

Journal of Organometallic Chemistry, 383 (1990) C1–C6
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20363

Preliminary communication

Reactions of sodium pentacarbonylrhenate(1 –) with activated acetylenes. Formation of rhenacyclobutenone complexes

Laura L. Padolik, Judith Gallucci, and Andrew Wojcicki *

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received June 26th, 1989)

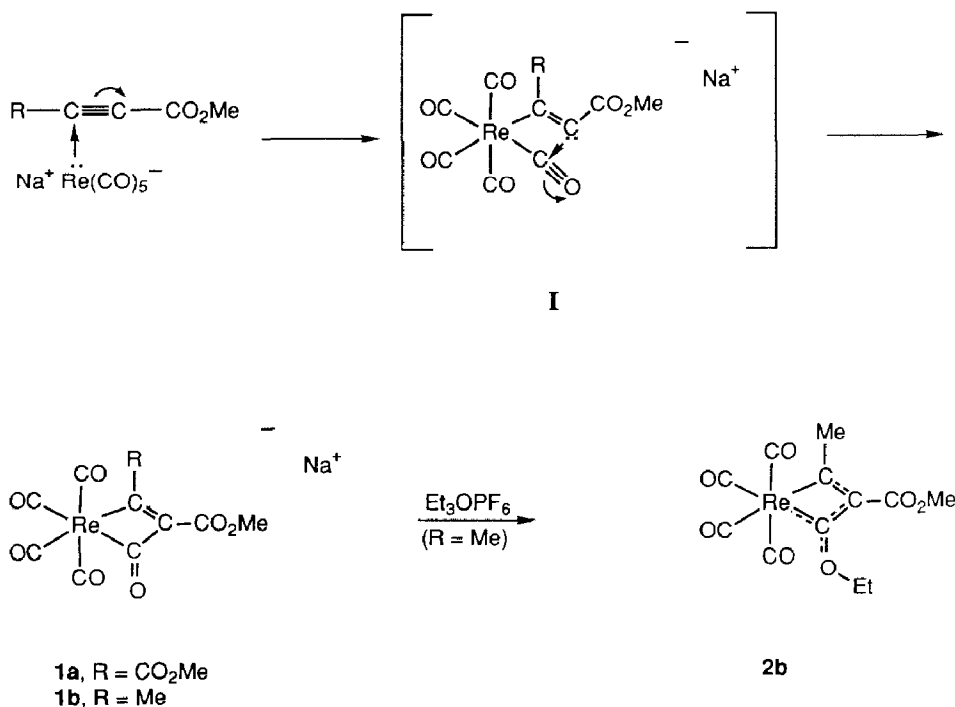
Abstract

The complexes $\text{Na}[(\text{CO})_4\overline{\text{ReC(R)=C(CO}_2\text{Me)C(O)}}]$ (**1a**, R = CO₂Me; **1b**, R = Me) are formed in the reaction of Na[Re(CO)₅] with RC≡CCO₂Me at room temperature. The structure of **1a** has been shown by X-ray diffraction to contain a rhenacyclobutenone ring. Complex **1b** is alkylated by Et₃OPF₆ at the ketonic oxygen, as determined crystallographically.

Recently we have reported [1] the preparation of substituted derivatives of Na[Mn(CO)₅] by its photochemical reactions with the activated olefins RO₂CCH=CHCO₂R. When we sought to extend this work to activated acetylenes, we discovered to our surprise that Na[Mn(CO)₅] rapidly reacts at room temperature with MeO₂CC≡CCO₂Me (DMAD). Unfortunately, the product proved insufficiently stable for full characterization. In an effort to obtain a more stable analogue, we turned to the corresponding reaction of Na[Re(CO)₅]. Reported here are our preliminary results on this and related reactions as well as the alkylation of the product with Et₃OPF₆.

Treatment of a THF solution of Re₂(CO)₁₀ with Na sand under argon affords an orange solution of Na[Re(CO)₅] *. Addition of DMAD (1 equiv.) with stirring at room temperature causes an immediate darkening of the solution. The product (**1a**, Scheme 1) was isolated after a few minutes as a brown solid by removal of the solvent in vacuo and was washed with pentane. It can be recrystallized by slow diffusion of hexane into a solution of **1a** in 5/1 diethyl ether/THF to give an orange, air-stable solid in 60% isolated yield. Crystals suitable for an X-ray diffraction study were also obtained in this manner.

* This solution contains a small amount of a polynuclear rhenium carbonyl species which is difficult to remove; however, its presence does not interfere with subsequent reactions.



Scheme 1.

Spectroscopic data for **1a** point to the addition of the alkyne to rhenium and a CO ligand. Accordingly, the IR spectrum in THF solution shows $\nu(\text{CO})$ bands attributed to ReCO (2059w , 1961s , 1917s cm^{-1}) as well as ligand CO_2Me and non-terminal ReC(=O) (1716w , 1698s cm^{-1}). The inequivalence of the CO_2Me groups is reflected in the appearance of two singlet resonances (δ 3.52, 3.72 ppm) of equal intensity in the ^1H NMR spectrum (acetone- d_6). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the Me signals coincidentally overlap at δ 50.9 ppm as indicated by 2D C–H correlation studies. The remainder of the spectrum is fully consistent with the structure of the anion. Thus two resonances are observed for each of the indicated carbon atoms CCO_2Me and CO_2Me at δ 159.3 and 187.0 ppm and δ 160.5 and 175.9 ppm, respectively. ReCO signals occur at δ 195.5, 196.2, and 197.4 ppm in a ratio of 1/1/2, and the signal of ReC(=O) is at δ 227.9 ppm.

The mode of addition of DMAD to Re(CO)_5^- to give a rhenacyclobutenone ring was unequivocally demonstrated by X-ray crystallography*, which also revealed

* Crystal data: $\text{C}_{26}\text{H}_{20}\text{O}_{19}\text{Na}_2\text{Re}_2$, $M = 1054.83$, triclinic, space group $P\bar{1}$, a 12.642(2), b 12.986(2), c 11.179(1) Å, α 104.81(1), β 98.00(1), γ 88.06(1)°, U 1757 Å³, $Z = 2$, D_c 1.99 g cm^{-3} , $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, μ 70.75 cm^{-1} , orange rectangular prism, $0.15 \times 0.27 \times 0.50$ mm. Rigaku AFC5S diffractometer, 8087 unique intensities to $2\theta_{\text{max}}$ 55°, ω - 2θ scans, analytical absorption correction with transmission factors 0.211–0.356, decay correction based on average 12% decrease in intensities of six standards. Full-matrix least-squares refinement based on F for 4927 reflections with $F_0^2 > 3\sigma(F_0^2)$, 445 variables, non-hydrogen atoms anisotropic, hydrogen atoms fixed in calculated positions. Final $R = 0.033$, $R_w = 0.035$, weighting scheme $w = 1/\sigma^2(F_0)$, $S = 1.17$ e. There are two Re complexes and a solvent molecule of THF in the asymmetric unit. Two Na^+ ions lie on crystallographic inversion centers and a third Na^+ ion is in a general position to give a total of four Na^+ ions in the unit cell.

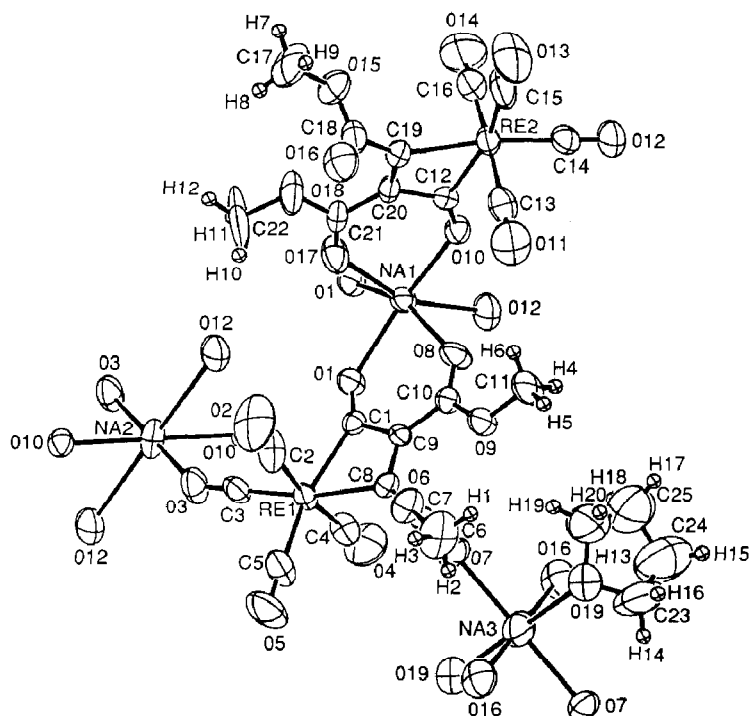


Fig. 1. ORTEP drawing of the asymmetric unit of the crystal structure of $(\mathbf{1a})_2 \cdot \text{THF}$ showing the two different rhenium carbonyl anions and the coordination geometry around the three unique Na^+ ions.

the composition of the solid as $2\text{Na}[\text{Re}(\text{CO})_5] \cdot 2\text{DMAD} \cdot \text{THF}$ ($(\mathbf{1a})_2 \cdot \text{THF}$, Fig. 1), consistent with the elemental analysis*. The crystal structure contains two kinds of rhenium carbonyl anions and three unique six-coordinate Na^+ cations. The former are rendered inequivalent by the manner in which the Na^+ ions are positioned around their periphery. One THF molecule is present for every two rhenium carbonyl anions.

In Fig. 2, a monomeric unit of $(\mathbf{1a})_2 \cdot \text{THF}$ (i.e., $\mathbf{1a}$) is drawn, with the Na^+ ions omitted for clarity. The geometry around each Re atom is a distorted octahedron. The rhenacyclobutenone ring is very nearly planar, and the average $\text{Re}-\text{C}(\text{O})$ and $\text{Re}-\text{C}(\text{CO}_2\text{Me})$ bond distances are equal (2.194 and 2.196 Å, respectively). The average $\text{C}(\text{CO}_2\text{Me})-\text{C}(\text{CO}_2\text{Me})$ length of 1.352 Å corresponds to a double bond.

To elucidate the regiochemistry of this [2 + 2] cycloaddition, we investigated the reaction of $\text{Na}[\text{Re}(\text{CO})_5]$ with methyl 2-butynoate. This reaction proceeds considerably more slowly than that involving DMAD and requires several hours at room temperature to reach completion. Work-up in a manner similar to that described for $\mathbf{1a}$ yielded an orange solid which could not be freed of a small amount of the polynuclear rhenium carbonyl impurity. Nevertheless, it was possible partially to characterize the product as $\mathbf{1b}$ (Scheme 1) by spectroscopy**. The similarity of the spectral data for $\mathbf{1a}$ and $\mathbf{1b}$ strongly implicates a rhenacyclobutenone structure for

* Found: C, 30.01; H, 1.98. $\text{C}_{26}\text{H}_{20}\text{Na}_2\text{O}_{19}\text{Re}_2$ ($(\mathbf{1a})_2 \cdot \text{THF}$) calcd.: C, 29.61; H, 1.91%.

** IR $\nu(\text{CO})$ (THF): 2045 w, 1957 s, 1906 s, 1717 m, 1675 cm^{-1} . ^1H NMR (acetone- d_6): δ 2.81 s, 3.57 s ppm (2 Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6): δ 32.5, 49.7 (Me), 160.8 (CO_2), 163.0 (MeC=C), 197.5, 197.7, 200.0 (C=O), 214.1 (C=C CO_2Me), 224.6 ppm (C=O).

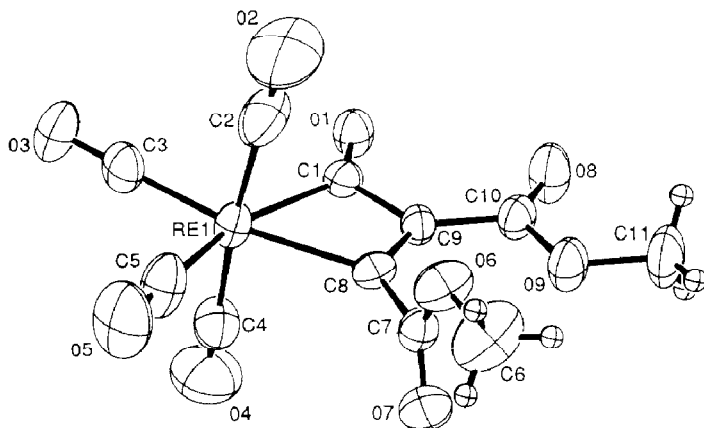


Fig. 2. ORTEP drawing of monomeric fragment **1a** with the Na^+ ions removed for clarity. Selected bond distances: $\text{Re}(1)\text{-C}(1)$ 2.193(7), $\text{Re}(1)\text{-C}(8)$ 2.200(6), $\text{C}(1)\text{-C}(9)$ 1.491(9), $\text{C}(8)\text{-C}(9)$ 1.342(9), $\text{C}(1)\text{-O}(1)$ 1.222(8) Å. Selected bond angles: $\text{C}(1)\text{-Re}(1)\text{-C}(8)$ 61.1(2), $\text{Re}(1)\text{-C}(8)\text{-C}(9)$ 99.6(4), $\text{C}(1)\text{-C}(9)\text{-C}(8)$ 104.0(5), $\text{Re}(1)\text{-C}(1)\text{-C}(9)$ 95.2(4)°.

1b as well, but does not resolve the question of regiochemistry for the addition of methyl butyrate to $\text{Re}\text{-CO}$.

Complex **1b** rapidly reacts at room temperature with Et_3OPF_6 in CH_2Cl_2 solution to afford a yellow solid (40% yield) after removal of the solvent, extraction of the residue with hexane, and evaporation to dryness. The solid gives satisfactory elemental analysis for **2b** (Scheme 1) *. Its spectroscopic data ** are in accord with this structure and suggest that ethylation occurred at the ketonic oxygen. However, again, the regiochemistry of the cycloaddition between $\text{Na}[\text{Re}(\text{CO})_5]$ and $\text{MeC}\equiv\text{CCO}_2\text{Me}$ cannot be inferred from these data.

The molecular structure of **2b** was elucidated by X-ray crystallography *** and is shown in Fig. 3. As suggested by the spectral data, ethylation took place at the rhenacyclobutenone oxygen, and the four-membered ring retained its planarity. The bond $\text{Re}\text{-C}(5)$ (2.13(1) Å) is shorter than $\text{Re}\text{-C}(7)$ (2.18(1) Å), and $\text{C}(5)\text{-C}(6)$, $\text{C}(6)\text{-C}(7)$, and $\text{C}(5)\text{-O}(5)$ measure 1.45(2), 1.36(2), and 1.30(1) Å, respectively, all indicative of π bonding. These data, along with the downfield ^{13}C chemical shift of COEt , reflect electron delocalization over the $\text{Re}\text{-C}(5)\text{-O}(5)\text{-C}(6)\text{-C}(7)$ fragment

* Found: C, 31.63; H, 2.23. $\text{C}_{12}\text{H}_{11}\text{O}_7\text{Re}$ (**2b**) calcd.: C, 31.79; H, 2.44%.

** IR $\nu(\text{CO})$ (THF): 2082 m, 1991 vs., 1937 s, 1704 m cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 1.59 t (J 7.18 Hz), 3.03 s, 3.07 s (3 Me), 4.70 q (J 7.18 Hz) ppm (CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6): δ 15.0 (Me), 35.2 (CH_2), 50.6, 81.6 (Me), 156.9 (CO_2), 159.4 ($\text{MeC}=\text{C}$), 191.2, 193.0, 194.5 ($\text{C}=\text{O}$), 243.7 ($\text{C}=\text{C}\text{CO}_2\text{Me}$), 246.4 ppm ($\text{C}=\text{O}$).

*** Crystals were obtained by slow evaporation of a pentane solution of **2b**. Crystal data: $\text{C}_{12}\text{H}_{11}\text{O}_7\text{Re}$, $M = 453.42$, monoclinic, space group $P2_1/c$, a 7.265(2), b 27.695(2), c 7.378(3) Å, β 95.86(3)°, U 1477 Å³, $Z = 4$, D_c 2.04 g cm^{-3} , $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, μ 83.64 cm^{-1} , yellow rectangular plate, 0.04 \times 0.19 \times 0.35 mm. Rigaku AFC5S diffractometer, 3486 unique intensities to $2\theta_{\text{max}}$ 55°, ω scans, decay correction applied to account for average percentage decrease in standard intensities of 48%. ψ scan absorption correction with transmission factors 0.464 to 1.000. Full-matrix least-squares refinement based on F for 1574 reflections with $F_0^2 > 3\sigma(F_0^2)$, 181 variables, non-hydrogen atoms anisotropic, hydrogen atoms fixed in calculated positions. Final $R = 0.041$, $R_w = 0.041$, weighting scheme $w = 1/\sigma^2(F_0)$, $S = 1.20$ e.

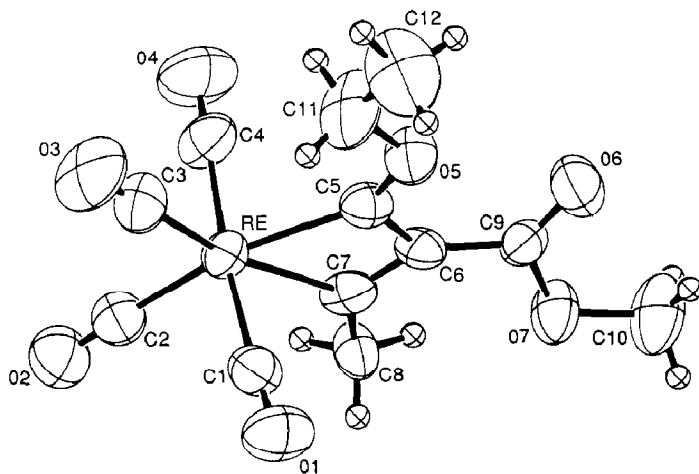


Fig. 3. ORTEP drawing of **2b**. Selected bond lengths: Re–C(5) 2.13(1), Re–C(7) 2.18(1), C(5)–C(6) 1.45(2), C(6)–C(7) 1.36(2), O(5)–C(5) 1.30(1), O(5)–C(11) 1.46(1) Å. Selected bond angles: C(5)–Re–C(7) 59.8(5), Re–C(5)–C(6) 99.8(8), Re–C(7)–C(6) 100.5(8), C(5)–O(5)–C(11) 116(1), Re–C(5)–O(5) 141(1)°.

of the molecule (Scheme 1). The regiochemistry of the formation of **1b** is established as involving the addition of CMe to Re and CCO₂Me to a CO.

Unlike the reactions of Na[Mn(CO)₅] with activated olefins which require photochemical conditions, reactions of Na[Re(CO)₅] with activated acetylenes proceed under ambient thermal conditions to afford the first examples of anionic metallacyclobutenone complexes. The proposed mechanism for their formation is depicted in Scheme 1. The first step involves nucleophilic attack of Re(CO)₅[−] at the positive alkyne carbon atom to generate the intermediate I. The negatively charged adjacent carbon atom then attacks a *cis*-CO to form the metallacycle. When the alkyne carries two different substituents, nucleophilic attack occurs at the less positive carbon atom, thereby placing the developing negative charge on the carbon bearing the ester group where it receives better stabilization.

Although anionic metallacyclobutenone complexes had not been previously synthesized, examples of related neutral compounds have been reported. Green [2] prepared the first metallacyclobutenone complex (CO)₂[P(OMe)₃]₂RuC(CF₃)=C(CF₃)C(O), which is formed in the photochemical reaction of Ru(CO)₃[P(OMe)₃]₂ with hexafluoro-2-butyne. Since then, several dinuclear metallacyclobutenone complexes have appeared in the literature [3].

The nucleophilicity of Na[Re(CO)₅] toward other unsaturated organic compounds has been observed; in two cases, metallacyclic products were obtained. King and Hodges [4] reported the reaction of Na[Re(CO)₅] with α -chloroenamines, Me₂C=C(NR₂)Cl, to give (CO)₄ReC(NR₂)C(Me)₂C(O). Ketenimines undergo cycloaddition reaction with Na[Re(CO)₅] to afford four-membered metallacycles, Na[(CO)₄ReC(=CPh₂)N(R)C(O)] [5]. These rhenacycles add electrophilic reagents at the ketonic oxygen with the formation of neutral complexes, similarly to **1b**.

Studies in progress are concerned with reactions of other metal carbonyl anions with activated acetylenes and with the chemistry of resultant metallacyclobutenone products.

Acknowledgements. We gratefully acknowledge financial support of the National Science Foundation (Grant CHE-8420806). Discussions with Dr. Ferenc Ungváry in the early stages of this research proved to be most helpful and are much appreciated. We also acknowledge Mr. Andrew Kuzmission's assistance with the solution and refinement of the two structures. Finally, we thank Professors M.D. Rausch and R.B. King for their invitation to write this article for the Mond Centennial Volume of the Journal of Organometallic Chemistry.

References

- 1 L.L. Padolik and A. Wojcicki, Abstr., 21st Central Regional Meeting Am. Chem. Soc., Cleveland, OH, June 1-2, 1989, No. 248.
- 2 R. Burt, M. Cooke and M. Green, *J. Chem. Soc. (A)*, (1970) 2981.
- 3 (a) N.M. Boag, R.J. Goodfellow, M. Green, B. Hessner, J.A.K. Howard and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1983) 2585; (b) S.R. Finimore, S.A.R. Knox and G.E. Taylor, *ibid.*, (1982) 1783; (c) R.S. Dickson, G.S. Evans and G.D. Fallon, *J. Organomet. Chem.* 236 (1982) C49; (d) M.J. Chetcuti and K.A. Green, *Organometallics*, 7 (1988) 2450.
- 4 R.B. King and K.C. Hodges, *J. Am. Chem. Soc.*, 97 (1975) 2702.
- 5 W.P. Fehlhammer, P. Hirschmann and A. Völkl, *J. Organomet. Chem.*, 294 (1985) 251.