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Chemistry of Fischer-type rhenacyclobutadiene complexes. II. Reactions with alkynes and sulfonium ylides, and rearrangements induced by nitriles and pyridine

Véronique Plantevin [1], Andrew Wojcicki *

Department of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, OH 43210-1185, USA

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Abstract

Further investigations into the chemistry of the rhenacyclobutadiene complexes $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(X))$ (**1**: R = Me, X = OEt (**1a**), $O(CH_2)_3C{\equiv}CH$ (**1b**), NEt_2 (**1c**); R = $CHEt_2$, X = OEt (**1d**); R = Ph, X = OEt (**1e**)) are reported. Reactions of **1** with alkynes at reflux temperature of toluene and at ambient temperature either under photochemical conditions or in the presence of PdO yield ring-substituted η^5-cyclopentadienylrhenium tricarbonyl complexes, **2**. The symmetrical alkynes $R'C{\equiv}CR'$ (R' = Ph, Me, CO_2Me) afford the pentasubstituted complexes $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Ph)(Ph))Re(CO)_3$ (**2d**), $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Me)(Me))Re(CO)_3$ (**2e**), $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(CO_2Me)(CO_2Me))Re(CO)_3$ (**2f**), and $(\eta^5\text{-}C_5(Me)(CO_2Me)(NEt_2)(CO_2Me)(CO_2Me))Re(CO)_3$ (**2i**) on reaction with the appropriate **1**, whereas the unsymmetrical alkynes $R'C{\equiv}CR''$ (R' = Ph; R'' = H, Me) give either only one, $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Ph)H)Re(CO)_3$ (**2a**)), or both, $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Ph)(Me))Re(CO)_3$ (**2b**) and $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Me)(Ph))Re(CO)_3$ (**2c**), $(\eta^5\text{-}C_5(Ph)(CO_2Me)(OEt)(Ph)H)Re(CO)_3$ (**2g**) and $(\eta^5\text{-}C_5(Ph)(CO_2Me)(OEt)(H)(Ph))Re(CO)_3$ (**2h**), of the possible products of [3 + 2] cycloaddition of alkyne to $\eta^2\text{-}C(R)C(CO_2Me)C(X)$. Thermolysis of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(O(CH_2)_3C{\equiv}CH))$ (**1b**) containing a pendant alkynyl group proceeds to $(\eta^5\text{-}C_5(Me)(CO_2Me)(O(CH_2)_3)H)Re(CO)_3$ (**2j**), a η^5-cyclopentadienyl-dihydropyran fused-ring product. Competition experiments showed that each of PhC≡CH and $MeO_2CC{\equiv}CCO_2Me$ reacts faster than PhC≡CPh with **1a**. The results with unsymmetrical alkynes are rationalized by steric properties of substituents at the C≡C and Re=C bonds and by a preference of Re=C(Me) over Re=C(OEt) to undergo alkyne insertion. A mechanism is proposed that involves substitution of a *trans* CO by alkyne in **1**, insertion of alkyne into Re=C bond to give a rhenabenzene intermediate, and collapse of the latter to **2**. Complexes **1a** and **1d** undergo rearrangement in MeCN at reflux temperature to give rhenafuran-like products, $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(CH{=}CR_2)C(OEt))$ (R = H (**3a**) or Et (**3b**)). The reaction of **1d** also proceeds in EtCN, PhCN, and *t*-BuCN at comparable temperature, but is slower (especially in *t*-BuCN) than in MeCN. In pyridine at reflux temperature, **1a** undergoes a similar rearrangement, with CO substitution, to give $(CO)_3(py)Re(\kappa^2\text{-}OC(OMe)C(CH{=}CEt_2)C(OEt))$ (**4**). A mechanism is proposed for these reactions. The sulfonium ylides $Me_2S{=}CHC(O)Ph$ and $Me_2S{=}C(CN)_2$ ($Me_2S{=}CRR'$) react with **1a** in acetonitrile at reflux temperature by nucleophilic addition of the ylide to the Re=C(Me) carbon, loss of Me_2S, and rearrangement to a rhenafuran-type structure to yield $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}CRR')C(OEt))$ (R = H, R' = C(O)Ph (**5a**); R = R'=CN (**5b**)). All new compounds were characterized by a combination of elemental analysis, mass spectrometry, and IR and NMR spectroscopy.

Keywords: Rhenium complexes; Metallacyclobutadiene complexes; Fischer carbene complexes; Cyclopentadienyl complexes; Rearrangement reactions; Nucleophilic addition

1. Introduction

In the accompanying paper we reported a general synthetic method for Fischer rhenacyclobutadiene complexes of the type $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(OR'))$ (**1**). Also presented were a number of reactions of

* Corresponding author. Tel.: +1-614-292-4750; fax: +1-614-292-1685.
E-mail address: wojcicki@chemistry.ohio-state.edu (A. Wojcicki).
[1] Celgene, Signal Research Division, 4550 Towne Centre Court, San Diego, CA 92121, USA.

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1, viz., deprotonation followed by alkylation at R (R = alkyl), aminolysis at *C*(OR′), nucleophilic addition (at *C*(R)) and substitution (at Re) by tertiary phosphine, and insertion of oxygen atom and the isoelectronic NH fragment into the Re=C bonds [1]. This paper focuses on additional chemistry of **1** and derivatives, including reactions with alkynes to yield tetra- and pentasubstituted η^5-cyclopentadienylrhenium complexes ($Cp^{\ddagger}Re(CO)_3$ (**2**)) and with sulfonium ylides to give nucleophilic addition at *C*(R) followed by rearrangement, as well as rearrangements induced by nitriles and pyridine.

2. Experimental

2.1. General procedures and measurements

All general procedures were the same as those described in the immediately preceding paper [1]. IR and NMR spectra were obtained as reported earlier [2,3]. Mass spectra were recorded on a Kratos VG70-250S spectrometer by using either electron impact (EI) or fast atom bombardment (FAB) techniques. All listed mass peaks are those of ions containing ^{187}Re. Photochemical experiments were conducted on ca. 10^{-4} M solutions with 300-nm lamps in a Rayonet reactor.

2.2. Materials

Reagents were obtained from various commercial sources and used as received except as indicated below. The sulfonium ylides $Me_2S{=}CHC(O)Ph$ and $Me_2S{=}C(CN)_2$ were prepared by reported procedures [4,5]. The rhenacyclobutadienes $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(X))$ (R = Me, X = OEt (**1a**), $O(CH_2)_3C{\equiv}CH$ (**1b**), NEt_2 (**1c**); R = $CHEt_2$, X = OEt (**1d**); R = Ph, X = OEt (**1e**)) were synthesized as described in the accompanying paper [1].

2.3. Reactions of $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(X))$ (*1*) with alkynes

2.3.1. Synthesis of $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Ph)H)Re(CO)_3$ (*2a*) from $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (*1a*) and PhC≡CH

To a solution of **1a** (0.244 g, 0.538 mmol) in 20 ml of toluene was added ca. 1 equivalent of PhC≡CH (0.059 ml, 0.055 g), and the mixture was heated at reflux temperature. After 4 h the solvent was removed under reduced pressure, and the brown residue was extracted with 10-ml portions of hexane. The extracts were filtered, and the filtrate was concentrated to a brown oil under reduced pressure. The oil partially solidified upon storage at room temperature overnight. Further purification was achieved by dissolution in hexane and filtration through a plug of grade III deactivated alumina using first hexane and then hexane/CH_2Cl_2 as the eluent. Yields of (η^5-C_5(Me)(CO_2Me)(OEt)(Ph)H)Re$(CO)_3$ (**2a**) were typically higher than 0.26 g (ca. 90%). IR (hexane): *ν*(CO) 2025 (m), 1945 (s), 1729 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.7–7.1 (m, 5H, Ph), 5.29 (s, 1H, CH), 3.87 (s, 3H, CO_2Me), 3.80 (m, 2H, CH_2Me), 2.49 (s, 3H, CMe), 1.25 (t, ^3J = 7.0 Hz, 3H, OCH_2Me). ^{13}C NMR ($CDCl_3$): δ 192.5 (s, CO), 165.3 (s, CO_2Me), 137.5 (s, *C*OEt), 130.8 (s, C of Cp), 128.9, 128.6, 128.4, 127.8 (s, 3d, C of Ph), 101.6, 95.3, 79.2 (2s, d, C of Cp), 74.9 (t, OCH_2Me), 51.9 (q, CO_2Me), 15.3 (q, C*Me*), 14.8 (q, OCH_2Me). MS (FAB): *m*/*z* 528 (M^+). Anal. Found: C, 43.42; H, 3.12%. Calc. for $C_{19}H_{17}O_6Re$: C, 43.26; H, 3.25%.

Alternatively, **2a** was prepared from **1a** (0.300 g, 0.662 mmol) and PhC≡CH (0.075 ml, 0.068 g) in 1.5 ml of toluene in a sealed tube heated at 120 °C overnight. Workup was similar to that detailed above. Yield: 0.315 g (90%).

Complex **2a** was also synthesized at ambient temperature from **1a** (0.162 g, 0.357 mmol) and PhC≡CH (0.040 ml, 0.037 mmol, 1 equivalent) in MeCN (7 ml) in the presence of PdO (0.044 g). The resulting yellow solution with suspended black particles of PdO turned green within 1 h of stirring. Completion of the reaction required 2 days. The solvent was then evaporated and the residue was extracted with 20 ml of hexane. The rest of the workup paralleled that for the thermal reaction. Product **2a** was isolated as an oil that did not readily crystallize. Typical yields were ca. 90%.

2.3.2. Synthesis of $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Ph)(Me))Re(CO)_3$ (*2b*) and $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Me)(Ph))Re(CO)_3$ (*2c*) from $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (*1a*) and PhC≡CMe

A solution of **1a** (0.060 g, 0.13 mmol) in 5 ml of toluene was treated with 1 equivalent of PhC≡CMe (0.017 ml, 0.015 g), and the mixture was heated at reflux temperature for 5 h. The workup was similar to that described in Section 2.3.1. Chromatography on a grade III alumina column using CH_2Cl_2 as the eluent afforded after solvent removal a 3:1 mixture of η^5-C_5(Me)(CO_2Me)(OEt)(Ph)(Me))Re$(CO)_3$ (**2b**) and (η^5-C_5(Me)(CO_2Me)(OEt)(Me)(Ph))Re$(CO)_3$ (**2c**) as a yellow oil. Yield: 0.044 g (62%). ^{1}H NMR ($CDCl_3$): δ 7.7–7.1 (m, 5H, Ph), 3.97 (minor), 3.88 (2m, 2H, OCH_2Me), 3.82 (minor), 3.80 (2s, 3H, CO_2Me), 2.40, 2.16 (minor), 1.97 (minor), 1.95 (4s, 6H, CMe), 1.30 (minor), 1.00 (2t, ^3J = 7.0 Hz, 3H, OCH_2Me).

2.3.3. Synthesis of $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(Ph)(Ph))Re(CO)_3$ (*2d*) from $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (*1a*) and PhC≡CPh

A solution of **1a** (0.100 g, 0.221 mmol) in 10 ml of toluene was treated with 1 equivalent of PhC≡CPh (0.040 g), and the mixutre was heated at reflux

temperature for 3 h. The workup procedure followed that given in Section 2.3.1. After chromatography on grade III alumina with CH_2Cl_2/hexane as the eluent, 0.107 g (80%) of (η^5-C_5(Me)(CO_2Me)(OEt)(Ph)(Ph))-Re(CO)$_3$ (**2d**) was obtained. IR (hexane): *ν*(CO) 2016 (m), 1971 (s), 1720 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.5–7.0 (m, 10H, Ph), 3.90 (s, 3H, CO_2Me), 3.70 (m, 2H, OC*H*$_2$Me), 2.43 (s, 3H, CMe), 1.17 (t, $^3J = 7.0$ Hz, OCH$_2$*Me*). ^{13}C NMR ($CDCl_3$): δ 194.0 (s, CO), 165.6 (s, *C*O_2Me), 123.3 (s, *C*OEt), 103.7, 100.1, 97.2 (3s, *C*Ph), 89.3 (s, *C*CO_2Me), 75.0 (t, O*C*H$_2$Me), 52.0 (q, CO_2*Me*), 15.1 (q, C*Me*), 12.8 (q, OCH$_2$*Me*).

Complex **2d** was also prepared by irradiating a solution of **1a** and PhC≡CPh (1 equivalent) in hexane. After ca. 12 h, a mixture of 60% **2d** and 40% unreacted **1a** was observed by ^{1}H NMR spectroscopy.

2.3.4. Synthesis of (η^5-C_5(Me)(CO_2Me)(OEt)(Me)-(Me))Re(CO)$_3$ (**2e**) from (CO)$_4$Re(η^2-C(Me)C(CO_2-Me)C(OEt)) (**1a**) and MeC≡CMe

A solution of **1a** (0.100 g, 0.221 mmol) and MeC≡CMe (0.090 ml, 0.060 g, 5 equivalents) in 2 ml of toluene in a sealed tube was heated at 110 °C overnight. The contents were cooled to room temperature, evaporated to dryness, and extracted with two 10-ml portions of hexane. The extracts were filtered, and hexane was removed from the filtrate to yield a yellow oil. Further purification was effected by chromatography on alumina with CH_2Cl_2 as the eluent. The pale yellow oil solidified under vacuum overnight to furnish 0.060 g (57% yield) of pure (η^5-C_5(Me)(CO_2Me)(OEt)(Me)(Me))Re(CO)$_3$ (**2e**). IR (hexane): *ν*(CO) 2098 (m), 1977 (s), 1729 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.97, 3.88 (2m, 2H, OC*H*$_2$Me), 3.80 (s, 3H, CO_2Me), 2.41, 2.16, 2.15 (3s, 9H, CMe), 1.33 (t, $^3J = 7.0$ Hz, OCH$_2$*Me*). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 194.8 (s, CO), 165.6 (s, *C*O_2Me), 137.6 (s, *C*OEt), 98.3, 95.3, 92.3 (3s, *C*Me), 75.3 (s, O*C*H$_2$Me), 75.2 (s, *C*CO_2Me), 51.7 (s, CO_2*Me*), 15.4 (s, OCH$_2$*Me*), 11.8, 10.5, 9.4 (3s, C*Me*). MS (EI): *m*/*z* 480 (M$^+$).

2.3.5. Synthesis of (η^5-C_5(Me)(CO_2Me)(OEt)(CO_2-Me)(CO_2Me))Re(CO)$_3$ (**2f**) from (CO)$_4$Re(η^2-C(Me)C(CO_2Me)C(OEt)) (**1a**) and $MeO_2CC{\equiv}CCO_2Me$

A solution of **1a** (0.060 g, 0.13 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (0.016 ml, 0.019 g, 1 equivalent) in 2 ml of toluene in a sealed tube was heated at 120 °C for 4 h. Cooling to room temperature, evaporation to dryness, and extraction of the residue with 10-ml portions of hexane afforded 0.049 g (65% yield) of (η^5-C_5(Me)(CO_2Me)(OEt)(CO_2Me)(CO_2Me))Re(CO)$_3$ (**2f**) as a yellowish green oil upon removal of the solvent. IR (toluene): *ν*(CO) 2031 (m), 1952 (s), 1743 (w), 1732 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.07, 3.92 (2m, 2H, OC*H*$_2$Me), 3.83, 3.82, 3.80 (3s, 9H, CO_2Me), 2.68 (s, 3H, CMe), 1.31 (t, $^3J = 7.0$ Hz, 3H, OCH$_2$*Me*. ^{13}C NMR ($CDCl_3$): δ 192.1 (s, CO), 163.8, 163.7, 163.5 (3s, *C*O_2Me), 140.0 (s, *C*OEt), 105.6 (s, *C*Me), 84.2, 84.1, 79.4 (3s, *C*CO_2Me), 73.7 (t, O*C*H$_2$Me), 53.1, 51.8, 51.2 (3q, CO_2*Me*), 15.0 (q, C*Me*), 12.7 (q, OCH$_2$*Me*). MS (FAB): *m*/*z* 568 (M$^+$).

2.3.6. Synthesis of (η^5-C_5(Ph)(CO_2Me)(OEt)(Ph)H)-Re(CO)$_3$ (**2g**) and (η^5-C_5(Ph)(CO_2Me)(OEt)(H)-(Ph))Re(CO)$_3$ (**2h**) from (CO)$_4$Re(η^2-C(Ph)C(CO_2-Me)C(OEt)) (**1e**) and PhC≡CH

The reaction in a sealed tube and workup were conducted as in Section 2.3.1 by using **1e** (0.100 g, 0.194 mmol) and PhC≡CH (0.021 ml, 0.020 g, 1 equivalent) in toluene (2 ml). The resulting orange oil was identified by ^{1}H NMR spectroscopy as a 2:1 mixture of isomers (η^5-C_5(Ph)(CO_2Me)(OEt)(Ph)H)Re(CO)$_3$ (**2g**) and (η^5-C_5(Ph)(CO_2Me)(OEt)(H)(Ph))Re(CO)$_3$ (**2h**). Yield: 0.075 g (65%). ^{1}H NMR ($CDCl_3$): δ 7.6–6.9 (m, 10H, Ph), 5.62, 5.32 (minor) (2s, 2H, CH), 4.2–3.9 (m, 2H, OC*H*$_2$Me), 3.74, 3.62 (minor) (2s, 3H, CO_2Me), 1.48 (minor), 1.32 (2t, $^3J = 7.1$ Hz, OCH$_2$*Me*).

2.3.7. Synthesis of (η^5-C_5(Me)(CO_2Me)(NEt_2)-(CO_2Me)(CO_2Me))Re(CO)$_3$ (**2i**) from (CO)$_4$Re(η^2-C(Me)C(CO_2Me)C(NEt_2)) (**1c**) and $MeO_2CC{\equiv}C$-CO_2Me

To a solution of **1c** (0.125 g, 0.260 mmol) in 10 ml of toluene was added $MeO_2CC{\equiv}CCO_2Me$ (0.048 ml, 0.055 g, 1.5 equivalents), and the mixture was heated at reflux temperature for 2 h. Workup was similar to that in Section 2.3.1. The yield of (η^5-C_5(Me)(CO_2Me)(NEt_2)(CO_2Me)(CO_2Me))Re(CO)$_3$ (**2i**), a green solid, was 0.102 g (66%). IR (toluene): *ν*(CO) 2025 (m), 1978 (s), 1730 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.84, 3.83, 3.81 (3s, 9H, CO_2Me), 3.05 (m, 4H, NC*H*$_2$Me), 2.62 (s, 3H, CMe), 1.06 (t, $^3J = 7.2$ Hz, 6H, NCH$_2$*Me*). ^{13}C NMR ($CDCl_3$): δ 192.4 (s, CO), 165.2, 165.1, 164.6 (3s, *C*O_2Me), 134.5 (s, *C*NEt_2), 106.2 (s, *C*Me), 83.0, 82.7, 82.6 (3s, *C*CO_2Me), 53.6, 53.4, 52.4 (3q, CO_2*Me*), 46.2 (t, N*C*H$_2$Me), 12.8 (q, C*Me*), 12.2 (q, NCH$_2$*Me*). MS (FAB): *m*/*z* 595 (M$^+$). Anal. Found: C, 38.51; H, 3.91%. Calc. for $C_{19}H_{22}NO_9Re$: C, 38.38; H, 3.73%.

2.3.8. Synthesis of (η^5-C_5(Me)(CO_2Me)(O(CH_2)$_3$)H)-Re(CO)$_3$ (**2j**) by thermolysis of (CO)$_4$Re(η^2-C(Me)C-(CO_2Me)C(O(CH_2)$_3$C≡CH)) (**1b**)

A solution of **1b** (0.312 g, 0.640 mmol) in 20 ml of toluene was heated at reflux temperature for 4 h. After evaporation of the solvent, the crude product was dissolved in a minimum volume of hexane, and the solution was filtered and cooled to −78 °C. Yellowish green crystals of (η^5-C_5(Me)(CO_2Me)(O(CH_2)$_3$)H)Re(CO)$_3$ (**2j**) were isolated by filtration in 56% yield (0.166 g). IR (toluene): *ν*(CO) 2065 (m), 2006 (s), 1972 (m), 1935 (m), 1720 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.01 (s, 1H, CH),

4.3, 4.1 (2m, 2H, $OCH_2(CH_2)_2$), 3.84 (s, 3 H, CO_2Me), 2.65 (m, 2H, $O(CH_2)_2CH_2$), 2.47 (s, 3H, CMe), 1.95 (m, 2H, $OCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 194.0 (s, CO), 190.9 (br s, CO), 165.6 (s, CO_2Me), 139.3 (s, $COCH_2$), 100.2 (s, *C*Me), 82.5 (s, C of Cp), 78.0 (d, CH), 71.9 (s, C of Cp), 68.6 (t, $OCH_2(CH_2)_2$), 51.8 (q, CO_2Me), 21.6 (t, $O(CH_2)_2CH_2$), 19.9 (t, $OCH_2CH_2CH_2$), 14.6 (q, C*Me*). MS (FAB): m/z 464 (M^+).

2.3.9. Competition reaction of $(CO)_4Re(\eta^2$-C(Me)-C(CO_2Me)C(OEt)) (**1a**) with 1:1 PhC≡CH and PhC≡CPh

A solution of **1a** (0.050 g, 0.11 mmol) in 10 ml of toluene at room temperature was treated with both PhC≡CH (0.014 ml, 0.013 g, 1 equivalent) and PhC≡CPh (0.020 g, 1 equivalent). The mixture was then heated at reflux temperature for 4 h. Solvent was removed under reduced pressure, and the residue was extracted with 10-ml portions of hexane. Examination of the extracts by ^1H NMR spectroscopy showed the exclusive formation of the phenylacetylene-derived product, (η^5-C_5(Me)(CO_2Me)(OEt)(Ph)H)Re(CO)$_3$ (**2a**).

2.3.10. Competition reaction of $(CO)_4Re(\eta^2$-C(Me)-C(CO_2Me)C(OEt)) (**1a**) with 1:1 PhC≡CPh and $MeO_2CC{\equiv}CCO_2Me$

This reaction was conducted similarly to that in Section 2.3.9 and utilized **1a** (0.050 g, 0.11 mmol), PhC≡CPh (0.020 g, 1 equivalent), and $MeO_2CC{\equiv}C$-CO_2Me (0.014 ml, 0.016 g, 1 equivalent) in 10 ml of toluene. Only (η^5-C_5(Me)(CO_2Me)(OEt)(CO_2Me)(CO_2Me))Re(CO)$_3$ (**2f**) was observed by ^1H NMR spectroscopy.

2.4. Rearrangement reactions of $(CO)_4Re(\eta^2$-C(R)C(CO_2Me)C(OEt)) (R = Me (**1a**), $CHEt_2$ (**1d**)) in nitriles and pyridine

2.4.1. Synthesis of $(CO)_4Re(\kappa^2$-OC(OMe)C-(CH=CH_2)C(OEt)) (**3a**) from $(CO)_4Re(\eta^2$-C(Me)C-(CO_2Me)C(OEt)) (**1a**) in MeCN

A solution of **1a** (0.105 g, 0.232 mmol) in 10 ml of MeCN was heated at reflux temperature for 2 h, with the reaction being monitored by ^1H NMR spectroscopy. The solvent was removed under reduced pressure, and the residue was extracted with 10-ml portions of hexane. A green oil was isolated upon removal of hexane from the extracts. Yield: 0.074 g (70%). The proposed structure of $(CO)_4Re(\kappa^2$-OC(OMe)C(CH=CH_2)C(OEt)) (**3a**) is based on ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The product was insufficiently stable for chemical analysis. IR (hexane): ν(CO) 2092 (w), 1998 (s), 1947 (s), 1726 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.43 (dd, $^3J_{cis} = 12.1$ Hz, $^3J_{trans} = 18.0$ Hz, 1H, C*H*=CH_2), 5.58 (dd, $^2J = 2.67$ Hz, $^3J_{trans} = 18.0$ Hz, 1H, CH=CH_2), 4.95 (dd, $^2J = 2.67$ Hz, $^3J_{cis} = 12.1$ Hz, 1H, CH=CH_2), 4.38 (q, $^3J = 7.1$ Hz, 2H, OCH_2Me), 3.89 (s, 3H, CO_2Me), 1.50 (t, $^3J = 7.1$ Hz, 3H, OCH_2Me). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 234.3 (s, Re*C*OEt), 191.5, 190.5, 186.37 (3s, CO), 186.36 (s, *C*OMe), 126.4 (s, *C*CH=CH_2), 114.9 (s, *C*H=CH_2), 110.8 (s, CH=*C*H_2), 75.4 (s, O*C*H_2Me), 53.4 (s, CO*Me*), 15.3 (s, OCH_2Me).

2.4.2. Synthesis of $(CO)_4Re(\kappa^2$-OC(OMe)C-(CH=CEt_2)C(OEt)) (**3b**) from $(CO)_4Re(\eta^2$-C(CH-Et_2)C(CO_2Me)C(OEt)) (**1d**) in CD_3CN

A solution of **1d** (0.051 g, 0.10 mmol) in 0.5 ml of CD_3CN in a pressure NMR tube was heated at 78–80 °C, with the reaction being monitored by ^1H NMR spectroscopy. After 5 days, the reaction was essentially complete. The solvent was evaporated from the reaction mixture, the residue was extracted with 0.5 ml of CH_2Cl_2, and the extract was layered with hexane. Evaporation of hexane afforded a yellow oil. The oil crystallized on dissolution in hexane and cooling at 0 °C for a few hours. The isolated yield of $(CO)_4Re(\kappa^2$-OC(OMe)C(CH=CEt_2)C(OEt)) (**3b**) was 0.028 g (55%). IR (hexane): ν(CO) 2018 (m), 1938 (s), 1899 (s) cm^{-1}. ^1H NMR (CD_3CN): δ 5.34 (br s, 1H, =CH), 4.35 (q, $^3J = 7.1$ Hz, 2H, OCH_2Me), 3.78 (s, 3H, OMe), 2.08 (qd, $^3J = 7.5$ Hz, $^4J = 1.34$ Hz, 2H, =CCH_2Me), 1.92 (q, $^3J = 7.6$ Hz, 2H, =CCH_2Me), 1.32 (t, $^3J = 7.1$ Hz, 3H, OCH_2Me), 1.02 (t, $^3J = 7.5$ Hz, 3H, =CCH_2Me), 0.92 (t, $^3J = 7.5$ Hz, 3H, =CCH_2Me). ^{13}C NMR (CD_3CN): δ 242.2 (s, Re*C*OEt), 199.4, 197.4, 194.7 (3 s, CO), 188.3 (s, *C*OMe), 146.0 (s, *C*CH=CEt_2), 116.1 (d, *C*H=CEt_2), 114.5 (s, =*C*Et_2), 74.4 (t, O*C*H_2Me), 53.7 (q, OMe), 29.0, 25.4 (2t, =C*C*H_2Me), 16.3 (q, OCH_2Me), 13.2, 12.5 (2q, =CCH_2Me). MS (EI): m/z 510 (M^+), 482 (M^+–CO). Anal. Found: C, 37.63; H, 3.80%. Calc. for $C_{16}H_{19}O_7Re$: C, 37.72; H, 3.76%.

2.4.3. Synthesis of $(CO)_4Re(\kappa^2$-OC(OMe)C(CH=CEt_2)C(OEt)) (**3b**) from $(CO)_4Re(\eta^2$-C($CHEt_2$)C-(CO_2Me)C(OEt)) (**1d**) in other nitriles

Solutions of **1d** (0.020 g, 0.039 mmol) in 0.5 ml of EtCN, PhCN, or *t*-BuCN in a pressure NMR tube were heated at 78–80 °C for 5 days. In each case, the mixture was evaporated to dryness, and the residue was extracted with hexane. The extract was filtered and freed of the solvent under reduced pressure. ^1H NMR spectra of the residue showed presence of $(CO)_4Re(\kappa^2$-OC(OMe)C(CH=CEt_2)C(OEt)) (**3b**) and some nitrile for the reactions of **1d** in EtCN and PhCN. For the reaction in *t*-BuCN, more than 60% unreacted **1d** was observed as well.

2.4.4. Synthesis of $(CO)_3(py)Re(\kappa^2$-OC(OMe)C-(CH=CEt_2)C(OEt)) (**4**) from $(CO)_4Re(\eta^2$-C(CH-Et_2)C(CO_2Me)C(OEt)) (**1d**) and pyridine

A solution of **1d** (0.020 g, 0.039 mmol) in 0.5 ml (ca. 6 mmol) of pyridine in a pressure NMR tube was heated

at 78–80 °C for 2 days. The mixture was concentrated to an oil and extracted by slow diffusion into 5 ml of hexane. The yellowish green hexane solution was filtered, the solvent was removed under reduced pressure, and the residue was dried under vacuum to afford $(CO)_3(py)Re(\kappa^2\text{-}OC(OMe)C(CH{=}CEt_2)C(OEt))$ (**4**) as a green solid in 69% yield (0.015 g). IR (hexane): *ν*(CO) 2014 (m), 1928 (s), 1898 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.7–7.3 (m, 5H, py), 5.37 (br s, 1 H, =CH), 4.54 (m, 2H, OCH_2Me), 3.80 (s, 3H, OMe), 2.07 (qd, $^3J = 7.5$ Hz, 2H, $=CCH_2Me$), 1.68 (q, $^3J = 7.6$ Hz, 2H, $=CCH_2Me$, 1.43 (t, $^3J = 7.1$ Hz, 3H, OCH_2Me), 1.02 (t, $^3J = 7.5$ Hz, 3H, $=CCH_2Me$), 0.80 (t, $^3J = 7.5$ Hz, 3H, $=CCH_2Me$). ^{13}C NMR ($CDCl_3$): δ 247.4 (s, Re*C*OEt), 200.9, 198.6, 194.7 (3s, CO), 187.4 (s, *C*OMe), 153.7 (d, py), 145.8 (s, $CCH{=}CEt_2$), 144.3 (d, $CH{=}CEt_2$), 137.7, 125.4 (2d, py), 114.0 (s, $=CEt_2$), 73.8 (t, OCH_2Me), 53.2 (q, OMe), 28.3, 24.7 (2t, $=CCH_2Me$), 15.8 (q, OCH_2Me), 12.8, 12.1 (2q, $=CCH_2Me$). MS (EI): *m*/*z* 561 (M^+), 533 (M^+–CO), 504 (M^+–CO–Et), 476 (M^+–2CO–Et). Anal. Found: C, 42.87; H, 4.15%. Calc. for $C_{20}H_{24}NO_6Re$: C, 42.85; H, 4.31%.

2.5. Reactions of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**1a**) with sulfonium ylides

2.5.1. Synthesis of $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}CHC(O)Ph)C(OEt))$ (**5a**) from $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**1a**) and $Me_2S{=}CHC(O)Ph$

A solution of **1a** (0.123 g, 0.270 mmol) and 1 equivalent of $Me_2S{=}CHC(O)Ph$ (0.049 g, 0.27 mmol) in 12 ml of MeCN was heated at reflux temperature. Within 15 min, the color of the solution turned orange, and after 30 min complete conversion to the product was observed by IR spectroscopy. Acetonitrile was removed under reduced pressure, and the residue was extracted with 10-ml portions of hexane. The extracts were filtered, and the filtrate was evaporated to leave a yellow oil of $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}CHC(O)Ph)C(OEt))$ (**5a**) in 49% yield (0.075 g). The product undergoes slow decomposition even on storage under argon. IR (hexane): *ν*(CO) 2096 (w), 2001 (s), 1996 (s), 1941 (m), 1665 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.8–7.4 (m, 5H, Ph), 6.59 (q, $^4J \sim 1$ Hz, 1H, =CH), 4.20 (q, $^3J = 7.1$ Hz, 2H, OCH_2Me), 3.72 (s, 3 H, COMe), 2.05 (d, $^4J \sim 1$ Hz, 3H, =CMe), 1.29 (t, $^3J = 7.1$ Hz, 3H, OCH_2Me). (nOe: irradiation of the signal at δ 2.05 resulted in a 4% enhancement of the signal at δ 6.59). ^{13}C NMR ($CDCl_3$): δ 214.7 (s, Re*C*OEt), 191.9, 191.7, 190.7 (3s, CO), 186.5, 185.1 (2s, *C*(O)Ph, *C*OMe), 147.4 (s, *C*C(Me)=CH), 138.9 (s, ipso C of Ph), 132.1, 128.25, 128.17 (3d, other C of Ph), 124.3 (d, C(Me)=*C*H), 117.4 (s, *C*(Me)=CH), 74.7 (t, OCH_2Me), 53.4 (q, CO*Me*), 25.0 (q, =C*Me*), 15.4 (q, OCH_2Me).

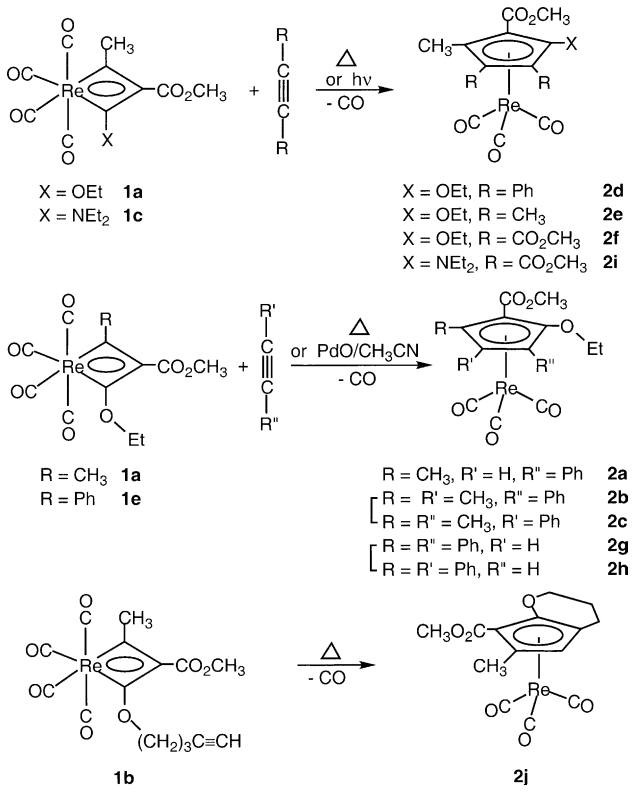
2.5.2. Synthesis of $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}C(CN)_2)C(OEt))$ (**5b**) from $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**1a**) and $Me_2S{=}C(CN)_2$

A solution of **1a** (0.231 g, 0.510 mmol) and 1 equivalent of $Me_2S{=}C(CN)_2$ (0.063 g) in 10 ml of MeCN was treated for 6 h as described in Section 2.5.1. The ^1H NMR spectrum of the oil residue from evaporation of the initial hexane extracts indicated a mixture of three products. The major one was obtained by further extraction of this mixture using 2 ml of THF and a layer of hexane. The product $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}C(CN)_2)C(OEt))$ (**5b**) was isolated from the hexane layer by evaporation of the solvent. The yield was 0.063 g (24%). IR (CH_2Cl_2): *ν*(CO) 2102 (w), 2067 (s), 2004 (s), 1972 (m), 1943 (m), 1723 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.46 (q, $^3J = 7.1$ Hz, 2H, OCH_2Me), 3.91 (s, 3H, CO_2Me), 2.32 (s, 3 H, =CMe), 1.48 (t, $^3J = 7.1$ Hz, 3H, OCH_2Me). ^{13}C NMR ($CDCl_3$): δ 239.8 (s, Re*C*OEt), 194.1, 190.3, 189.7 (3s, CO), 185.5 (s, *C*OMe), 114.3 (s, $=C(CN)_2$), 113.3, 112.3 (2 s, CN), 87.0 (s, *C*(Me)=C), 76.8 (t, OCH_2Me), 54.1 (q, CO*Me*), 23.2 (q, =C*Me*), 15.2 (q, OCH_2Me). MS (EI): *m*/*z* 518 (M^+), 490 (M^+–CO), 462 (M^+–2CO), 434 (M^+–3CO), 406 (M^+–4CO).

3. Results and discussion

3.1. Formation of substituted η^5-cyclopentadienylrhenium tricarbonyl complexes from $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(X))$ (**1**) and alkynes

Reactions of **1** with 1 equivalent of alkyne in toluene at reflux temperature for 2–5 h were found to proceed as illustrated in Scheme 1. The alkynes employed include both electron-rich (e.g., MeC≡CMe) and electron-deficient (e.g., $MeO_2CC{\equiv}CCO_2Me$), symmetrical (e.g., PhC≡CPh) and unsymmetrical (e.g., PhC≡CH, PhC≡CMe), as well as a pendant alkynyl group on the rhenacyclobutadiene ring ($O(CH_2)_3C{\equiv}CH$). After workup, tetra- and pentasubstituted η^5-cyclopentadienylrhenium complexes **2** were obtained as yellow or green oils or solids in 56–90% isolated yields. Most losses were sustained on purification by extraction and chromatography. Thermal reactions were also conducted, with similar results, in a sealed tube at 110–120 °C; this procedure is particularly applicable to the more volatile alkynes such as MeC≡CMe. Synthesis of **2** from **1** and alkyne was also effected at ambient temperature under photochemical conditions or by use of PdO for abstraction of CO from **1** [6]. Irradiation of **1a** and $MeO_2CC{\equiv}CCO_2Me$ in hexane for 1 h afforded a large amount of decomposition material as well as some $(\eta^5\text{-}C_5(Me)(CO_2Me)(OEt)(CO_2Me)(CO_2Me))Re(CO)_3$ (**2f**); however, the method has no synthetic advantage over the thermal one. Corresponding reaction of **1a** with



Scheme 1.

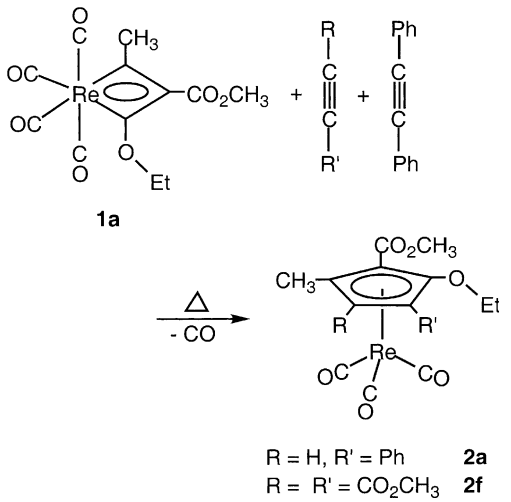
PhC≡CPh proceeded cleanly but slowly, and after 12 h only 60% of **1a** was converted to (η^5-C_5(Me)(CO_2Me)(OEt)(Ph)(Ph))Re(CO)$_3$ (**2d**).

Complexes **1** and each of the symmetrical alkynes PhC≡CPh, MeC≡CMe, and $MeO_2CC{\equiv}CCO_2Me$ afforded only one product **2**, as expected in such [3 + 2] cycloadditions without rearrangement of the ring carbon atoms. ^{1}H and ^{13}C NMR spectra showed that **1a** and the unsymmetrical alkyne PhC≡CH also gave only one product **2** (cf. Section 2.3.1), which was assigned the isomeric structure (η^5-C_5(Me)(CO_2Me)(OEt)(Ph)H)Re(CO)$_3$ (**2a**) from a ^{1}H NMR nOe experiment. Irradiation of the CH signal at δ 5.29 enhanced the intensity of the CMe signal at δ 2.49 to show proximity of H and Me on the ring. Similarly to the reaction of **1a** with PhC≡CH, thermolysis of **1b**, containing pendant alkynyl group O(CH_2)$_3$C≡CH, afforded also a single product, a η^5-cyclopentadienyl-dihydropyran fused-ring complex, (η^5-C_5(Me)(CO_2Me)(O(CH_2)$_3$)H)Re(CO)$_3$ (**2j**). In contrast, reactions of **1a** with PhC≡CMe and of **1e** with PhC≡CH gave mixtures of two products each – (η^5-C_5(Me)(CO_2Me)(OEt)(Ph)(Me))Re(CO)$_3$ (**2b**)/(η^5-C_5(Me)(CO_2Me)(OEt)(Me)(Ph))Re(CO)$_3$ (**2c**) and (η^5-C_5(Ph)(CO_2Me)(OEt)(Ph)H)Re(CO)$_3$ (**2g**)/(η^5-C_5(Ph)(CO_2Me)(OEt)(H)(Ph))Re(CO)$_3$ (**2h**) – in 3:1 and 2:1 respective ratios based on the intensities of the ^{1}H NMR signals in their spectra. However, it was not possible to assign structure to the major and minor isomers from spectroscopic data. Two regioisomers are expected from [3 + 2] cycloaddition of an unsymmetrical alkyne to the η^2-C(R)C(CO_2Me)C(OEt) ligand of **1**.

Complexes **2a**–**2j** were characterized by a combination of IR and NMR spectroscopy, mass spectrometry, and elemental analysis. The IR spectra feature two metal carbonyl ν(CO) bands, generally at 2031–2016 (m) and 1978–1945 (s) cm^{-1}, as reported for other ring-substituted derivatives of CpRe(CO)$_3$ [7,8]. In addition, a weaker ν(CO) band is observed at 1745–1720 cm^{-1}, and is attributed to the CO_2Me substituent(s) on the ring. For complex **2j**, four metal carbonyl ν(CO) absorptions are noted, probably owing to the presence of two conformers. Conformational isomerism has been implicated by IR spectra for other η^5-cyclopentadienylmetal carbonyl complexes [9].

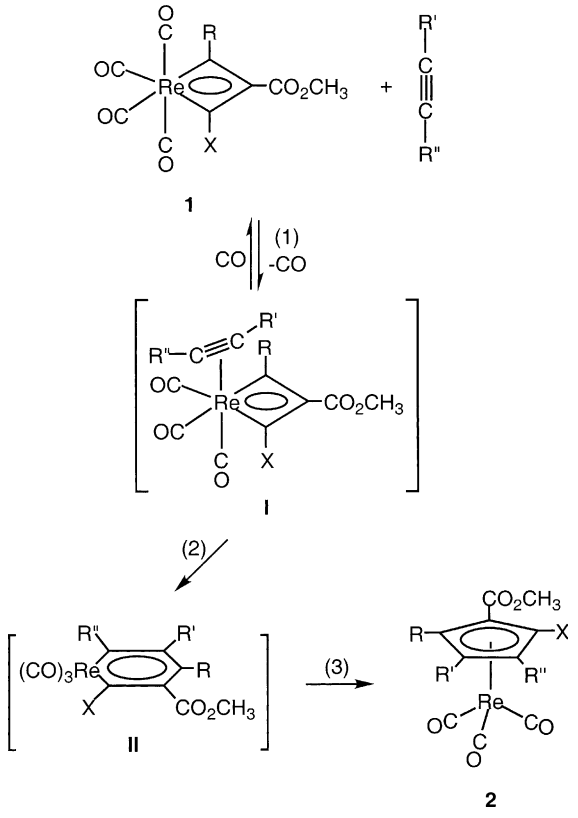
The ^{1}H NMR spectra are in accord with the structures assigned to **2**. Thus, the η^5-cyclopentadienyl CH of **2a**, **2g**, **2h**, and **2j** resonates at δ 5.62–5.01, in agreement with the literature reports on related compounds [7,8,10]. In the complexes containing more than one Me group as CMe or CO_2Me, each Me group gives rise to a separate resonance, as expected for these structures. All of the ^{13}C NMR spectra show five resonances for their five inequivalent η^5-cyclopentadienyl carbon atoms; they occur in the range δ 140–75, depending on the substituent. Accordingly, the *C*OR or *C*NEt_2 carbon resonates at the lowest field (δ 140–123), followed by the *C*Ph, *C*CO_2Me, *C*Me (δ 106–75), and *C*H (δ 79–78), again in agreement with the literature [8–10]. However, in some cases, unambiguous assignment is not possible owing to overlap of the chemical shift ranges. For the CH ring carbon, ^{13}C DEPT NMR experiments provide a definitive signal attribution. Like the ring carbons, all of the C*Me*, *C*O_2Me, and CO_2*Me* carbons display separate resonances for every appropriate complex. With the exception of **2j**, all complexes **2** show one ^{13}C NMR signal of CO at δ 194.9–192.1 to indicate that ring rotation is rapid on the NMR time scale. For **2j**, two singlet CO resonances are observed, again suggesting presence of rotational isomers.

A limited study was carried out on relative reactivity of **1a** toward alkynes by competition reactions with mixtures of two acetylenes as described in Sections 2.3.9 and 2.3.10 (Scheme 2). These experiments showed that when PhC≡CH and PhC≡CPh were used together, only **2a** was observed by ^{1}H NMR spectroscopy. With $MeO_2CC{\equiv}CCO_2Me$ and PhC≡CPh, **2f** was the sole detected product. Thus, each of PhC≡CH and $MeO_2CC{\equiv}CCO_2Me$ reacts faster than PhC≡CPh. Steric considerations seem to be important assuming that insertion of alkyne into Re=C bond represents the discriminating step in the reaction. The electrophilic nature of $MeO_2CC{\equiv}CCO_2Me$ also appears to play a role, although steric factors control the reactivity order PhC≡CH > PhC≡CPh.



Scheme 2.

We now turn to mechanistic considerations of the reactions presented in Scheme 1. A pathway consistent with the formation of complexes **2** and with related chemistry, including reactions of other metallacyclobutadienes with alkynes [10b,11,12], is set out in Scheme 3. It represents an adaptation of the mechanism proposed in similar studies and consists of 3 steps:



Scheme 3.

(i) replacement of CO with alkyne in **1** to generate intermediate **I**,
(ii) insertion of coordinated alkyne into Re=C bond to give a rhenabenzene complex, intermediate **II**, and
(iii) extrusion of Re from the rhenabenzene ring of **II** and coordination to resultant cyclopentadienyl ligand to afford **2**.

Step 1 requires that the reactions be conducted at elevated temperatures such as reflux temperature of toluene for 2–5 h to reach completion. Less stringent conditions are not effective; for example, use of THF at reflux (66 °C) afforded no reaction of **1a** with $MeO_2CC{\equiv}CCO_2Me$, and use of boiling hexane (69 °C) with the same reactants gave only partial conversion to **2f** in 4 h. Reversible loss of CO followed by coordination of alkyne is also the rate determining step in annulation reactions of $(CO)_5Cr$(carbene) complexes with alkynes [13]. Under the high-temperature conditions employed, no reaction intermediate could be observed with **1a** and alkynes. To possibly detect such species, reactions were carried out at ambient temperature in the presence of PdO, an effective reagent for abstraction of CO from metal carbonyls [6]. When a suspension of PdO in a MeCN solution of **1a** and PhC≡CH was stirred for 2 days, complete conversion to **2a** was achieved. However, no reaction intermediates were detected. Significantly, as in the thermal reaction, only one regioisomer, **2a**, was obtained. Use of **1e** with PhC≡CH and PdO under similar conditions resulted in the formation of a mixture of **2g** and **2h**, again as in the reaction at elevated temperature. These results support the proposal that loss of CO from **1** is the initial step in the conversion of **1** to **2** by alkynes.

Coordination of alkyne to Re leads to its insertion into one of the Re=C bonds to give a rhenabenzene intermediate **II** (step 2). Since the report of an osmabenzene complex by Roper and co-workers in 1982 [14], a number of stable metallabenzenes have been prepared and characterized [15]. Rhenabenzene carbonyl complexes have been proposed as intermediates in several investigations [8,16], including those concerned with synthesis of η^5-$Cp^{\ddagger}Re(CO)_3$ ($Cp^{\ddagger}$ = multisubstituted Cp) from $(CO)_4Re(\eta^2$-C(Ph)C(Ph)C(Ph)) and alkynes [10] and from $Re(CO)_4(PPh_3)Br$ and 1,4-dilithio-1,4-diphenyl-1,3-butadiene [8], but were not isolated, presumably owing to their relative instability. Schrock-type metal alkylidynes and metallacyclobutadienes react with alkynes also to yield η^5-cyclopentadienylmetal complexes [11,12,17], and intermediacy of metallabenzenes has been proposed in some cases. However, other intermediates are possible as well [11,18].

There is an additional point that we want to address. It concerns structure of intermediate **I** and regiochemistry of its conversion to **II**. Since mutually *trans* CO's are substitutionally more labile than those *trans* to η^2-C(R)C(CO_2Me)C(X) [19], we propose that the

entering alkyne is positioned *cis* to the bidentate ligand in **I** (overall *fac*-tricarbonyl geometry). When coordinated in this position, its C–C≡C–C backbone can assume an orientation that either eclipses one of the OC–Re–C(R or X) vectors (as drawn in Scheme 3) or staggers them. Although for a d^4 (or $d^{<4}$) octahedral complex, eclipsed alkyne orientation is favored because a vacant t_{2g} d orbital on metal participates in bonding [20], in intermediate **I** of d^6 configuration no such bonding interaction occurs, and electronic stabilization of any possible alkyne orientation appears to be insignificant. Nevertheless, alkyne orientation for further reaction is important to the understanding of observed regiochemistry in the formation of **2** (and presumably **II**) from **I**. Answers to the questions of which carbon atom of R′C≡CR″ is directed toward η^2-C(R)C(CO_2Me)C(X) during the insertion and which Re=C bond interacts with the alkyne may provide clues as to why certain regioisomers arise from **I** and an unsymmetrical alkyne. Of the reactions examined here, three are relevant in this context, viz., **1a** with PhC≡CMe to afford **2a**, **1a** with PhC≡CMe to give **2b** and **2c**, and **1e** with PhC≡CH to yield **2g** and **2h**. The conversion of **1b** to **2j** is a special case, since ring constraints associated with the formation of a bicyclic system dictate regiochemical course of the reaction.

The foregoing results may be rationalized by one or both of the following factors: increased steric crowding on going from PhC≡CH to PhC≡CMe and to PhC≡CPh, and a preference for insertion into Re=C(R) rather than Re=C(OEt). The exclusive formation of **2a** from **1a** suggests that the unsubstituted end of PhC≡*C*H interacts with the organic ligand of **I** for steric reasons and that it forms a CH–C(Me) bond during insertion into Re=C(Me). The observation that PhC≡CH reacts faster than PhC≡CPh supports the importance of steric factors. The formation of both **2b** and **2c** from **1a** and PhC≡CMe may be attributed to a greater steric repulsion of PhC≡*C*Me than of PhC≡ *C*H with Re=C(Me). This could lead to insertion of PhC≡*C*Me into Re=C(OEt) as well as into Re=C(Me). A similar rationalization may apply to the formation of both **2g** and **2h** from **1e** and PhC≡CH. It is relevant that annulation reactions of $(CO)_5$Cr(carbene) complexes with unsymmetrical alkynes proceed by ineraction of the smaller ≡CR fragment of the latter with the carbene carbon [13]. Also, insertion of oxygen atom or the NH group into Re=C bond of **1** involves either Re=C(Me) or Re=C(OEt) depending on the nature of reactant and/or reaction conditions; however, insertion into Re=C(Me) is more common [1,19,21].

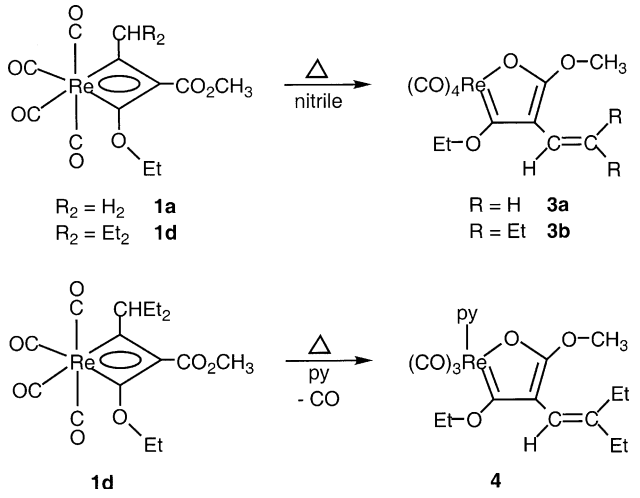
Little can be said about step 3 in Scheme 3. Very likely conversion of **II** to **2** occurs rapidly, since no rhenabenzene complex was detected when reaction of **1a** or **1b** with PhC≡CH was conducted at room temperature in the presence of PdO. The fact that **II** is a 16-electron species may promote this conversion. Scrambling of the ring carbon atoms in going from metallacyclobutadiene to η^5-cyclopentadienyl product, reported for reactions of Schrock-type complexes of tungsten [11], in all probability does not occur here. This is because the number of products **2** observed by ^{1}H and ^{13}C NMR spectroscopy for each reaction never exceeds that predicted for rearrangement-free [3 + 2] cycloaddition of alkyne to the η^2-C(R)C(CO_2Me)C(X) ligand of **1**.

The reactions of **1** with alkynes reported herein, together with the preparation of **1** described elsewhere [1,19], represent a new synthetic approach to a variety of ring-substituted η^5-cyclopentadienylrhenium carbonyl complexes, **2**. Substituted η^5-cyclopentadienylmetal complexes have been the subject of considerable interest [22], especially in connection with their application in alkene polymerization reactions. The scope of the chemistry described in our studies, including extensions to other transition metals, still needs to be elaborated.

*3.2. Rearrangement reactions of $(CO)_4Re(\eta^2$-C(R)C(CO_2Me)C(OEt)) (**1**) in nitriles and pyridine*

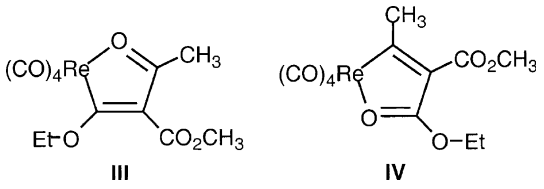
Fischer carbene complexes are known to undergo insertion of RC≡N into the M=C bond [23]. Since complexes **1** react with alkynes to afford $Cp^‡Re(CO)_3$ (**2**), similar reactions with nitriles would be expected to result in substituted heterocyclic compounds of rhenium.

We find that acetonitrile solutions of **1a** maintain their integrity on storage at ambient temperature. However, heating at reflux temperature for 2 h affords $(CO)_4Re(\kappa^2$-OC(OMe)C(CH=CH_2)C(OEt)) (**3a**) as a moderately stable oil in 70% yield (Scheme 4). Use of deuteriated acetonitrile leads to **3a** that shows no incorporation of deuterium by ^{2}H NMR spectroscopy.



Scheme 4.

Complex **3a** was characterized by ^{1}H and ^{13}C NMR spectroscopy to possess a rhenafuran ring structure. It may be considered as derived from **1a** by cleavage of the Re=C(Me) bond with transfer of one Me hydrogen to the Re=C carbon followed by formation of a 5-membered ring via coordination of the terminal C(O)OMe oxygen to rhenium. The IR spectrum of **3a** shows three metal carbonyl ν(CO) bands at 2092 (w), 1998 (s), and 1947 (s) cm^{-1}; these bands are very similar in position and relative intensity to those observed for **III** and **IV**, derived from oxygen atom insertion into Re=C bond of **1a** [19]. The absence of the methyl group as Re=C(Me) and the presence of a vinyl group CH=CH$_2$ in its place are demonstrated by the ^{1}H NMR spectrum (cf. Section 2.4.1). In support of the assigned rhenafuran structure, the ester carbonyl *C*O$_2$Me ^{13}C resonance occurs at δ 186.36 and replaces the corresponding signal of **1a** at δ 159.4 [19]. The new position is identical with that of the *O*-coordinated *C*O$_2$Et in **IV**. Furthermore, the signal at δ 234.3, assigned to Re=*C*(OEt), comes close to that at δ 243.7 for the corresponding carbon nucleus of **1a**.

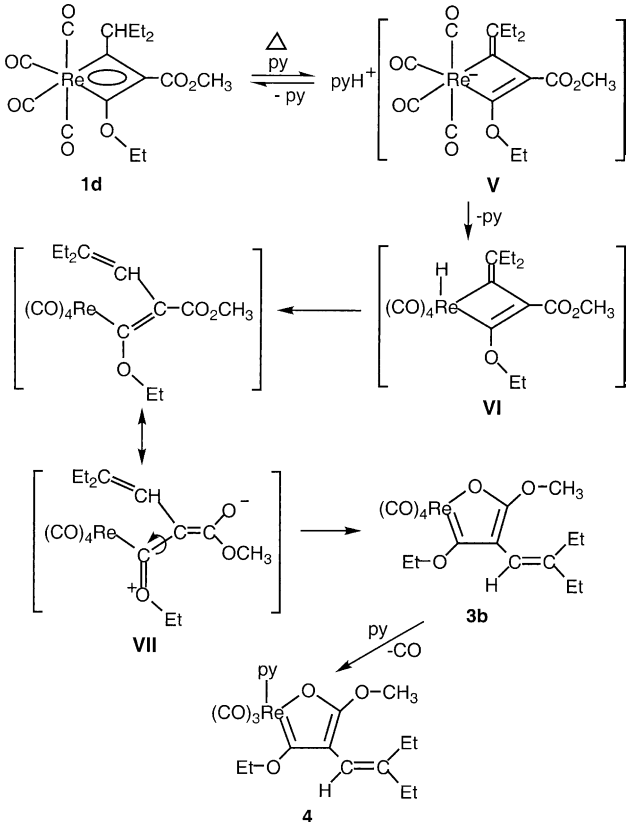


Since **3a** decomposes on storage, we turned to the corresponding reaction of **1d** to seek a more stable product. A similar rearrangement of **1d** would lead to the trisubstituted double bond CCH=CEt$_2$ instead of CCH=CH$_2$ in **3a**, and therefore confer additional stability on the resulting rhenafuran complex. The reaction of **1d** in MeCN solution is cleaner but slower than that of **1a**. When carried out in CD$_3$CN at 78–80 °C, it was essentially complete in 5 days (Scheme 4). Again, the product (CO)$_4$Re(κ^2-OC(OMe)C(CH=CEt$_2$)C(OEt)) (**3b**) contained no deuterium from the nitrile. Use of EtCN or PhCN in place of MeCN at the same temperature resulted in a greater than 90% yield of **3b** in 5 days. In *t*-BuCN under similar conditions, 40% **3b** and 60% unreacted **1d** were observed by ^{1}H NMR spectroscopy. No reaction occurs of **1d** in benzene in the absence of RCN at comparable temperature.

The assigned structure of **3b** is based on IR and ^{1}H and ^{13}C NMR spectroscopic evidence, and its chemical composition is supported by mass spectrometric and elemental analysis. The structure is strictly analogous to that of **3a**, with the vinyl substituent on the rhenafuran ring being, as expected, CH=CEt$_2$. Two separate ^{1}H and ^{13}C NMR signals are observed for the CH$_2$ and Me parts of each Et group. In the ^{13}C NMR spectrum, the signals of *C*O$_2$Me at δ 188.3 and of Re=C(OEt) at δ 242.2 compare well with those noted for **3a**. The rest of the spectroscopic data (cf. Section 2.4.2) is also in good agreement with the proposed structure.

Behavior of **1d** toward pyridine was investigated, since the latter is known to displace carbene ligand from its complexes [24,25]; for example, reaction between (CO)$_5$Cr=C(OMe)(CHRR′) and pyridine produces (CO)$_5$Cr(py) and (MeO)CH=CRR′, where shift of hydrogen occurred to the adjacent carbon atom [24]. Heating a solution of **1d** in pyridine at 78–80 °C for 2 days afforded after workup a green solid, (CO)$_3$(py)Re(κ^2-OC(OMe)C(CH=CEt$_2$)C(OEt)) (**4**), in 69% yield (cf. Scheme 4). The IR spectrum of **4** in the metal carbonyl ν(CO) region features three medium- or strong-intensity bands between 2014 and 1898 cm^{-1}, consistent with such a six-coordinate *fac*-tricarbonyl structure [26]. Its ^{1}H and ^{13}C NMR spectra, presented in Section 2.4.4, are very similar to those of **3b**, except for the presence of additional signals assigned to coordinated pyridine. The structure receives further support from the observed parent molecular ion and the fragmentation pattern in the mass spectrum.

A proposed mechanism of formation of **4** from **1d** and pyridine is set out in Scheme 5. The initial role of pyridine is to abstract the methine hydrogen of Re=C(C*H*Et$_2$) as H$^+$ to form pyH$^+$ and the conjugate base of **1d**, **V**. The latter then undergoes protonation by pyH$^+$ at rhenium to afford a metal hydrido intermediate,



Scheme 5.

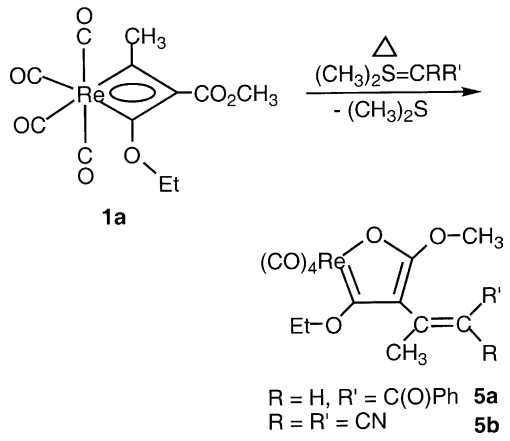
VI. Reductive elimination of H and the $C(=CEt_2)$-$C(CO_2Me)C(OEt)$ end of the chelate converts **VI** to **VII**, which, after rotation about the (EtO)C–C bond, generates a rhenafuran ring of **3b** by coordination of the *O*C(OMe) oxygen to rhenium. Substitution of a carbonyl ligand by pyridine yields **4**. Precedence exists in the literature for pyridine-promoted deprotonation of a carbene ligand and reprotonation at adjacent carbon atom [24,25], presumably by intermediacy of a metal hydrido complex. The step in Scheme 5 involving rotation about the C–C bond is driven by the formation of a stable 5-membered rhenafuran ring, a process proposed for a similar ruthenium system [27].

The nitrile-promoted rearrangement of **1a** and **1d** to **3a** and **3b**, respectively, probably proceeds by a mechanism similar to that depicted in Scheme 5, but does not involve replacement of CO with nitrile. A troublesome step in such a pathway, however, is deprotonation of **1** with RCN, a very weak base compared to pyridine (pK_a of $MeCNH^+ = -10.1$ vs. pK_a of $pyH^+ = 5.2$ [28]). Nevertheless, involvement of RCN in the reaction must occur, since **1d** in benzene alone does not undergo rearrangement, and the reaction shows dependence on steric bulk of RCN, with the rate increasing as a function of R in the order *t*-Bu < Ph, Et < Me. [2]

3.3. Reactions of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**1a**) with sulfonium ylides

The acidity of the Me substituent on the rhenacyclobutadiene ring in **1a** precludes addition of organolithium or similar basic reagents [1]. Wittig reagents probably would also be too basic to undergo addition [29]; however, sulfur-stabilized carbanions (sulfonium ylides), which possess lower basicity, present themselves as suitable candidates for such a reaction. Cleavage of the organic ligand by sulfonium ylides with no deprotonation has been reported to proceed under thermal or photochemical conditions for chromium Fischer carbene complexes [30]. Accordingly, we extended our studies on the chemistry of **1a** to reactions with $Me_2S{=}CHC(O)Ph$ [4] and $Me_2S{=}C(CN)_2$ [5].

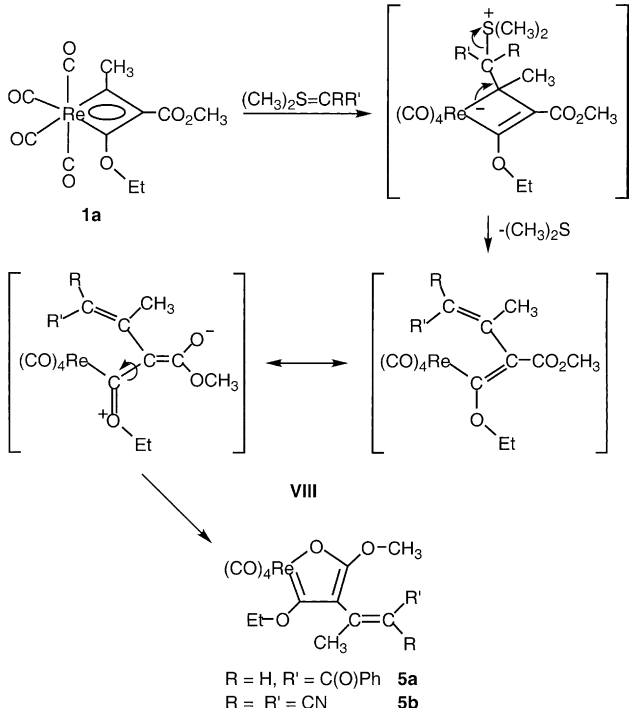
Reaction of **1a** with $Me_2S{=}CHC(O)Ph$ in acetonitrile at reflux temperature was complete in 30 min, and after workup resulted in the isolation of $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}CHC(O)Ph)C(OEt))$ (**5a**) as a yellow oil in 49% yield (Scheme 6). The product undergoes slow decomposition even if kept under argon. The corresponding reaction of **1a** with $Me_2S{=}C(CN)_2$ proceeded



Scheme 6.

more slowly than that with $Me_2S{=}CHC(O)Ph$ and required 6 h to reach completion under similar conditions. Three products were detected by ^1H NMR spectroscopy, but only the major one, $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}C(CN)_2)C(OEt))$ (**5b**), could be isolated (24% yield) after extensive extraction of the crude reaction mixture.

Complexes **5a** and **5b** were characterized by a combination of IR and ^1H and ^{13}C NMR spectroscopic and mass spectrometric techniques. Their ^1H and ^{13}C NMR spectra show striking similarities to those of **3a**, **3b**, and **4** to implicate a rhenafuran structure in each case. For example, ^{13}C resonances of **5a** and **5b** occur at δ 214.7 and 239.8 and at δ 185.1 and 185.5 for $Re{=}C(OEt)$ and *C*OMe, respectively, as expected [19]. Only one double

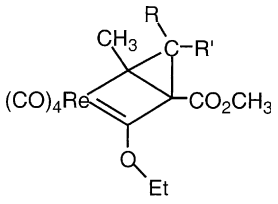


Scheme 7.

[2] As an alternative mechanism, it was suggested by a reviewer that the $CHEt_2$ proton could possibly be transferred to the adjacent carbon via an agostic interaction with Re. The resulting alkene group would most likely be η^2 bound to the Re center, but would be easily displaced by either pyridine or nitrile. The rest of the mechanism is similar to that in Scheme 5.

bond geometry was observed for C(Me)=CHC(O)Ph in **5a**, and the assigned *cis* disposition of Me and H is supported by a ^{1}H NMR nOe experiment (cf. Section 2.5.1).

A proposed mechanism for the reactions of **1a** with $Me_2S{=}CHC(O)Ph$ and $Me_2S{=}C(CN)_2$ ($Me_2S{=}CRR'$) is presented in Scheme 7. It consists of nucleophilic addition of $Me_2S{=}CRR'$ to the Re=C(Me) carbon, formation of intermediate **VIII** by dissociation of the Re–C bond and release of Me_2S, and ring closure to give the rhenafuran structure in **5**. Intermediate **VIII** is strictly analogous to **VII** in Scheme 5. Likewise, the ring closure step occurs as depicted in Scheme 5. An alternative to this pathway involves cyclopropanation reaction between the $ReC(Me){=}C(CO_2Me)$ double bond of **1a** and $Me_2S{=}CRR'$. Sulfur-stabilized carbanions are known to undergo addition to α,β-unsaturated carbonyl compounds to afford cyclopropane products [31]. If one considers **1a** as an α,β-unsaturated ester equivalent, then addition of $Me_2S{=}CRR'$ might yield a highly strained cyclopropane, **IX**, which is likely to rearrange to a rhenafuran product.



IX

4. Summary

In this paper we have reported additional chemical transformations of Fischer rhenacyclobutadiene complexes of the type $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(X))$ (**1**). The new reactions, in a broad sense, fall into two classes. The first class is comprised of reactions with alkynes which lead to the formation of ring-substituted η^5-cyclopentadienylrhenium tricarbonyl products, $Cp^{\ddagger}Re(CO)_3$ (**2**). A number of tetra- and pentasubstituted complexes were synthesized by this methodology through use of various symmetrical and unsymmetrical alkynes as well as a pendant alkynyl group on **1**. A second group of reactions features rearrangement with expansion of the 4-membered rhenacyclobutadiene ring of **1** to a 5-membered rhenafuran ring in product complexes. This transformation is made possible by the presence of a CO_2Me group on C(2) of **1**, and can be effected by nitriles and pyridine on heating, or by use of sulfonium ylides. In the former reactions, $(CO)_4Re(\eta^2\text{-}C(CHR_2)C(CO_2Me)C(OEt))$ ($R_2{=}H_2$ (**1a**), Et_2 (**1d**)) undergo conversion to $(CO)_3(L)Re(\kappa^2\text{-}OC(OMe)C(CH{=}CR_2)C(OEt))$ (L = CO (**3**), py (**4**)), whereas in the latter reactions **1a** and $Me_2S{=}CR'R''$ furnish analogous $(CO)_4Re(\kappa^2\text{-}OC(OMe)C(C(Me){=}CR'R'')C(OEt))$ (**5**).

Acknowledgements

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