Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 2000–2012
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Chemistry of Fischer-type rhenacyclobutadiene complexes. I. Deprotonation, addition/substitution of nucleophilic reagents at α-carbon, and insertion of heteroatoms into rhenium–carbon bonds

Véronique Plantevin [a,1], Andrew Wojcicki [a,*]

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

Received 29 December 2003; accepted 8 March 2004

Abstract

The rhenacyclobutadienes $(CO)_4Re(\eta^2$- C(R)C(CO_2Me)C(OR′)) (**2**) undergo a number of reactions that mirror those of Fischer alkoxycarbene complexes. Thus, $(CO)_4Re(\eta^2$-C(Me)C(CO_2Me)C(OEt)) (**2a**) can be deprotonated by LDA, Na[OBu-*t*], or Na[$CH(CO_2Me)_2$] to give the ylide-like conjugate base $[(CO)_4Re(\eta^2$-C(=CH_2)C(CO_2Me)C(OEt)]$^-$ (**3**), which was isolated as PPN(**3**). Li(**3**) undergoes deuteriation with DCl/D_2O and alkylation with Et_3OPF_6 at ReC=CH_2, with the latter reaction affording $(CO)_4Re(\eta^2$-C(CH_2Et)C(CO_2Me)C(OEt)) (**4**). Repetition of the sequence deprotonation-ethylation on **4** generates $(CO)_4Re(\eta^2$-C($CHEt_2$)C(CO_2Me)C(OEt)) (**5**). The nature of the alkoxy substituent in **2** can be varied by use of the rhenacyclobutenones Na[$(CO)_4Re(\eta^2$-C(R)C(CO_2Me)C(O))] (Na(**1**)) in conjunction with AcCl and R′OH to produce a series of new complexes (R = Ph, R′ = Et (**2b**); R = Me, R′ = CH_2CH=CH_2 (**2c**), $(CH_2)_3$C≡CH (**2d**), Me (**2e**)). Aminolysis of **2a** with the primary and secondary amines $PhNH_2$, $HO(CH_2)_2NH$, *p*-TolNH_2, and Et_2NH yields the aminorhenacyclobutadiene complexes $(CO)_4Re(\eta^2$-C(Me)C(CO_2Me)C(NHR′ or NR'_2)) ($R'_2 = Et_2$ (**6a**); R′ = Ph (**6b**), $(CH_2)_2OH$ (**6c**), *p*-Tol (**6d**)). These complexes display lesser carbene-like character than their alkoxy counterparts **2**, as evidenced by ^1H and ^{13}C NMR spectroscopic properties and lack of reactivity toward LDA by **6a**. Reactions of each **2a** and **6a** with $PPhMe_2$ at low temperature afford $(CO)_4Re(\eta^2$-C(Me)($PPhMe_2$)C(CO_2Me)C(OEt)) (**7**) and $(CO)_3(PPhMe_2)Re(\eta^2$-C(Me)C(CO_2Me)C(NEt_2)) (**9**), respectively, further in agreement with the more carbenoid nature of **2a** than **6a**. **7** undergoes conversion to $(CO)_3(PPhMe_2)Re(\eta^2$-C(Me)C(CO_2Me)C(OEt)) (**8**) upon heating. **2a** reacts with each of $(NH_4)_2[Ce(NO_3)_6]$, DMSO, $EtNO_2/Et_3N$, and Me_3NO under various conditions to afford one or both of the oxygen atom insertion products into the Re=C bonds, $(CO)_4Re(\kappa^2$-OC(Me)C(CO_2Me)C(OEt)) (**10**) and $(CO)_4Re(\kappa^2$-C(Me)C(CO_2Me)C(OEt)O) (**11**). In contrast, no reaction occurred between **2a** and S_8 on heating. However, **6a** was converted to the NH insertion product $(CO)_4Re(\kappa^2$-NHC(Me)C(CO_2Me)C(NEt_2)) (**12**) by the action of $H_2NNH_2 \cdot H_2O$ at 0 °C. 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; Deprotonation reactions; Aminolysis reactions; Insertion reactions

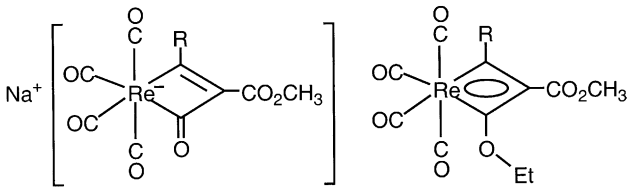
1. Introduction

We have previously reported the synthesis of rhenacyclobutenone complexes Na[$(CO)_4Re(\eta^2$-C(R)C(CO_2Me)C(O))] (Na(**1**)) by reaction of Na[$Re(CO)_5$] with the activated alkynes RC≡CCO_2Me (R = H, Me, CO_2Me) [1,2]. Alkylation of Na(**1**) with Et_3OPF_6 furnished the

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

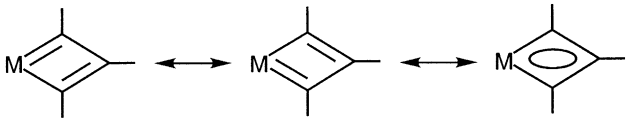
0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.03.026

corresponding rhenacyclobutadiene complexes $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(OEt))$ (**2**).



Na(**1**) **2**

Structural, spectroscopic [1,2] and limited reaction chemistry studies on **2** [1–3] have indicated that these complexes may be regarded as metallacyclobutadiene analogues of Fischer-type carbenes [4], in the same sense that Schrock metallacyclobutadienes [5] are related to Schrock-type carbenes (alkylidenes) [6] (cf. **I** and **II**). Fischer carbene and metallacyclobutadiene complexes generally contain a low oxidation state transition metal in conjunction with carbonyl ligands, are often stabilized by the presence of a heteroatom bonded to carbene carbon, and show electrophilic properties. In contrast, Schrock alkylidene and metallacyclobutadiene complexes incorporate metal in a high formal oxidation state and behave as nucleophiles. [2]



I

metallacyclobutadiene

II

metal carbene/alkylidene

Since their discovery in 1964 [8], Fischer carbene complexes have shown extensive reaction chemistry and are considered to be one of the most versatile reagents in organic synthesis [9,10]. To explore chemical analogies between Fischer carbene and metallacyclobutadiene complexes, we have investigated several aspects of reaction chemistry of **2** and related rhenacyclobutadienes. Reported in this paper are our studies directed at developing further methods of synthesis of Fischer rhenacyclopentadiene complexes and at expanding the scope of their addition/substitution reactions with nucleophiles as well as insertion reactions of heteroatoms into Re=C bonds. The accompanying paper is concerned with reactions of **2** and derivatives with alkynes and sulfonium ylides and with rearrangements induced by nitriles and pyridine [11].

[2] However, some metal carbene/alkylidene complexes show amphiphilic properties [7].

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of air-sensitive compounds were conducted under an atmosphere of dry argon by use of standard procedures [12]. Solvents were dried [13], distilled under argon, and degassed before use. Elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ and Guelph Chemical Laboratories Ltd, London, Ont., Canada. IR and NMR (^1H, ^2H, ^{13}C, and ^{31}P) spectra were obtained as previously described [14,15]. 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. Column chromatography was done on silica gel (Merck grade 60, 230–240 mesh).

2.2. Materials

Reagents were procured from various commercial sources and used as received. A solution of $Na[Re(CO)_5]$ in THF was prepared as described previously [2]. Rhenacyclobutenone $Na[(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(O)]$ (Na(**1a**))) was synthesized according to a procedure reported in the literature [2], but generally on a larger (ca. 4 times) scale, which resulted in the formation of purer product (less polynuclear rhenium carbonyl impurity). The complex $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**2a**) was obtained by treatment of Na(**1a**) with Et_3OPF_6 [2] (Method 1) or with AcCl and EtOH (Method 2, cf. Section 2.4.1.).

2.3. Deprotonation reactions of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**2a**) and deuteriation or alkylation of resultant $M[(CO)_4Re(\eta^2\text{-}C(=CH_2)C(CO_2Me)C(OEt))]$ (M(**3**): M = Li, Na, PPN)

2.3.1. Synthesis of $PPN[(CO)_4Re(\eta^2\text{-}C(=CH_2)C(CO_2Me)C(OEt))]$ (PPN(**3**): $PPN=(Ph_3P)_2N$)

A solution of **2a** (0.349 g, 0.770 mmol) in 20 ml of THF at −78 °C was treated with 1 equivalent of LDA (lithium diisopropylamide) in hexane (0.970 ml, 0.8 M)

to produce an immediate color change to orange. The reaction mixture was stirred at −78 °C for 1 h, at which time complete disappearance of **2a** was observed by IR spectroscopy, and new ν(CO) bands were noted at 2058 (w), 1960 (s), 1901 (s), and 1630 (m) cm^{-1}. One equivalent (0.442 g) of PPNCl was then added and stirring was continued while the mixture was allowed to warm to room temperature. Insoluble matter was removed by filtration, and the orange filtrate was concentrated. Addition of hexane (60 ml) with cooling to 0 °C induced the precipitation of an orange solid which was collected, washed with 20-ml portions of hexane, and dried in vacuo for 24 h. The yield of PPN[$(CO)_4Re(\eta^2$-C(=CH_2)C(CO_2Me)C(OEt))] (PPN(**3**)) was 0.330g (94%). ^{1}H NMR (THF-d_8): δ 7.8–7.2 (m, 30 H, Ph), 6.3 (d, $^2J = 4.5$ Hz, 1 H, =CH_2), 4.67 (d, $^2J = 4.5$ Hz, 1 H, =CH_2), 4.02 (q, $^3J = 7.02$ Hz, 2 H, OCH_2), 3.36 (s, 3 H, CO_2Me), 1.21 (t, $^3J = 7.02$ Hz, 3 H, OCH_2*Me*). The complex decomposes slowly in solution.

2.3.2. Reaction of **2a** with LDA followed by addition of DCl/D_2O

A solution of Li(**3**) in THF at −78 °C was prepared from **2a** (0.349 g, 0.770 mmol) and LDA as described in Section 2.3.1. To this solution was then added ca. 5-fold excess of DCl (20% w/w in D_2O) resulting in the formation of a white precipitate which was removed by filtration. The filtrate was pumped down to dryness, and the residue was extracted with 20-ml portions of hexane. A bright yellow solid, obtained in yields $\geqslant$95% ($\geqslant$0.332 g) upon evaporation of hexane, was spectroscopically characterized as a mixture of **2a** and $(CO)_4Re(\eta^2$-C(Me-d_1)C(CO_2Me)C(OEt)) (up to 87% D incorporation determined by integration). ^{1}H NMR ($CDCl_3$): δ 4.69 (q, $^3J = 7.10$ Hz, 2 H, OCH_2), 3.69 (s, 3 H, CO_2Me), 3.06 (s, 3 H, ReCMe), 3.02 (t, $^2J_{DH} = 2.2$ Hz, 2 H, ReCCH_2D), 1.58 (t, $^3J = 7.10$ Hz, 3 H, OCH_2*Me*). ^{2}H NMR (CH_2Cl_2): δ 3.04 (t, $^2J_{DH} = 2.3$ Hz, CH_2D). In some trials, **2a**-d_2 was observed in minute amounts.

2.3.3. Reaction of **2a** with Na[$CH(CO_2Me)_2$] followed by addition of DCl/D_2O

A freshly prepared solution of Na[$CH(CO_2Me)_2$] (0.039 g, 0.300 mmol) in 5 ml of THF was slowly added to **2a** (0.113 g, 0.250 mmol) in 15 ml of THF at 0 °C. The reaction mixture was stirred for 30 min as its color became deep yellow and its IR spectrum indicated that all starting material had reacted. The solution was concentrated to 2 ml, and hexane (50 ml) was added to induce the precipitation of Na(**3**), characterized by ^{1}H NMR spectroscopy (cf. Section 2.3.1). Complex Na(**3**) was then treated with DCl/D_2O as described in Section 2.3.2 for Li(**3**). A similar workup yielded a mixture of **2a** and **2a**-d_1 (0.096 g).

2.3.4. Synthesis of $(CO)_4Re(\eta^2$-C(CH_2Et)C(CO_2Me)C(OEt)) (**4**)

A solution of **2a** (0.205 g, 0.450 mmol) in 15 ml of THF at −78 °C was treated with 1 equivalent (0.135 ml, 1.5 M) of LDA in hexane. The reaction and workup were conducted as described in Section 2.3.1. After the volatiles were removed under reduced pressure, the brown oil was dissolved in 15 ml of CH_2Cl_2. A solution of Et_3OPF_6 (0.112 g, 1 equivalent) in 5 ml of CH_2Cl_2 was added, and the mixture was stirred at room temperature for 1 h. The solvent was evaporated, and the residue was extracted with 10 ml of hexane. Filtration and removal of the solvent from the filtrate afforded a yellow oil (0.109 g) that contained **2a** and the alkylated products, mainly $(CO)_4Re(\eta^2$-C(CH_2Et)C(CO_2Me)C(OEt)) (**4**). Repeated chromatography on silica gel afforded (29% yield) pure yellow **4**. ^{1}H NMR ($CDCl_3$): δ 4.69 (q, $^3J = 7.2$ Hz, 2 H, OCH_2), 3.70 (s, 3 H, CO_2Me), 3.17 (t, $^3J = 7.3$ Hz, 2 H, CH_2Et), 1.85 (sept, $^3J \sim 7.5$ Hz, 2 H, CH_2CH_2Me), 1.58 (t, $^3J = 7.2$ Hz, 3 H, OCH_2*Me*), 1.05 (t, $^3J = 7.3$ Hz, 3 H, CH_2CH_2*Me*). ^{13}C{1H} NMR ($CDCl_3$): δ 253.6 (s, Re*C*OEt), 243.1 (s, Re*C*CH_2Et), 193.4, 191.9 (2 s, *cis*-CO), 190.1 (s, *trans*-CO), 159.2 (s, *C*O_2Me), 155.1 (s, *C*CO_2Me), 79.8 (s, OCH_2), 50.6 (s, CO_2*Me*), 47.8 (s, *C*H_2Et), 24.1 (s, CH_2*C*H_2Me), 14.8 (s, OCH_2*Me*), 14.4 (s, CH_2CH_2*Me*). MS (EI): *m*/*z* 482 (M^+), 454 ($M^+ - CO$), 426 ($M^+ - 2CO$), 398 ($M^+ - 3CO$), 370 ($M^+ - 4CO$), 339 ($M^+ - 4CO - OMe$), 311 ($M^+ - 4CO - CO_2Me$).

2.3.5. Synthesis of $(CO)_4Re(\eta^2$-C($CHEt_2$)C(CO_2Me)C(OEt)) (**5**)

The sequence deprotonation of **2a** (0.204 g, 0.450 mmol) in THF with 1 equivalent of LDA to generate Li(**3**) followed by addition of Et_3OPF_6 (0.112 g, 1 equivalent) was carried out as described in Section 2.3.1. The resultant impure **4** was then similarly subjected to sequential treatment with LDA (0.5 equivalent) and Et_3OPF_6 (0.056 g). Solvent was removed from the reaction mixture, and the crude product was dissolved in 1–2 ml of 2:1 hexane/CH_2Cl_2 and loaded on top of a silica gel column packed with the same solvent mixture. The product was eluted off as a homogeneous yellow band. The dialkylated complex $(CO)_4Re(\eta^2$-C($CHEt_2$)C(CO_2Me)C(OEt)) (**5**) was isolated as a yellow oil that solidified when subjected to pumping. Yield: 0.060 g (44%). IR (hexane): ν(CO) 2079 (w), 1993 (s), 1948 (s), 1719 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.71 (q, $^3J = 7.2$ Hz, 2 H, OCH_2), 3.70 (s, 3 H, CO_2Me), 3.53 (m, 1 H, C*H*Et_2), 1.60 (t, $^3J = 7.15$ Hz, 3 H, OCH_2*Me*), 1.77–1.26 (m, 4 H, CHCH_2Me), 0.87 (t, $^3J = 7.4$ Hz, 6 H, $CHCH_2$*Me*). ^{13}C NMR ($CDCl_3$): δ 255.7 (s, Re*C*OEt), 242.9 (s, Re*C*CHEt_2), 193.4, 191.4 (2s, *cis*-CO), 190.3 (s, *trans*-CO), 159.6 (s, *C*O_2Me), 156.7 (s, C*C*O_2Me), 79.6 (t, OCH_2), 54.3 (d, *C*HEt_2), 50.5 (q, CO_2*Me*), 29.3 (t, CH*C*H_2Me), 14.8 (q, OCH_2*Me*), 12.5 (q, $CHCH_2$*Me*).

MS (EI): *m/z* 510 (M^+), 482 ($M^+ - CO$). Anal. Found: C, 37.64; H, 4.00%. Calc. for $C_{16}H_{19}O_7Re$: C, 37.72; H, 3.76%.

2.4. Reactions of Na[(CO)$_4$Re(η^2-C(R)C(CO$_2$Me)C(O))] (Na (**1**)) with AcCl/R′OH

2.4.1. Synthesis of (CO)$_4$Re(η^2-C(Me)C(CO$_2$Me)C(OEt)) (**2a**) (Method 2)

Rhenacyclobutenone Na[(CO)$_4$Re(η^2-C(Me)C(CO$_2$Me)C(O))] (Na(**1a**)), obtained by reduction of $Re_2(CO)_{10}$ (1.00 g, 1.53 mmol) with sodium (ca. 0.5 g) followed by treatment with an excess of MeC≡CCO$_2$Me (0.307 ml, 0.300 g, 3.06 mmol) [1,2], was added to 20 ml of CH_2Cl_2, and the resulting suspension was cooled to −15 °C and treated with AcCl (0.130 ml, 0.118 g, 1 equivalent). The mixture turned bright yellow within minutes. After 20 min of stirring, EtOH (0.359 ml, 0.432 g, 2 equivalents) was added, and the contents were allowed to warm to room temperature. Insoluble material was removed by filtration, and the filtrate was evaporated to dryness. Extraction of the residue with 20-ml portions of hexane and removal of solvent resulted in the isolation of (CO)$_4$Re(η^2-C(Me)C(CO$_2$Me)C(OEt)) (**2a**) as a bright yellow solid in 80% yield (0.650 g). Further purification can be achieved by chromatography on silica gel with 1:1 hexane/CH_2Cl_2 as the eluent. Spectroscopic properties of the product matched those of **2a** reported in the literature [2].

2.4.2. Synthesis of (CO)$_4$Re(η^2-C(Ph)C(CO$_2$Me)C(OEt)) (**2b**) (Method 2)

The precursor of **2b**, Na[(CO)$_4$Re(η^2-C(Ph)C(CO$_2$Me)(C(O))] (Na(**1b**)), was prepared by an adaptation of the general procedure reported for Na(**1a**) [2], from $Re_2(CO)_{10}$ (2.00 g, 3.06 mmol), sodium (ca. 1.0 g), and PhC≡CCO$_2$Me (0.0850 ml, 0.981 g, 1 equivalent). It was isolated as bright orange needles (2.50 g, 80% yield) after recrystallization from Et$_2$O/THF/hexane at room temperature. IR (THF): *ν*(CO) 2054 (w), 2005 (s), 1940 (s), 1904 (m), 1608 (w) cm^{-1}. ^{1}H NMR (acetone-d$_6$): *δ* 7.4–7.2 (m, 5 H, Ph), 3.63 (s, 3 H, Me). ^{13}C{^{1}H} NMR (acetone-d$_6$): 225.7 (s, ReC=O), 202.4 (s, Re*C*Ph), 199.6, 197.4, 196.9 (3s, CO), 161.7 (s, *C*O$_2$Me), 149.3 (s, *C*CO$_2$Me), 128.1, 127.8, 127.0, 126.6 (4s, Ph), 49.6 (s, CO$_2$*Me*).

The synthesis of **2b** was carried out in a manner strictly analogous to that of **2a** (Section 2.4.1). By using 0.500 g (0.980 mmol) of Na(**1b**), 1 equivalent of AcCl (0.070 ml, 0.052 g), and an excess of EtOH (0.200 ml), (CO)$_4$Re(η^2-C(Ph)C(CO$_2$Me)C(OEt)) (**2b**) was obtained as a bright orange solid in 77% yield (0.387 g, 0.760 mmol). IR (hexane): *ν*(CO) 2079 (w), 1995 (s), 1946 (s), 1725 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 7.49–7.41 (m, 5 H, Ph), 4.76 (q, ^3J = 7.2 Hz, 2 H, OC*H*$_2$Me), 3.64 (s, 3 H, CO$_2$Me), 1.63 (t, ^3J = 7.2 Hz, 3 H, OCH$_2$*Me*). ^{13}C{^{1}H} NMR (CDCl$_3$): *δ* 243.5 (s, Re*C*OEt), 227.4 (s, Re*C*Ph), 193.3, 191.5 (2s, *cis*-CO), 189.9 (s, *trans*-CO), 160.5 (s, *C*O$_2$Me), 152.1 (s, *C*CO$_2$Me), 145.5 (s, ipso C of Ph), 130.6 (s, p C of Ph), 128.6, 128.1 (2s, other C of Ph), 79.7 (s, O*C*H$_2$Me), 50.8 (s, CO$_2$*Me*), 14.8 (s, OCH$_2$*Me*). MS (EI): *m/z* 516 (M^+), 488 ($M^+ - CO$), 460 ($M^+ - 2CO$), 429 ($M^+ - 2CO - OMe$), 401 ($M^+ - 3CO - OMe$).

2.4.3. Synthesis of (CO)$_4$Re(η^2-C(Me)C(CO$_2$Me)C(OCH$_2$CH=CH$_2$)) (**2c**) (Method 2)

Rhenacyclobutenone Na(**1a**), obtained from 0.250 g (0.385 mmol) of $Re_2(CO)_{10}$ and an excess of each sodium and MeC≡CCO$_2$Me [2], was reacted with AcCl (0.055 ml, 0.060 g, 1.06 equivalents) and CH$_2$=CHCH$_2$OH (0.055 ml, 0.045 g, 1 equivalent) as described in Section 2.4.1 for **2a**. Product (CO)$_4$Re(η^2-C(Me)C(CO$_2$Me)C(OCH$_2$CH=CH$_2$)) (**2c**) was isolated as a yellow crystalline solid in 76% yield (0.270 g). IR (hexane): *ν*(CO) 2080 (w), 1994 (s), 1949 (s), 1717 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 6.11 (m, $^3J_{cis}$ = 10.6 Hz, $^3J_{trans}$ = 17.2 Hz, $^3J_{allylic}$ = 4.7 Hz, 1 H, CH$_2$C*H*=CH$_2$), 5.52 (m, $^3J_{trans}$ = 17.2 Hz, $^2J_{gem}$ = 1.5 Hz, 1 H, CH$_2$CH=C*H*$_2$), 5.42 (m, 1 H, CH$_2$CH=C*H*$_2$), 5.13 (m, $^4J_{allylic}$ = 0.7 Hz, 2 H, C*H*$_2$CH=CH$_2$), 3.70 (s, CO$_2$Me), 3.07 (s, ReCMe) (*J*'s determined by selective decoupling). ^{13}C{^{1}H} NMR (CDCl$_3$): *δ* 249.8, 244.5 (2s, Re*C*OEt, Re*C*Me), 193.1, 192.3, 189.9 (3s, CO) 159.9 (s, *C*O$_2$Me), 155.7 (*C*CO$_2$Me), 130.6 (s, OCH$_2$*C*H=CH$_2$), 120.2 (s, OCH$_2$CH=*C*H$_2$), 83.6 (s, O*C*H$_2$CH=CH$_2$), 50.6 (s, CO$_2$*Me*), 35.8 (s, ReC*Me*). MS (FAB): *m/z* 467 ($M^+ + 1$), 452 ($M^+ + 1 - Me$), 369 ($M^+ + 1 - CO - OC_3H_5$), 341 ($M^+ + 1 - 2CO - OC_3H_5$). Anal. Found: C, 33.4; H, 2.53%. Calc. for $C_{13}H_{11}O_7Re$: C, 33.55; H, 2.38%.

2.4.4. Synthesis of (CO)$_4$Re(η^2-C(Me)C(CO$_2$Me)C(O(CH$_2$)$_3$C≡CH)) (**2d**) (Method 2)

Rhenacyclobutenone Na(**1a**), obtained from 0.250 g (0.385 mmol) of $Re_2(CO)_{10}$ and an excess of each sodium and MeC≡CCO$_2$Me [2], was reacted with AcCl (0.055 ml, 0.060 g, 1 equivalent) and 4-pentyn-1-ol (0.070 ml, 0.065 g, 1 equivalent) as described in Section 2.4.1 for **2a**. Product (CO)$_4$Re(η^2-C(Me)C(CO$_2$Me)C(O(CH$_2$)$_3$C≡CH)) (**2d**) was isolated in 83% yield (0.312 g) after recrystallization from hexane. IR (hexane): *ν*(CO) 2066 (w), 2011 (m), 1982 (s), 1950 (s); *ν*(C≡C) 1995 cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 4.73 (t, ^3J = 6.31 Hz, 2 H, OCH$_2$), 3.69 (s, 3 H, CO$_2$Me), 3.06 (s, 3 H, ReCMe), 2.44 (td, ^3J = 6.8 Hz, ^4J = 2.5 Hz, 2 H, C*H*$_2$C≡CH), 2.16 (quint, ^3J = 6.8 Hz, 2 H, CH$_2$C*H*$_2$CH$_2$), 2.03 (t, ^3J = 2.5 Hz, 1 H, C≡CH). ^{13}C{^{1}H} NMR (CDCl$_3$): *δ* 249.0, 244.1 (2s, Re*C*OCH$_2$, Re*C*Me), 193.1, 192.1 (2s, *cis*-CO), 190.0 (s, *trans*-CO), 158.9 (s, *C*O$_2$Me), 155.6 (s, *C*CO$_2$Me), 82.1 (s, OCH$_2$), 82.0 (s, *C*≡CH), 69.9 (s, C≡*C*H), 50.5 (s, CO$_2$*Me*), 36.6 (s, ReC*Me*), 27.8 (s, CH$_2$*C*H$_2$CH$_2$), 14.8 (s,

$CH_2C{\equiv}CH$). MS (FAB): *m/z* 492 (M^+), 464 ($M^+ - CO$), 436 ($M^+ - 2CO$), 380 ($M^+ - 4CO$).

2.4.5. Synthesis of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OMe))$ (**2e**) (Method 2)

Product $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OMe))$ (**2e**) was obtained as a green solid in 76% yield from Na(**1a**), AcCl, and MeOH by a procedure similar to that described in Section 2.4.1 for **2a**. IR (hexane): *v*(CO) 2081 (w), 1995 (s), 1951 (s), 1719 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.44 (s, 3 H, OMe), 3.71 (s, 3 H, CO_2Me), 3.08 (s, 3 H, ReCMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 249.6, 246.6 (2s, Re*C*OMe, Re*C*Me), 193.2, 192.2 (2s, *cis*-CO), 189.9 (s, *trans*-CO), 158.9 (s, *C*O_2Me), 155.4 (s, *C*CO_2Me), 69.0 (s, OMe), 50.6 (s, CO_2*Me*), 35.8 (s, ReC*Me*). Anal. Found: C, 30.23; H, 2.06%. Calc. for $C_{11}H_9O_7Re$: C, 30.07; H, 2.06%.

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

2.5.1. Synthesis of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NEt_2))$ (6a)

A solution of **2a** (0.480 g, 1.06 mml) in 20 mol of THF was treated with 1 equivalent of Et_2NH (0.11 ml, 0.078 g), and the mixture was stirred at 0 °C. After 2 h, the IR spectrum (*v*(CO)) showed that **2a** had been consumed. Evaporation of the solvent yielded a bright yellow oil which was dissolved in 1 ml of CH_2Cl_2, layered with hexane, and stored at −23 °C for 2 h. The product diffused into hexane and was obtained therefrom by evaporation. The yield of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NEt_2))$ (**6a**) ranged from 74% to 85% in various trials. IR (hexane): *v*(CO) 2066 (w), 2004 (s), 1974 (s), 1924 (m), 1712 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.71 (s, 3 H, CO_2Me), 3.70 (m, 4 H, NCH_2Me), 2.69 (s, 3 H, ReCMe), 1.37 (t, ^3J = 7.2 Hz, 3 H, NCH_2Me), 1.26 (t, ^3J = 7.2 Hz, 3 H, NCH_2Me). ^{13}C NMR ($CDCl_3$): δ 210.1 (s, Re*C*NEt_2), 193.7 (s, Re*C*Me), 193.2, 191.3, 191.1 (3s, CO), 163.7 (s, *C*O_2Me), 147.9 (s, *C*CO_2Me), 56.8 (q, CO_2*Me*), 50.8, 47.8 (2t, NCH_2Me), 31.3 (q, ReC*Me*), 14.0, 13.7 (2q, NCH_2Me). MS (FAB): *m/z* 481 (M^+), 453 ($M^+ - CO$), 425 ($M^+ - 2CO$).

2.5.2. Synthesis of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NHPh))$ (6b)

Complex **6b** was isolated in 70–86% yield as a green solid from reaction of **2a** (0.376 g, 0.83 mmol) with $PhNH_2$ (0.075 ml, 0.035 g, 1 equivalent) by use of a procedure similar to that described in Section 2.5.1. IR (hexane): *v*(CO) 2060 (w), 2002 (s), 1975 (s), 1935 (m), 1710 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4 (m, 5 H, Ph), 3.77 (s, 3 H, CO_2Me), 2.99 (s, 3 H, ReCMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 230.5 (s, Re*C*NHPh), 197.4 (s, Re*C*Me), 193.6, 191.4, 190.9 (3s, CO), 162.8 (s, *C*O_2Me), 145.8(s, *C*CO_2Me), 140.4 (s, ipso C of Ph), 129.4, 128.0, 123.1 (3s, other C of Ph), 50.8 (s, CO_2*Me*), 33.5 (s, ReC*Me*). MS (FAB): *m/z* 501 (M^+), 473 ($M^+ - CO$), 417 ($M^+ - 3CO$), 389 ($M^+ - 4CO$).

2.5.3. Synthesis of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NH(CH_2)_2OH))$ (6c)

Complex **6c** was isolated as a yellow-green solid from reaction of **2a** (0.254 g, 0.560 mmol) and 2-aminoethanol (0.034 ml, 0.034 g, 1 equivalent) by use of a procedure similar to that described in Section 2.5.1. IR (hexane): *v*(CO) 2060 (w), 2000 (s), 1975 (s), 1930 (m), 1675 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.94 (t, 2 H, OCH_2), 3.72 (s, 3 H, CO_2Me), 3.69 (m, 2 H, NCH_2), 2.92 (s, 3 H, ReCMe), 1.88 (br s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 224.1 (s, Re*C*$NHCH_2$), 197.8 (s, Re*C*Me), 193.5, 192.7 (2s, *cis*-CO), 190.1 (s, *trans*-CO), 162.5 (s, *C*O_2Me), 145.0 (s, *C*CO_2Me), 61.8 (s, OCH_2), 58.9 (s, NCH_2), 50.4 (s, CO_2*Me*), 32.7 (s, ReC*Me*). MS (FAB): *m/z* 471 ($M^+ + 2$), 442 ($M^+ - CO + 1$), 414 ($M^+ - 2CO + 1$), 386 ($M^+ - 3CO + 1$), 358 ($M^+ - 4CO + 1$).

2.5.4. Synthesis of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NHTol\text{-}p))$ (6d)

Complex **6d** was isolated in 95% yield as a green solid from reaction of **2a** (0.100 g, 0.221 mmol) and *p*-toluidine (0.024 g, 1 equivalent) by use of a procedure similar to that described in Section 2.5.1. IR (THF): *v*(CO) 2052 (w), 1953 (s), 1914 (s), 1651 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 12.31 (br s, 1 H, NH), 7.4–7.3 (m, 4 H, C_6H_4), 3.78 (s, 3 H, CO_2Me), 2.99 (s, 3 H, ReCMe), 2.41 (s, 3 H, C_6H_4*Me*). ^{13}C NMR ($CDCl_3$): δ 229.8 (s, Re*C*NTol), 196.4 (s, Re*C*Me), 193.7, 191.6 (2s, *cis*-CO), 191.0 (s, *trans*-CO), 162.9 (s, *C*O_2Me), 145.8 (s, *C*CO_2Me), 138.0, 137.9 (2s, C of Ph), 130.0, 122.8 (2d, CH of Ph), 50.5 (q, CO_2*Me*), 33.4 (q, ReC*Me*), 21.1 (q, C_6H_4*Me*). MS (EI): *m/z* 515 (M^+). Anal. Found: C, 39.86; H, 2.95%. Calc. for $C_{17}H_{14}NO_6Re$: C, 39.69; H, 2.74%.

2.6. Reactions of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(X))$ ($X = OEt$ (**2a**), NEt_2 (**6a**)) with $PPhMe_2$

2.6.1. Synthesis of $(CO)_4Re(\eta^2\text{-}C(Me)(PPhMe_2)C(CO_2Me)C(OEt))$ (7)

To a solution of **2a** (0.117 g, 0.258 mmol) in 10 ml of CH_2Cl_2 at −78 °C was added by syringe $PPhMe_2$ (0.058 ml, 0.054 g, 1 equivalent). The yellow color faded as the solution was stirred for 1 h. The solvent was then removed under reduced pressure at low temperature. The residue was purified by dissolution in 1 ml of 1:1 Et_2O/THF, layering with hexane, and cooling at −23 °C for 3 days. The product $(CO)_4Re(\eta^2\text{-}C(Me)(PPhMe_2)C(CO_2Me)C(OEt))$ (**7**) goes into solution while impurities oil out; it was isolated upon removal of the solvent. Yield: 0.122 g (53%). IR (THF): *v*(CO) 2059 (m), 1969

(s), 1943 (s), 1919 (s), 1649 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.68–7.53 (m, 5 H, Ph), 4.01 (q, $^3J=$ 7.1 Hz, 2 H, OCH_2Me), 3.66 (s, 3 H, CO_2Me), 2.28 (d, $^3J_{PH}=19.9$ Hz, 3 H, ReCMe), 2.10 (d, $^2J_{PH}=11.8$ Hz, 3 H, PMe), 1.89 (d, $^2J_{PH}=12.07$ Hz, 3 H, PMe), 1.36 (t, $^3J=$ 7.1 Hz, 3 H, OCH_2Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 195.1 (d, $^3J_{PC}=17.7$ Hz, Re*C*OEt), 194.4, 191.1, 190.8, 189.9 (4s, CO), 164.6 (s, CO_2Me), 133–129 (m, Ph), 114.0 (d, $^2J_{PC}=5.5$ Hz, CCO_2Me), 73.4 (s, OCH_2Me), 50.3 (s, CO_2Me), 27.2 (d, $^2J_{PC}=6.6$ Hz, ReC*Me*), 15.2 (s, OCH_2Me), 10.9 (d, $^1J_{PC}=48.3$ Hz, PMe), 8.2 (d, $^1J_{PC}=62.2$ Hz, PMe), −4.3 (d, $^1J_{PC}=30.5$ Hz, ReCP). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.34 (s). MS (FAB): *m/z* 592 (M^+).

2.6.2. Conversion of 7 to $(CO)_3(PPhMe_2)Re(\eta^2$-C(Me)C(CO_2Me)C(OEt)) (8)

A solution of **7** (0.122 g, 0.206 mmol) in 15 ml of THF was maintained at reflux temperature for 1 h. The solvent was then evaporated, and the residue was extracted with hexane. The yellow oil obtained by evaporation of the extracts solidified upon storage for 10 h. Yield of $(CO)_3(PPhMe_2)Re(\eta^2$-C(Me)C(CO_2Me) C(OEt)) (**8**): 0.090 g (80%). IR (hexane): *v*(CO) 2007 (s), 1939 (s), 1904 (s), 1708 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4–7.2 (m, 5 H, Ph), 4.37 (q, $^3J=7.2$ Hz, 2 H, OCH_2Me), 3.63 (s, 3 H, CO_2Me), 2.73 (d, $^4J_{PH}=1.8$ Hz, 3 H, ReCMe), 1.86–1.80 (overlapping 2d, $^2J_{PH}\sim{}^2J_{PH}\sim9$ Hz, 6 H, PMe_2), 1.43 (t, $^3J=7.2$ Hz 3 H, OCH_2Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 258.6, 252.9 (2d, $^2J_{PC}={}^2J_{PC}=12.2$ Hz, Re*C*OEt, Re*C*Me), 200.8 (d, $^2J_{PC}=8.2$ Hz, CO *cis* to P), 199.3 (d, $^2J_{PC}=7.2$ Hz, CO *cis* to P), 197.6 (d, $^2J_{PC}=58.3$ Hz, CO *trans* to P), 159.1 (d, $^4J_{PC}=3.8$ Hz, CO_2Me), 152.8 (d, $^3J_{PC}=8.4$ Hz, CCO_2Me), 136.7 (d, $^1J_{PC}=43.8$ Hz, ipso C of Ph), 130-128 (m, other C of Ph), 78.6 (s, OCH_2Me), 50.0 (s, CO_2Me), 34.7 (s, Re*C*Me), 17.2 (d, $^1J_{PC}=31.3$ Hz, PMe), 16.2 (d, $^1J_{PC}=30.9$ Hz, PMe), 14.6 (s, OCH_2Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −26.17 (s). MS (FAB): *m/z* 564 (M^+).

2.6.3. Synthesis of $(CO)_3(PPhMe_2)Re(\eta^2$-C(Me)C(CO_2Me)C(NEt_2)) (9)

To a solution of **6a** (0.197 g, 0.410 mmol) in 5 ml of CH_2Cl_2 at −78 °C was added by syringe 1 equivalent of $PPhMe_2$ (0.067 ml, 0.057 g), and the reaction mixture was stirred at low temperature for 2 h. The solvent was then removed under reduced pressure, and the remaining oil was treated with 5 ml of hexane at −78 °C. Complex $(CO)_3(PPhMe_2)Re(\eta^2$-C(Me)C(CO_2Me)C(NEt_2)) (**9**) precipitated out and was filtered off and washed with hexane. Yield: 0.042 g (18%). No attempt was made to obtain further product from the supernatant solution. IR (hexane): *v*(CO) 2000 (m), 1923 (s), 1890 (s), 1680 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.6–7.1 (m, 5 H, Ph), 3.68 (s, 3 H, CO_2Me), 3.48 (q, $^3J=7.2$ Hz, 2 H, NCH_2Me), 3.37 (m, 2 H, NCH_2Me), 2.43 (d, $^4J_{PH}=2.0$ Hz, 3 H, ReCMe), 1.78 (d, $^2J_{PH}=7.8$ Hz, 3 H, PMe), 1.72 (d, $^2J_{PH}=7.8$ Hz, 3 H, PMe), 1.32 (t, $^3J=$ 7.2 Hz, 3 H, NCH_2Me), 1.15 (t, $^3J=$ 7.2 Hz, 3 H, NCH_2Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 223.1 (d, $^2J_{PC}=13.1$ Hz, Re*C*NEt_2), 201.4 (d, $^2J_{PC}=12.0$ Hz, Re*C*Me), 201.1 (d, $^2J_{PC}=7.8$ Hz, CO *cis* to P), 200.1 (d, $^2J_{PC}=7.1$ Hz, CO *cis* to P), 197.6 (d, $^2J_{PC}=61.6$ Hz, CO *trans* to P), 163.9 (s, CO_2Me), 145.1 (d, $^3J_{PC}=8.5$ Hz, CCO_2Me), 137.9 (d, $^1J_{PC}=40.1$ Hz, ipso C of Ph), 129.8–128.1 (m, other C of Ph), 55.3 (s, NCH_2Me), 50.5 (s, CO_2Me), 46.9 (s, NCH_2Me), 30.6 (s, ReC*Me*), 16.6 (d, $^1J_{PC}=30.1$ Hz, PMe), 15.6 (d, $^1J_{PC}=29.5$ Hz, PMe), 13.7, 13.1 (2s, NCH_2Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −25.2 (s). Anal. Found: C, 42.79; H, 4.50%. Calc. for $C_{21}H_{27}O_5NPRe$: C, 42.70; H, 4.61%.

2.7. Reactions of $(CO)_4Re(\eta^2$-C(Me)C(CO_2Me) C(OEt)) (2a) with oxygen-transfer reagents

2.7.1. Reaction of 2a with $EtNO_2/Et_3N$

A solution of **2a** (0.250 g, 0.55 mmol) in 15 ml of THF was treated with an equimolar mixture of $EtNO_2$ (0.040 ml, 0.55 mmol) and Et_3N (0.084 ml, 0.55 mmol). The contents were stirred overnight at room temperature, and the solvent was evaporated under reduced pressure. The residue was extracted with 10-ml portions of hexane, and the extracts were evaporated to afford 0.211 g of a yellow oil which was shown by ^1H NMR spectroscopy to be a mixture of unreacted **2a** and known [2] $(CO)_4Re(\kappa^2$-OC(Me)C(CO_2Me)C(OEt)) (**10**). The two complexes were separated by column chromatography using hexane to elute **2a**, and CH_2Cl_2 to elute **10**. The latter was isolated in 43% yield (0.110 g) by evaporation of the solvent and characterized by comparison of its IR, ^1H and $^{13}C\{^1H\}$ NMR, and MS FAB data with those reported earlier [2].

2.7.2. Reaction of 2a with $(NH_4)_2[Ce(NO_3)_6]$ in acetone at 0 °C

To a solution of **2a** (0.050 g, 0.11 mmol) in 5 ml of acetone at 0 °C was added $(NH_4)_2[Ce(NO_3)_6]$ (0.18 g, 0.33 mmol), also in 5 ml of acetone at the same temperature. The reaction mixture was stirred at 0 °C for 6 h and then allowed to warm to room temperature overnight. The solvent was removed under reduced pressure, and the crude product was extracted with 10 ml of CH_2Cl_2. Column chromatography eluting with CH_2Cl_2 followed by Et_2O afforded a yellow oil after removal of the solvent. A ^1H NMR spectrum of the oil showed it to contain **10** and $(CO)_4Re(\kappa^2$-C(Me)C(CO_2Me)C(OEt)O) (**11**), also previously reported [2], in a 7:1 ratio, respectively. A similar ratio was observed when 1 equivalent of $(NH_4)_2[Ce(NO_3)_6]$ was used under the same conditions.

*2.7.3. Reaction of **2a** with $(NH_4)_2[Ce(NO_3)_2]$ in acetone at reflux temperature*

A solution of **2a** (0.050 g, 0.11 mmol) and $(NH_4)_2[Ce(NO_3)_6]$ (0.18 g, 0.33 mmol) in 10 ml of acetone was kept at reflux temperature for 1 h. It was then allowed to cool to room temperature and treated as described in Section 2.7.2. A 4:1 ratio **10/11** was shown by ^{1}H NMR spectroscopy.

*2.7.4. Reaction of **2a** with Me_2SO (DMSO)*

A solution of **2a** (0.050 g, 0.11 mmol) in 0.5 ml of DMSO-d_6 at ambient temperature was monitored by ^{1}H NMR spectroscopy. After 1 h, a mixture of **2a**, **10**, and **11** (2.6:2.3:1.0 ratio) was observed, and after 5 h, only **10** and **11** (3:1 ratio) were noted. Solvent was then removed, and the residue was extracted with hexane. A mixture of **10** and **11** (same ratio) was isolated.

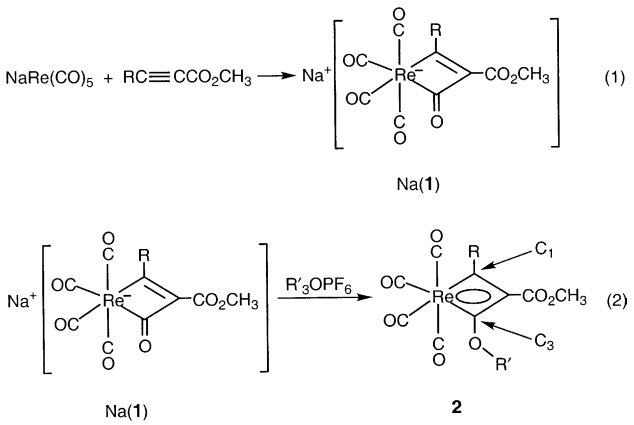
*2.8. Reaction of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NEt_2))$ (**6a**) with hydrazine monohydrate*

To a solution of **6a** (0.192 g, 0.400 mmol) in 10 ml of THF at 0 °C was added $H_2NNH_2 \cdot H_2O$ (0.020 ml, 0.020 g, 0.40 mmol), and the resulting mixture was stirred for 24 h as it warmed to room temperature. After evaporation of the solvent, the residue was extracted with hexane. Removal of hexane afforded an oil, which slowly crystallized under vacuum to give $(CO)_4Re(\kappa^2\text{-}(NHC(Me)C(CO_2Me)C(NEt_2))$ (**12**) as a bright yellow solid in 84% yield (0.166 g). IR (hexane): ν(NH) 3380 (w); ν(CO) 2087 (s), 1990 (s), 1938 (s); ν(CN) 1685 (m, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.85 (br s, 1 H, NH), 3.65 (s, 3 H, CO_2Me), 3.63 (q, ^3J = 7.1 Hz, 4 H, NCH_2Me), 2.25 (s, 3 H, NCMe), 1.22 (t, ^3J = 7.1 Hz, 6 H, NCH_2Me). (nOe: irradiation of signal at δ 2.25 resulted in a 4.4% enhancement of signal at δ 5.85). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 218.4 (s, ReCN), 192.4, 190.8, 187.2 (3s, CO), 186.7 (s, NCMe), 168.5 (s, CO_2Me), 113.4 (s, CCO_2Me), 52.3 (s, NCH_2Me), 50.5 (s, CO_2Me), 26.1 (s, NCMe), 14.3 (s, NCH_2Me). MS (EI): *m/z* 496 (M^+), 468 ($M^+ - CO$), 440 ($M^+ - 2CO$). Anal. Found: C, 33.88; H, 3.66, N, 5.54%. Calc. for $C_{14}H_{17}N_2O_6Re$: C, 33.93; H, 3.46; N, 5.65%.

3. Results and discussion

3.1. General considerations

As stated in the Introduction, at the start of this investigation the synthetic pathway to the subject rhenacyclobutadiene complexes **2** consisted of the two steps presented in Scheme 1. The first reaction requires that the alkyne contain at least one electron-withdrawing group. Accordingly, rhenacyclobutenone complexes Na(**1**) have been obtained from $Na[Re(CO)_5]$ and



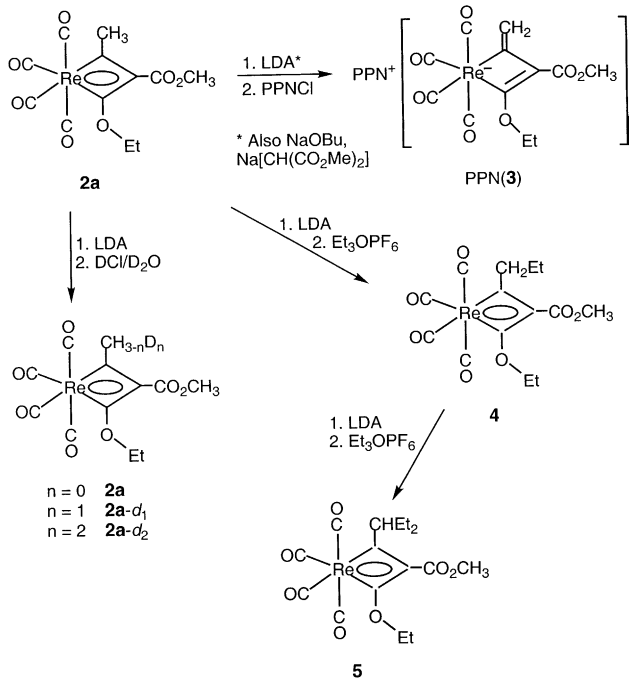
Scheme 1.

$RC{\equiv}CCO_2Me$ where R = H, Me, CO_2Me [1,2] and, in this study, Ph (Section 3.4.2), as well as from $Na[Re(CO_5]$ and $EtO_2CC{\equiv}CCO_2Et$ [16]. Step 2, viz., conversion of Na(**1**) to **2**, could be effected successfully only by use of Et_3OPF_6. Weaker alkylating reagents, e.g., MeI, are unreactive [2,16]. Thus, the preparative route in Scheme 1 provides access to few rhenacyclobutadienes **2**; in addition, it makes use of the hazardous and commercially very limited oxonium salts. We therefore sought other ways to modify the substituents R on C(1) and OR′ on C(3).

In the context of our investigation to develop chemistry of Fischer rhenacyclobutadienes for comparison with that of Fischer carbene complexes, we set out to explore electrophilic properties of C(1) (and its C_α) and C(3) in **2**. Nucleophilic substitutions at these carbon centers expand the range of available rhenacyclobutadiene complexes. Finally, of interest were further studies on insertion of heteroatoms into the Re=C(1) and/or Re=C(3) bonds [2,3], as similar reactions are well established for Fischer carbene complexes [4,9a,17].

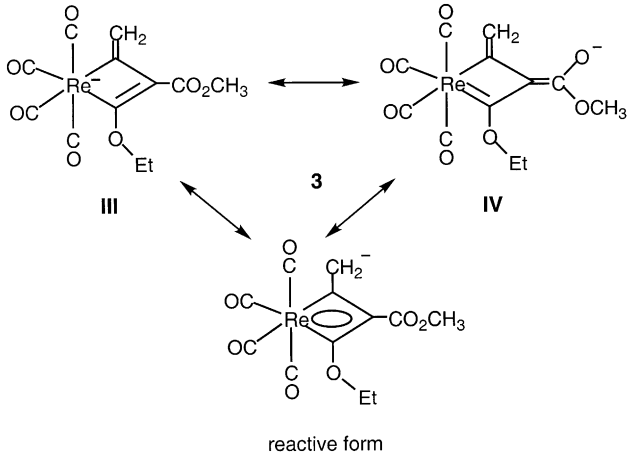
*3.2. Deprotonation of Me at C(1) in $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**2a**) and related chemistry*

Fischer carbene complexes are markedly acidic [9a,18,19]. For example, complexes of the type $(CO)_5M{=}C(Me)OR'$ (M = Cr, W) undergo rapid H–D exchange in the presence of base. We find that **2a** in THF at low temperature is readily deprotonated by LDA, Na[OBu-*t*], or $Na[CH(CO_2Me)_2]$ (Scheme 2). The deprotonation by LDA at −78 °C is evidenced by the shift in ν(C≡O) from 2080 (w), 1991 (s), and 1937 (s) cm^{-1} for **2a** to 2058 (w), 1960 (s), and 1901 (s) cm^{-1} for the product to reflect acquisition of negative charge at rhenium (cf. **III**). Moreover, the appearance of the carboxylate ν(C=O) band at 1630 cm^{-1} for $Li[(CO)_4Re(\eta^2\text{-}C(=CH_2)C(CO_2Me)C(OEt))]$ (Li(**3**)) compared to 1704 cm^{-1} for **2a** indicates that stabilization of the former can



Scheme 2.

be rationalized by the resonance structure **IV**, in addition to **III**. Addition of PPNCl to this solution resulted in the isolation of PPN[$(CO)_4Re(\eta^2\text{-}C(=CH_2)C(CO_2Me)C(OEt))$] (PPN(**3**)) in excellent yield. The ^1H NMR spectrum of PPN(**3**) shows that the ReCMe singlet of **2a** at δ 3.07 is absent; in its place two doublets are observed at δ 6.3 and 4.7 with a $^2J = 4.5$ Hz, consistent with the presence of a vinyl group, ReC=CH_2. The product decomposes slowly on storage in solution.



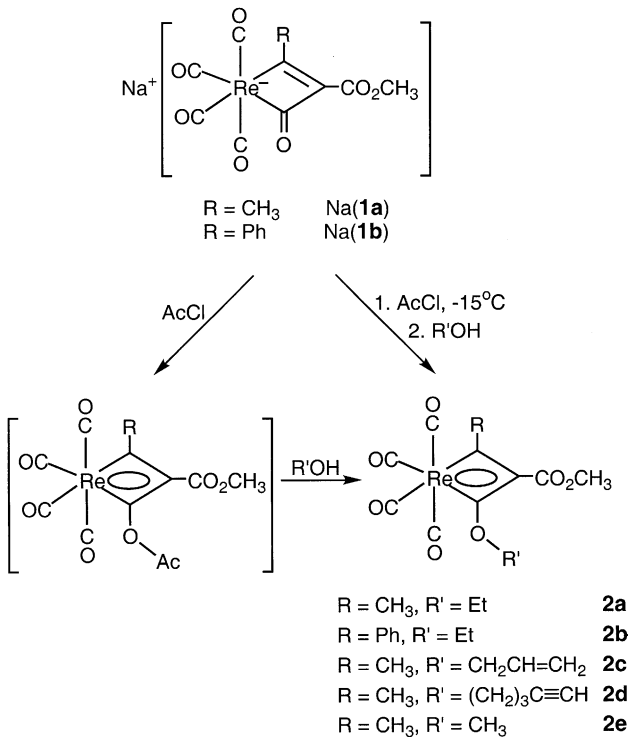
When solutions of Na(**3**) and Li(**3**) were treated with DCl/D_2O, a yellow solid was isolated after workup. Examination of the product by ^1H NMR spectroscopy revealed it to be a mixture of **2a** and **2a**-d_1, with a minute amount of **2a**-d_2 also observed in some runs (87% D incorporation in the ReCMe group for the Li(**3**) reaction). This behavior parallels that of metal carbene complexes [9a]; for example, Casey reported that deprotonation of $(CO)_5M{=}C(Me)OMe$ (M = Cr, W) with *n*-BuLi followed by acidification with DCl or DBr yielded ca. 90% $(CO)_5M{=}C(Me\text{-}d_1)OMe$ as well as the Me-d_0, Me-d_2, and Me-d_3 isotopomers [19].

Advantage can be taken of the acidity of the ReCMe protons of **2a** and the thermodynamic stability of **3** by derivatizing the former through deprotonation followed by alkylation (Scheme 2). Accordingly, treatment of **2a** with LDA and addition of Et_3OPF_6 to the resulting solution of Li(**3**) afforded after chromatography pure monoethylated derivative of **2a**, $(CO)_4Re(\eta^2\text{-}C(CH_2Et)(C(CO_2Me)C(OEt))$ (**4**). The composition of the product receives support from its EI mass spectrum, and its structure is evidenced by the ^1H and $^{13}C\{^1H\}$ NMR data, which are similar to those of **2a**, except for the signals relating to the replacement of ReC*Me* with ReC*CH_2Et*. By repeating the sequence deprotonation with LDA followed by addition of Et_3OPF_6 on crude **4**, the diethylated derivative of **2a**, $(CO)_4Re(\eta^2\text{-}C(CHEt_2)C(CO_2Me)C(OEt))$ (**5**) was obtained in 44% isolated yield after chromatographic removal of **2a** and **4**. Again, its spectroscopic data are similar to those of **2a** (and **4**), except for features due to a different substituent at C(1).

Disappointingly, attempts at modification of the substituent at C(1) of **2a** by using Li(**3**) in conjunction with reagents other than oxonium salts were fruitless. Reactions of Li(**3**) with each of MeI, PhC(O)Cl, and $MeC(O)CH{=}CH_2$ either did not proceed or furnished mixtures of inseparable compounds. In contrast, the corresponding conjugate bases of Fischer carbene complexes are useful reagents for the modification of the carbene side chain. Besides the oxonium salts and fluorosulfonates, a number of other reagents, including allyl and benzyl halides, α-bromoesters, aldehydes, and epoxides, inter alia, react readily and cleanly with various metal carbene derived anions [9,19,20].

3.3. Modification of alkoxy group at C(3) in $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(OR'))$ (2)

The rhenacyclobutadiene $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**2a**) reacts very slowly with neat methanol at room temperature to afford only 5% conversion to $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OMe))$ (**2e**) in 2 days. A much more practical route to diversification of the alkoxy group at C(3) in **2** proved to be reaction of Na[$(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(O))$] (Na(**1**)) with AcCl followed by R′OH (Scheme 3). This approach had been successfully applied by Connor and Jones toward the introduction of different OR′ groups in Fischer alkoxycarbene complexes [21].



Scheme 3.

Treatment of Na(**1**) with 1 equivalent of AcCl at −15 °C followed by the addition of R′OH afforded after workup 76–83% yield of the appropriate rhenacyclobutadiene **2** (R = Me, R′ = Et (**2a**), $CH_2CH{=}CH_2$ (**2c**), $(CH_2)_3C{\equiv}CH$ (**2d**), Me (**2e**); R = Ph, R′ = Et (**2b**)) (Method 2, cf. Section 2.4). However, this methodology could not be successfully applied to reactions of Na(**1**) with carboxylic amides such as acetamide or less nucleophilic alcohols such as trifluoroethanol, which yielded only intractable mixtures of products. The new complexes **2b**–**2e** show IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopic properties that are very similar to those of **2a**, except for the features due to the presence of different substituents at C(1) and/or C(3). For all complexes, the $^{13}C\{^1H\}$ NMR signals of the Re*C*R and Re*C*OR′ nuclei occur in the low-field region δ 249.8–227.4, as expected.

*3.4. Aminolysis at C(3) in $(CO)_4Re(\eta^2$-C(Me)C(CO_2Me)C(OEt)) (**2a**)*

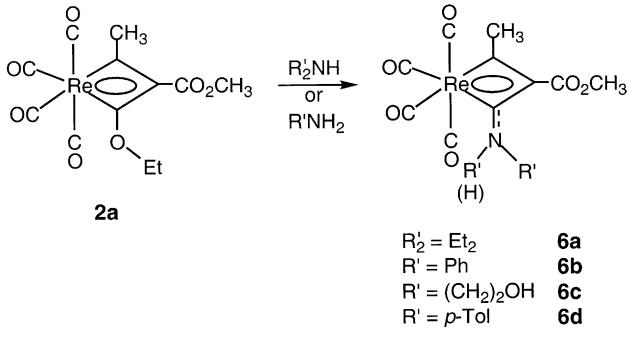
Alkoxy substituents at carbene carbon are excellent leaving groups, and Fischer carbene complexes of the type $L_nM{=}C(R)OR'$ undergo replacement of OR′ with NHR′ or NR'_2 upon respective reactions with primary and the less crowded secondary amines [9a,22].

We find that **2a** reacts with the primary amines $PhNH_2$, $HO(CH_2)_2NH_2$, and *p*-TolNH_2 at −78 °C followed by warming and with the secondary amine Et_2NH at 0 °C to afford the corresponding C(3)-substituted aminorhenacyclobutadiene $(CO)_4Re(\eta^2$-C(Me)C(CO_2Me)C(NHR′ or NR'_2)) products ($R'_2 = Et_2$ (**6a**); R′ = Ph (**6b**), $(CH_2)_2OH$ (**6c**), *p*-Tol (**6d**)) (Scheme 4). These conversions are thought to follow the same mechanism as the one implicated for Fischer carbene complexes, viz., nucleophilic attack of the amine at C(3) to yield an ylide-type structure (cf. Section 3.5), proton migration from the amino to the alkoxy substituent, and irreversible elimination of alcohol [23]. Attack at C(1) is also possible but has not been observed, possibly for thermodynamic reasons owing to its expected unproductive reversibility.

Complexes **6a**–**6d** were characterized by mass spectrometric/chemical analysis, and their proposed structures were inferred from the IR and ^1H and $^{13}C\{^1H\}$ NMR spectra. The IR ν(CO) region resembles that of the alkoxyrhenacyclobutadienes **2a** and **2c**–**2e**; however, the bands are shifted to lower energy by $\gtrsim$10 cm^{-1} to indicate a greater negative charge at Re in **6** than in **2**. Comparison of the $^{13}C\{^1H\}$ NMR Re*C*Me and Re*C*N signals of **6a**–**6d** (at δ 197.8–193.7 and 230.5–210.1) with the Re*C*Me and Re*C*OC signals of **2a** and **2c**–**2e** (at δ 249.8–246.4 and 246.6–243.7) shows considerably greater shielding in the amino-substituted complexes. Similar differences exist between Fischer alkoxycarbene and aminocarbene complexes, but the downfield chemical shifts are much larger [4].

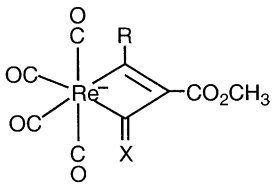
Another noteworthy feature in the NMR spectra of **6a** is the inequivalence of the Et groups of NEt_2. In the ^1H NMR spectrum, two NCH_2Me signals are observed while the NCH_2Me resonance is an unresolved multiplet. In the ^{13}C NMR spectrum, there are two signals for each of CH_2 and Me. The inequivalence of the Et groups indicates restricted rotation about the ReC–N bond owing to substantial C=N π-bonding. For Fischer aminocarbene complexes, such C=N bonding is significant; in fact, geometrical isomers have been observed by ^1H NMR spectroscopy when the amino group is NHR or NRR′ [22].

The aforementioned spectroscopic properties of **6** and the differences observed between **2** and **6** can be



Scheme 4.

rationalized by the relative contributions of the resonance structure **V** to the description of bonding. When $X = NHR'$ or NR'_2, this structure contributes more to the overall description of bonding (that also includes the structures depicted in **I**) than when $X = OR'$. This in turn reduces Fischer carbene character of **6** owing to lesser M=C-bonding. It also places a higher negative charge on Re and hence decreases ν(CO) of **6** relative to **2**. Similar trends hold for analogous Fischer carbene complexes [4,9].



X = OR', NR'_2 or NHR'

V

A decreased Fischer carbene character of **6** compared to **2** also manifests itself by the lack of reactivity of **6a** toward LDA in deprotonation. Under the conditions that mirrored those for the deprotonation followed by reaction with DCl/D_2O for **2a** (Section 2.3.2), no reaction was observed for **6a**. This result is consistent with the reports that Fischer aminocarbene complexes are substantially less acidic than corresponding Fischer alkoxycarbene complexes; for example, the pK_a of $(CO)_5Cr{=}C(Me)NMe_2$ in MeCN is about 10 units higher than that of $(CO)_5Cr{=}C(Me)OMe$ [9a]. Nevertheless, Fischer aminocarbene complexes still can be deprotonated [9,24].

In an attempt to extend the range of rhenacyclobutadiene complexes to C(3)-substituted sulfur analogues of **2**, **2a** was reacted with a large excess of PhSH in THF at room temperature for 2 days. However, no reaction occurred under these conditions.

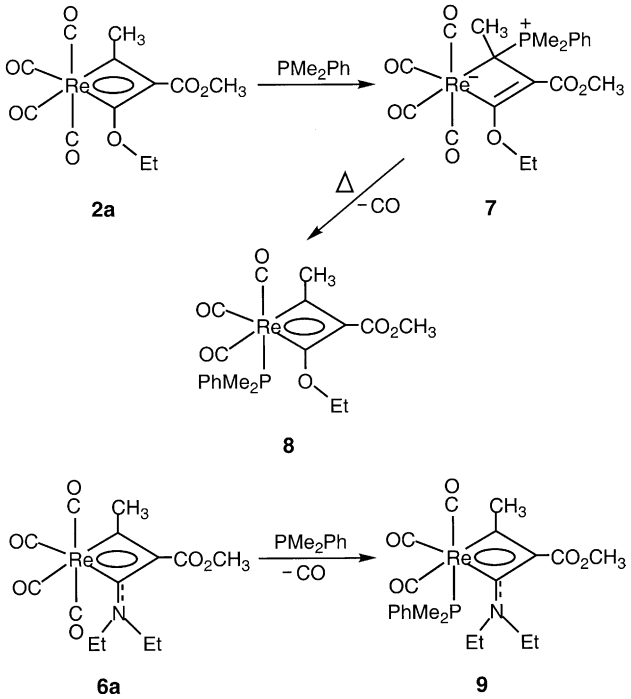
*3.5. Phosphine addition at C(1) and CO substitution in $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(X))$ (X = OEt (**2a**), NEt_2 (**6a**))*

Reactions of rhenacyclobutadiene complexes $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(OEt))$ (**2**: R = Me (**2a**), CO_2Me) with PR'_3 (R′ = Et, *p*-Tol) at ambient temperature were previously studied in our laboratory [2]. The outcome was either addition of PR'_3 to C(1) to give $(CO)_4Re(\eta^2\text{-}C(R)(PR'_3)C(CO_2Me)C(OEt))$ or replacement of a *trans*-CO with PR'_3 (when R = Me, R′ = *p*-Tol). Heating $(CO)_4Re(\eta^2\text{-}C(Me)(PEt_3)C(CO_2Me)C(OEt))$ in benzene at reflux afforded the CO substitution product $(CO)_3(PEt_3)Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$, but a similar prolonged treatment of $(CO)_4Re(\eta^2\text{-}C(CO_2Me)(PR'_3)C(CO_2Me)C(OEt))$ (R′ = Et, *p*-Tol resulted in no chemical change. These reactions are analogous to those reported for Fischer carbene complexes $(CO)_5M{=}C(R)OMe$ (M = Cr, W) and secondary or tertiary phosphines, where both addition to carbene carbon and CO substitution were observed [25].

The synthesis of aminorhenacyclobutadiene complexes **6** prompted us to extend the foregoing study to reactions of **2a** and **6a** with $PPhMe_2$. The objective of these additional experiments was to elucidate how the nature of X in $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(X))$ – OEt or NEt_2 – affects outcome of reaction with phosphine.

We find that **2a** and $PPhMe_2$ react at −78 °C with warming to ca. 0 °C to yield the product of addition of the phosphine to C(1), viz., $(CO)_4Re(\eta^2\text{-}C(Me)(PPhMe_2)C(CO_2Me)C(OEt))$ (**7**). Complex **7** on heating in THF at reflux afforded the CO-substitution derivative of **2**, $(CO)_3(PPhMe_2)Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**8**). In contrast, **6a** and $PPhMe_2$ under similar low-temperature reaction conditions gave directly the CO-substitution product $(CO)_3(PPhMe_2)Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NEt_2))$ (**9**) (Scheme 5). There was no spectroscopic evidence for intermediacy of a **6a**$PPhMe_2$ adduct.

The structure of **7** was inferred with the aid of IR and NMR spectroscopy (cf. Section 2.6.1) and by comparison with corresponding data for the related complexes $(CO)_4Re(\eta^2\text{-}C(R)(PR'_3)C(CO_2Me)C(OEt))$, one of which was characterized by X-ray diffraction techniques [2]. In the $^{13}C\{^1H\}$ NMR spectrum, four equal-intensity ReCO



Scheme 5.

singlet resonances are observed, which is consistent with the trans CO's being inequivalent owing to the presence of the chiral center Re*C*(Me)($PPhMe_2$). Also because of this chiral center, the $PPhMe_2$ shows diastereotopic Me groups in both ^1H and $^{13}C\{^1H\}$ NMR spectra. The $^{13}C\{^1H\}$ signal of Re*C*OEt is still observed at low field (δ 195.1); however, that of Re*C*(Me)($PPhMe_2$), which is no longer carbene-like in nature, is shifted dramatically upfield to δ −4.3, where it appears as a doublet ($^1J_{PC} = 30.5$ Hz). The coupling constants $^3J_{PH} = 19.9$ Hz and $^1J_{PC} = 6.6$ Hz observed, respectively, in the ^1H and $^{13}C\{^1H\}$ NMR spectra for ReC(*Me*)($PPhMe_2$) support nucleophilic addition of $PPhMe_2$ to the Re*C*Me carbene center.

Complexes **8** and **9** each show three strong IR *v*(CO) bands, a pattern characteristic of such a six-coordinate *fac*-tricarbonyl arrangement [26]. The absorption bands of **8** occur at a somewhat higher energy (~10 cm^{-1}) than those of **9**, as noted earlier (cf. Section 3.4) for the parent tetracarbonyls **2a** and **6a**. The appearance of three equal intensity ReCO signals at δ 201–197 in the $^{13}C\{^1H\}$ NMR spectra of **8** and **9** lends support to the assigned structures. The CO *trans* to $PPhMe_2$ resonates with a much larger $^2J_{PC}$ (58.3 and 61.6 Hz, respectively) than the two cis CO's ($^2J_{PC} = 7.2$–8.2 and 7.1–7.8 Hz, respectively), as expected [27]. A carbene-like nature of the two complexes is reflected in the $^{13}C\{^1H\}$ resonances of ReC at δ 258.6 and 252.9 for **8** and δ 223.1 and 201.4 for **9**. The alkoxyrhenacyclobutadiene **8** appears more carbene-like than the aminorhenacyclobutadiene **9**, as observed for their tetracarbonyl precursors and related complexes. Because the Re center is chiral, two ^1H and $^{13}C\{^1H\}$ signals occur for PMe_2 in the spectra of each **8** and **9**.

The reaction of **2a** with $PPhMe_2$ to aford **7** followed by conversion of the latter to **8** represents transformations that are similar to those reported earlier for alkoxyrhenacyclobutadiene complexes with other tertiary phosphines [2]. In contrast, **6a** yields a CO-substitution product directly upon reaction with $PPhMe_2$. This difference in behavior parallels that observed for corresponding Fischer carbene complexes. Whereas metal alkoxycarbene complexes afford addition complexes with phosphines [25], metal aminocarbene complexes fail to do so presumably owing to the reduced electrophilicity of their carbene carbon atoms [28].

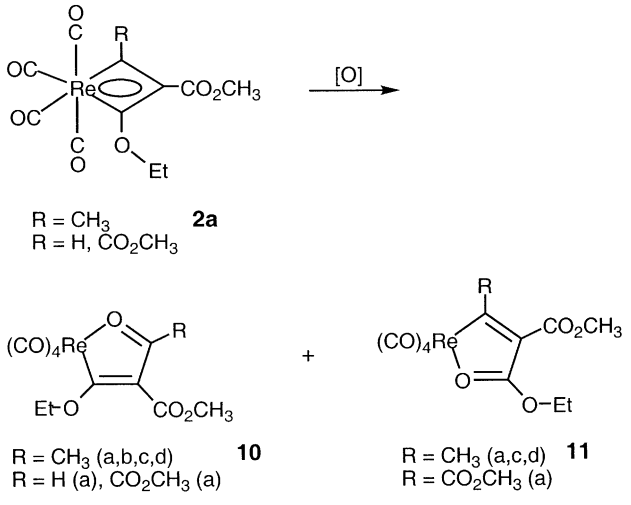
Finally, it is noteworthy that the *productive* addition of phosphines to Re*C*of **2** is at C(1) whereas the *productive* addition of amines to Re*C*of **2** is at C(3). Possibly, both reactions are orbital (rather than charge) controlled, as proposed for Fischer carbene complexes [29], and favor C(1). Nevertheless, *productive* addition of amines occurs at C(3), since it leads to the elimination of ethanol from ReC(OEt)(NH_2R' or NHR'_2) to provide a driving force for that reaction.

*3.6. Insertion of oxygen atom into Re=C bond of $(CO)_4Re(\eta^2$-C(Me)C(CO_2Me)C(OEt)) (**2a**)*

In a previous paper from this laboratory it was reported that **2a** and other alkoxyrhenacyclobutadiene complexes **2** react with $(NH_4)_2[Ce(NO_3)_6]$ to afford products of insertion of oxygen atom into Re=C bonds, $(CO)_4Re(\kappa^2$-OC(R)C(CO_2Me)C(OEt)) (R = H, Me (**10**), CO_2Me) and $(CO)_4Re(\kappa^2$-C(R)C(CO_2Me) C(OEt)O) (R = Me (**11**), CO_2Me) [2] (Scheme 6). The structure of **10** was ascertained by X-ray diffraction techniques. A similar reaction was reported for $(CO)_4Re(\eta^2$-$C_3Ph_3)$ and Me_3NO by Berke and coworkers [30]. The foregoing transformations are related to those of Fischer carbene complexes, which undergo oxidative cleavage by the action of $(NH_4)_2[Ce(NO_3)_6]$, DMSO, and Me_3NO, inter alia, to replace the M=C by O=C [31].

The goal of the present study was to augment the earlier investigation of oxygen atom insertion of **2a** by examining (a) the efficacy of other oxygen transfer reagents and (b) relative propensity for insertion into Re=C(1) and Re=C(3) to give **10** and **11**, respectively. In this context, further studies on reactions of **2a** with $(NH_4)_2[Ce(NO_3)_6]$ showed that product selectivity is affected to some extent by the temperature. Thus, by running the reaction at 0–25 °C in acetone solution, a ca. 7:1 mixture of **10/11** was obtained regardless of whether 1 or 3 equivalents of $(NH_4)_2[Ce(NO_3)_6]$ were employed. However, at reflux temperature of acetone the ratio of **10/11** decreased to 4:1. The relative amounts of **10** and **11** in a mixture of products do not change upon treatment with the cerium(IV) complex for several hours.

Other reagents are also effective in converting **2a** to one or both of **10** and **11** in THF solution (Scheme 6). Use of 1:1 $EtNO_2/Et_3N$ at room temperature affords **10** as the only product isolated in detectable quantity;



Scheme 6.

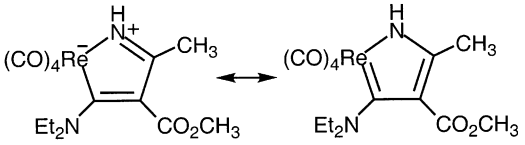
however, in DMSO at room temperature, a 3:1 mixture of **10/11** was obtained. Furthermore, with Me_3NO at ca. 25 °C, **11** was found as the major product. The reason for this unusual isomer preference is not clear.

Oxidative cleavage of the M=C bond in Fischer carbene complexes also can be effected with elemental sulfur [32]. However, attempts at extending this chemistry to **2a** by using an excess of S_8 in THF at reflux temperature resulted in no reaction.

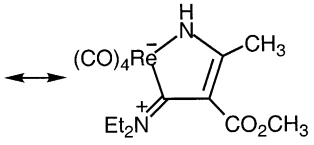
*3.7. Insertion of NH into Re=C bond of $(CO)_4Re(\eta^2$-$C(Me)C(CO_2Me)C(NEt_2))$ (**6a**)*

The alkoxyrhenacyclobutadiene **2a** reacts with $H_2NNH_2 \cdot H_2O$ in THF at 0 °C to afford $(CO)_4Re(\eta^2$-C(Me)C(CO_2Me)C(OEt)NH) and $(CO)_4Re(\eta^2$-NHC(Me)C(CO_2Me)C(OEt)) as the respective major and minor products of NH insertion into Re=C [3]. The structure of the latter product was elucidated, and a possible mechanism of the reaction was addressed. Fischer alkoxycarbene complexes also insert the NH from hydrazines [33], NH_2OH [17], and $NH{=}SPh_2$ [34] into their M=C bonds. Since the aminorhenacyclobutadiene **6a** shows less Fischer carbene character than **2a**, it was of interest to ascertain whether it would behave similarly to **2a** toward $H_2NNH_2 \cdot H_2O$.

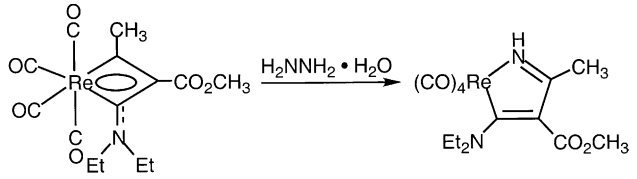
Reaction of **6a** with $H_2NNH_2 \cdot H_2O$ was carried out under conditions comparable to those for **2a**, and after workup afforded $(CO)_4Re(\kappa^2$-NHC(Me)C(CO_2Me)C(NEt_2)) (**12**) in 84% yield (Scheme 7). Complex **12** was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in conjunction with mass spectrometry and chemical analysis. The proposed regiochemistry of insertion of NH into the Re=CMe bond is based on a nOe experiment. Thus, irradiation of the ^1H signal of **12** at δ 2.25 (ReNCMe) resulted in a 4.4% enhancement of the signal at δ 5.85 (NH) to show spatial proximity of these protons. In the $^{13}C\{^1H\}$ NMR spectrum of **12**, the Re-*C*NEt_2 and ReNH*C*Me signals are observed at δ 218.4 and 186.7, respectively. For comparison, the Re*C*OEt and ReNH*C*Me carbon nuclei of $(CO)_4Re(\kappa^2$-NHC(Me)C(CO_2Me)C(OEt)) resonate at δ 239.3 and 190.4, respectively [3]. Furthermore, a complex related to **12**, $(\eta^5$-$C_5Me_5)(CO)_2W(\kappa^2$-N(Et)CHCHC(NHEt)), shows the ^{13}C resonance of W*C*NHEt at δ 221.8 and that of WN(Et)*C*H at δ 166.6 [35], in good agreement with the present data considering different metals and substituents at C and N. It is also noteworthy that only one signal occurs for each of the CH_2 and Me of the Et group in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **12**, unlike with **6a** which shows two signals for each (cf. Section 3.4). Hence, there appears little multiple bonding in ReC-NEt_2, and of the canonical structures **VI**–**VIII**, **VIII** seems relatively unimportant.



VI **VII**



VIII



6a **12**

Scheme 7.

4. Summary

Rhenacyclobutadiene complexes of the type $(CO)_4Re(\eta^2$-C(R)C(CO_2Me)C(OR′)) (**2**) show Fischer carbene-like NMR spectroscopic properties and, in many cases, parallel chemical behavior. When R = alkyl (Me, CH_2Et), they undergo deprotonation by LDA, Na[OBu-*t*], or Na[$CH(CO_2Me)_2$] to yield ylide-type conjugate bases **3** that can be deuteriated with DCl/D_2O or alkylated with Et_3OPF_6. The alkoxy substituent in **2** can be modified by treatment of $Na[(CO)_4Re(\eta^2$-C(R)C(CO_2Me)C(O))] (Na(**1**)) first with AcCl and then with R′OH. Aminolysis of **2a** (R = Me, R′ = Et) with R′NH_2 or R'_2NH affords the aminorhenacyclobutadienes $(CO)_4Re(\eta^2$-C(R)C(CO_2Me)C(NHR′ or NR'_2)) (**6**). Complexes **6** are less carbene-like than **2**, and **6a** (R = Me, R'_2-Et_2) could not be deprotonated with LDA. Both **2a** and **6a** react with $PPhMe_2$, the former by addition to Re*C*Me, and the latter by replacement of a CO. Likewise, both **2a** and **6a** insert oxygen atom or the isoelectronic NH fragment into their Re=C bonds. All of these reactions find precedence in the chemistry of Fischer carbene complexes. However, differences in chemical behavior have been found as well and include lack of reactivity of **2a** toward PhSH and S_8.

Acknowledgements

This research was supported in part by the National Science Foundation and The Ohio State University.

References

[1] L.L. Padolik, J. Gallucci, A. Wojcicki, J. Organomet. Chem. 338 (1990) C1.
[2] L.L. Padolik, J.C. Gallucci, A. Wojcicki, J. Am. Chem. Soc. 115 (1993) 9986.
[3] V. Plantevin, J.C. Gallucci, A. Wojcicki, Inorg. Chim. Acta 222 (1994) 199.
[4] E.O. Fischer, Adv. Organomet. Chem. 14 (1976) 1.
[5] (a) J.H. Wengrovius, J. Sancho, R.R. Schrock, J. Am. Chem. Soc. 103 (1981) 3932;
(b) R.R. Schrock, Acc. Chem. Res. 19 (1986) 342;
(c) I.A. Weinstock, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 113 (1991) 135.
[6] (a) R.R. Schrock, J. Am. Chem. Soc. 96 (1974) 9796;
(b) R.R. Schrock, Acc. Chem. Res. 12 (1979) 98.
[7] For example: C.P. Casey, P.C. Vosejpka, F.R. Askham, J. Am. Chem. Soc. 112 (1990) 3713, and references therein.
[8] E.O. Fischer, A. Maasböl, Angew. Chem., Int. Ed. Engl. 3 (1964) 580.
[9] Selected recent reviews: (a) C.F. Bernasconi, Adv. Phys. Org. Chem. 37 (2002) 137;
(b) J. Barluenga, Pure Appl. Chem. 74 (2002) 1317;
(c) G. Bertrand (Ed.), J. Organomet. Chem. 617–618 (2001) (special issue on transition-metal carbene complexes);
(d) A. de Meijere, H. Schirmer, M. Deutsch, Angew. Chem. Int. Ed. Engl. 39 (2000) 3964;
(e) J. Barluenga, F.J. Fananas, Tetrahedron 56 (2000) 4597;
(f) J.W. Herndon, Tetrahedron 56 (2000) 1257;
(g) K.H. Dötz, P. Tomuschat, Chem. Soc. Rev. 28 (1999) 187;
(h) F.Z. Dörwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999;
(i) W.D. Wulff, Organometallics 17 (1998) 3116;
(j) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 163;
(k) D.F. Harvey, D. Sigano, Chem. Rev. 96 (1996) 271;
(l) A. de Meijere, Pure Appl. Chem. 68 (1996) 61.
[10] Selected recent papers: (a) H. Wang, W.D. Wulff, A.L. Rheingold, J. Am. Chem. Soc. 125 (2003) 8980;
(b) K. Fuchibe, N. Isasawa, Chem. Eur. J. 9 (2003) 905;
(c) J. Zhang, T.B. Gunnoe, Organometallics 22 (2003) 2291;
(d) H. Werner, C. Grünwald, W. Stüer, J. Wolf, Organometallics 22 (2003) 1558;
(e) C.F. Bernasconi, S. Bhattacharya, Organometallics 22 (2003) 426;
(f) R. Aumann, X. Fu, C. Holst, R. Fröhlich, Organometallics 21 (2002) 4356;
(g) R. Stumpf, M. Jaeger, H. Fischer, Organometallics 20 (2001) 4040;
(h) J.P. Moretó, S. Ricart, K.H. Dötz, E. Molins, Organometallics 20 (2001) 62.
[11] V. Plantevin, A. Wojcicki, J. Organomet. Chem., X_{ref}: doi:10.1016/j.jorganchem.2004.03.024.
[12] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, second ed., Wiley, New York, 1986.
[13] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 1991.
[14] R.R. Willis, M. Calligaris, P. Faleschini, J.C. Gallucci, A. Wojcicki, J. Organomet. Chem. 193–194 (2000) 465.
[15] R.T. Dunsizer, V.M. Marsico, V. Plantevin, A. Wojcicki, Inorg. Chim. Acta 342 (2003) 279.
[16] L.L. Padolik, Ph.D. Dissertation, The Ohio State University, 1990.
[17] E.O. Fischer, R. Aumann, Chem. Ber. 101 (1968) 963.
[18] C.G. Kreiter, Angew. Chem., Int. Ed. Engl. 7 (1968) 147.
[19] (a) C.P. Casey, R.L. Anderson, J. Am. Chem. Soc. 96 (1974) 1230;
(b) C.P. Casey, W.R. Brunsvold, J. Organomet. Chem. 118 (1976) 309.
[20] (a) C.P. Casey, R.A. Boggs, R.L. Anderson, J. Am. Chem. Soc. 94 (1972) 8947;
(b) C.P. Casey, W.R. Brunsvold, J. Organomet. Chem. 102 (1975) 175;
(c) C.P. Casey, W.R. Brunsvold, D.M. Scheck, Inorg. Chem. 16 (1977) 3059.
[21] (a) J.A. Connor, E.M. Jones, J. Chem. Soc. D (1971) 570;
(b) J.A. Connor, E.M. Jones, J. Chem. Soc. A (1971) 3368.
[22] (a) U. Klabunde, E.O. Fischer, J. Am. Chem. Soc. 89 (1967) 7141;
(b) J.A. Connor, E.O. Fischer, J. Chem. Soc. A (1969) 578;
(c) E. Moser, E.O. Fischer, J. Organomet. Chem. 16 (1969) 275;
(d) E.O. Fischer, H.-J. Kollmeier, Chem. Ber. 104 (1971) 1339;
(e) E.O. Fischer, B. Heckl, H. Werner, J. Organomet. Chem. 28 (1971) 359.
[23] (a) B. Heckl, H. Werner, E.O. Fischer, Angew. Chem., Int. Ed. Engl. 7 (1968) 817;
(b) H. Werner, E.O. Fischer, B. Heckl, C.G. Kreiter, J. Organomet. Chem. 28 (1971) 367;
(c) C.F. Bernasconi, M.W. Stronah, J. Am. Chem. Soc. 115 (1993) 1341;
(d) C.F. Bernasconi, C. Whitesell, R.A. Johnson, Tetrahedron 56 (2000) 4917.
[24] W.D. Wulff, B.A. Anderson, A.J. Toole, Y.-C. Xu, Inorg. Chim. Acta 220 (1994) 215.
[25] (a) F.R. Kreissl, C.G. Kreiter, E.O. Fischer, Angew. Chem., Int. Ed. Engl. 11 (1972) 643;
(b) F.R. Kreissl, E.O. Fischer, C.G. Kreiter, H. Fischer, Chem. Ber. 106 (1973) 1262;
(c) H. Fischer, E.O. Fischer, C.G. Kreiter, H. Werner, Chem. Ber. 107 (1974) 2459;
(d) E.O. Fischer, T. Selmayr, F.R. Kreissl, Monatsh Chem. 108 (1977) 759;
(e) E.O. Fischer, T. Selmayr, F.R. Kreissl, Chem. Ber. 110 (1977) 2947.
[26] P.S. Braterman, Metal Carbonyl Spectra, Academic Press, New York, 1975.
[27] C. Elschenbroich, A. Salzer, in: Organometallics – A Concise Introduction, second ed., VCH, Weinheim, 1992, p. 302.
[28] K.H. Dötz, in: P.S. Braterman (Ed.), Reactions of Coordinated Ligands, vol. 1, Plenum Press, New York, 1986 (Chapter 4).
[29] (a) W.B. Perry, T.F. Schaaf, W.L. Jolly, L.J. Todd, D.L. Cronin, Inorg. Chem. 13 (1974) 2038;
(b) T.F. Block, R.F. Fenske, C.P. Casey, J. Am. Chem. Soc. 98 (1976) 441;
(c) T.F. Block, R.F. Fenske, J. Organomet. Chem. 139 (1977) 235.
[30] (a) C. Löwe, V. Shklover, H. Berke, Organometallics 10 (1991) 3396;
(b) C. Löwe, V. Shklover, H.W. Bosch, H. Berke, Chem. Ber. 126 (1993) 1769.
[31] (a) F.A. Cotton, C.M. Lukehart, J. Am. Chem. Soc. 93 (1971) 2672;
(b) C.M. Lukehart, J.V. Zeile, J. Organomet. Chem. 97 (1975) 421;
(c) C.M. Lukehart, J.V. Zeile, Inorg. Chim. Acta 17 (1976) L7;
(d) C.P. Casey, T.J. Burkhardt, C.A. Bunnell, J.C. Calabrese, J. Am. Chem. Soc. 99 (1977) 2127;
(e) C.P. Casey, W.R. Brunsvold, Inorg. Chem. 16 (1977) 391.
[32] E.O. Fischer, S. Riedmüller, Chem. Ber. 107 (1974) 915.
[33] R.G. Raubenheimer, S. Lotz, G. Kruger, G. Gafner, J. Organomet. Chem. 173 (1979) C1.
[34] R.G. Raubenheimer, G.J. Kruger, F. Scott, R. Otte, Organometallics 6 (1987) 1789.
[35] A.C. Filippou, C. Völkl, P. Kiprof, J. Organomet. Chem. 415 (1991) 375.