $Ru_2(dmpm)_2(CO)_4(\mu\text{-}\eta^1\text{:}\eta^1\text{-PhCCPh})$. That this facile chemistry requires a strongly electron deficient alkyne suggests that the pathway may involve an initial

(23) Spectroscopic data for **3**: IR (cm^{-1}, CH_2Cl_2) 1996 (m), 1968 (s), 1937 (m), 1912 (w), 1707 (w), 1674 (w), 1531 (w), 1431 (w); ^1H NMR (ppm, CD_2Cl_2) 1.12 (t, J_{HP} = 2.7 Hz, 6 H, Me), 1.2 (t, J_{HP} = 2.6 Hz, 6 H, Me), 1.46 (t, J_{HP} = 2.8 Hz, 6 H, Me), 1.57 (t, J_{HP} = 2.8 Hz, 6 H, Me), 1.86 (m, 2 H, CH_2), 3.2 (m, 2 H, CH_2), 3.5 (s, 3 H, OMe), 3.63 (s, 3 H, OMe); ^{13}C NMR (ppm, $CDCl_3$) 19.0 (m, 4 Me), 21.5 (m, 4 Me), 46.6 (m, CH_2), 50.3 (s, OCH_3), 51.1 (s, OCH_3), 162.5 (s), 166.9 (s), 178.6 (t, J_{CP} = 14 Hz), 181.4 (s), 192 (m, 2 C), 208.1 (m), 209.2 (m), 262.6 (m); ^{31}P NMR (ppm, $CDCl_3$, relative to H_3PO_4) aa'bb' pattern, δ_a = −0.90, δ_b = −2.26.

(24) X-ray diffraction data for **3**: FW 756.53; ρ_{calcd} = 1.695 g cm^{-1}; crystal system = monoclinic; space group = $P2_1/n$ (No. 14); T = −101 °C; a = 10.845 (5) Å; b = 27.82 (1) Å; c = 10.447 (5) Å; β = 109.90 (4)°; V = 2964 (5) Å^3; Z = 4; μ = 12.55 cm^{-1} (empirical correction applied); radiation = Mo Kα; scan range = 0° < 2θ < 56.0°; unique reflections collected = 7311; reflections used ($I > 2.0\sigma(I)$) = 5816; R = 0.033; R_w = 0.040. Thermal ellipsoids in Scheme I were drawn at the 50% probability level. Selected distances (Å): Ru1–Ru2, 2.936 (1); Ru1–C16, 2.156 (3); Ru2–C19, 2.132 (3); C13–C19, 1.496 (4); C13–C16, 1.340 (4); C19–O5, 1.235 (4).

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(27) Spectroscopic data for **5**: IR (cm^{-1}, toluene) 2033 (s), 1979 (s), 1933 (m), 1823 (w), 1700 (m), 1649 (w); ^1H NMR (ppm, C_6D_6) 0.905 (t, J_{HP} = 2.8 Hz, 6 H, Me), 1.085 (t, J_{HP} = 3.0 Hz, 6 H, Me), 1.186 (t, J_{HP} = 2.5 Hz, 6 H, Me), 1.421 (t, J_{HP} = 3.3 Hz, 6 H, Me), 1.8 (m, 4 H, CH_2), 3.540 (s, 3 H, OMe), 3.863 (s, 3 H, OMe); ^{31}P NMR (ppm, C_6D_6, relative to H_3PO_4) aa'bb' pattern, δ_a = 7.7, δ_b = 4.2.

electron-transfer step. A similar mechanistic proposal has been made regarding the reaction of **1** with dimethyl fumarate and dimethyl maleate.[28] Further work is focusing on the mechanism of the double carbonylation and on developing methods of removing these ligands from the metal centers.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-8714326). We are grateful to Doyle Britton and Christine Blaine for the X-ray crystallographic data.

Supplementary Material Available: Tables of atom positions, temperature factors, and bond distances and angles for **2** and **3** (25 pages). Ordering information is given on any current masthead page.

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DNA Cleavage by Oxygen Radicals Produced in the Absence of Metal Ions or Light

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Received January 16, 1991

The availability of molecules that mediate DNA strand scission has facilitated the implementation of strategies for DNA sequencing,[1] as well as studies of DNA conformation[2] and the way in which small molecules bind to DNA.[3] In addition to the exploration of novel mechanistic strategies for DNA cleavage,[4] new DNA cleaving agents are of substantial practical interest as potential antitumor agents[5] and as prosthetic groups for antisense oligonucleotides[6] that can destroy a bound target sequence in a site-selective fashion.[7] The latter two applications, however, require that DNA cleavage obtain efficiently under conditions compatible with physiological function, using only those cofactors normally present within a cell. Relatively few molecules meet this requirement; most of these are natural products[5,8] rather than designed reagents.

There are a number of examples of highly efficient DNA strand scission by reagents that effect the (metal-centered) generation of diffusible oxygen radicals,[2,3,9] but these typically require either a strong oxidant or high concentrations of a reducing agent for oxygen radical generation. Presently, we describe the preparation of a phenazine di-*N*-oxide derivative designed to produce diffusible oxygen radicals, and concomitant DNA strand scission, under physiological conditions.

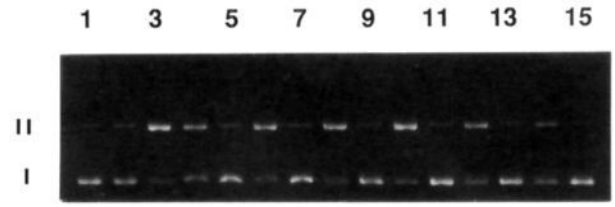


Figure 1. Cleavage of supercoiled ccc DNA by phenazine di-*N*-oxide **1** under aerobic conditions. A reaction mixture (40 μL total volume) containing 200 ng of replicative form *φX174* DNA in 2.5 mM sodium cacodylate, pH 7.5, was treated with compound **1** + 100 μM DTT at 37 °C for 1 h and then analyzed by agarose gel electrophoresis. Lane 1: DNA alone. Lane 2: 100 μM DTT. Lane 3: 10 μM Fe^{2+} + 0.03% H_2O_2. Lanes 4–15: DNA + **1** at 500 μM (lanes 4 and 5), 250 μM (lanes 6 and 7), 100 μM (lanes 8 and 9), 50 μM (lanes 10 and 11), 25 μM (lanes 12 and 13), and 10 μM (lanes 14 and 15) concentrations in the presence (even-numbered lanes) or absence (odd-numbered lanes) of 100 μM DTT.

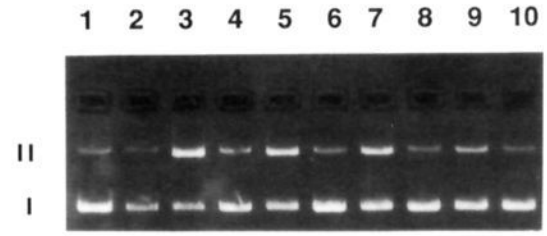
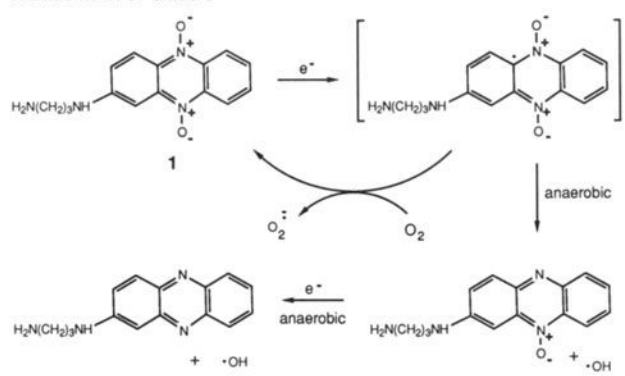


Figure 2. Cleavage of supercoiled DNA by **1** under anaerobic conditions in the presence of DTT and NADPH. Cleavage was carried out at 25 °C for 2 h. Lane 1: DNA alone. Lane 2: 1 mM DTT. Lane 3: 1 mM DTT + 50 μM **1**. Lane 4: 100 μM DTT. Lane 5: 100 μM DTT + 50 μM **1**. Lane 6: 1 mM NADPH. Lane 7: 1 mM NADPH + 50 μM **1**. Lane 8: 100 μM NADPH. Lane 9: 100 μM NADPH + 50 μM **1**. Lane 10: 50 μM **1**.

Scheme I. Proposed Mechanism for the Reductive Activation of Phenazine di-*N*-oxide **1**



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