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Fischer-Type Rhenacyclobutadiene Complexes: Synthesis, Structure, and Nucleophilic Addition/Substitution and Oxidation Reactions

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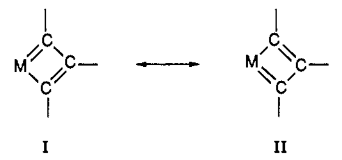
Abstract: Reactions of Na[Re(CO)$_5$] with the activated acetylenes RC≡CCO$_2$Me (R = CO$_2$Me (**a**), Me (**b**), H (**c**)) afford the rhenacyclobutenone complexes Na[(CO)$_4$ReC(R)C(CO$_2$Me)C(O)] (**1**), which undergo alkylation with Et$_3$OPF$_6$ to the novel Fischer-type rhenacyclobutadiene complexes (CO)$_4$ReC(R)C(CO$_2$Me)C(OEt) (**2**). A single-crystal X-ray diffraction analysis of **2b** revealed a planar unsymmetrical ring structure (C═C bond distances 1.45(2) and 1.36(2) Å) and Re—C(ring) bond lengths (2.13(1) and 2.18(1) Å) intermediate between those of Re—C and Re═C, as for the simple Fischer metal carbene complexes. The Fischer-type carbenoid character of **2** is further evidenced by the downfield position of the ^{13}C NMR signals of both Re═C(ring) atoms of **2**. **2a** reacts with PR$_3$ (R = Et or *p*-Tol) at ambient temperatures to give phosphine-addition products (CO)$_4$ReC(CO$_2$Me)(PR$_3$)C(CO$_2$Me)C(OEt) (**3a** and **4a**, respectively). The reaction of **2b** and PEt$_3$ affords the analogous addition product **3b**; however, that of **2b** and P(*p*-Tol)$_3$ yields the CO-substitution derivative *fac*-(CO)$_3$(P(*p*-Tol)$_3$)ReC(Me)C(CO$_2$Me)C(OEt) (**5b**). Upon heating in hexane at reflux, **3b** undergoes conversion to the CO-substitution product *fac*-(CO)$_3$(PEt$_3$)ReC(Me)C(CO$_2$Me)C(OEt) (**6b**), which reacts with additional PEt$_3$ to afford *fac*-(CO)$_3$(PEt$_3$)ReC(Me)(PEt$_3$)C(CO$_2$Me)C(OEt) (**7b**). Oxidation of **2** with (NH$_4$)$_2$[Ce(NO$_3$)$_6$] results in the insertion of an oxygen atom into the Re═C(ring) bonds to yield the five-membered oxametallacyclic products (CO)$_4$ReOC(R)C(CO$_2$Me)C(OEt) (**8**) and, for **2a**,**b**, also (CO)$_4$ReC(R)C(CO$_2$Me)C(OEt)O (**9**). The foregoing nucleophilic addition/substitution and oxygen atom insertion reactions are analogous to those of simple Fischer metal carbene complexes. The structures of (**1a**)$_2$·THF, **4a**, and **8b** were also elucidated by X-ray diffraction techniques.

Introduction

In recent years there has been considerable activity in the area of synthesis, structure, and reaction chemistry of metallacyclobutadiene complexes of d^0 transition metals,[1] e.g., tantalum(V), molybdenum(VI), tungsten(VI), and rhenium(VII). Investigations carried out by Schrock and co-workers have received much stimulus from the proposal[1a] and the finding[1d,e] that some of these complexes are effective catalysts for the metathesis of disubstituted acetylenes. Stable metallacyclobutadiene complexes have been isolated and characterized from reactions of metal-alkylidyne complexes with various acetylenes.[1b,d,e,h,i,l] Consideration of either a single localized structure or two equivalent resonance structures I and II of a delocalized metallacyclobutadiene ring reveals that these complexes possess metal-alkylidene bonding features. Since the metal occurs in a high formal oxidation state, the complexes in point may be regarded as Schrock-type metallacyclobutadienes, in analogy with Schrock-type metal alkylidenes.[2]



I II

In the 1970's Weaver[3] and Frisch[4] reported that oxidative addition reactions of Ir(CO)Cl(PMe$_3$)$_2$ and Rh(CO)Cl(PR$_3$)$_2$ (PR$_3$ = PMe$_3$, PMe$_2$Ph, PMePh$_2$) with triphenylpropenium salts yield iridacyclobutadiene and rhodacyclobutadiene complexes, respectively. The structures of [IrCl(CO)(PMe$_3$)$_2$(η^2-C$_3$Ph$_3$)]BF$_4$[3] and RhCl$_2$(PMe$_2$Ph)$_2$(η^2-C$_3$Ph$_3$),[4] like those of most of the Schrock-type complexes, were found to contain a planar metallacyclobutadiene ring.

We recently reported in a preliminary communication[5] that reaction of Na[Re(CO)$_5$] with the activated acetylenes RC≡C-CO$_2$Me (R = CO$_2$Me, Me) results in the formation of anionic rhenacyclobutenone complexes Na[(CO)$_4$ReC(R)═C(CO$_2$Me)C(O)] (**1**). Alkylation of **1** with Et$_3$OPF$_6$ affords the

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rhenacyclobutadienes $(CO)_4ReC(R)C(CO_2Me)C(OEt)$ (**2**). A related complex, $(CO)_4Re(\eta^2\text{-}C_3Ph_3)$, was subsequently obtained from $(CO)_5Re(\eta^1\text{-}C_3Ph_3)$ by Berke and co-workers.[6] The foregoing rhenium complexes are analogous to Fischer carbene complexes,[7] e.g., $(CO)_5Cr{=}C(R^1)OR^2$, with respect to structure and bonding, as Schrock metallacyclobutadienes are to Schrock alkylidenes. They characteristically contain a low oxidation state transition metal in conjunction with carbonyl ligands and are, in the case of **2**, stabilized by the presence of a heteroatom (oxygen) bonded to one α-carbon atom of the ring. Because of this apparent analogy to the Fischer carbene complexes, and because Fischer carbene complexes display rich chemistry that includes numerous applications to organic synthesis,[8] we have undertaken a study on reactions of the new Fischer-type rhenacyclobutadienes **2**. In this paper we report in detail the synthesis, characterization by spectroscopy and X-ray diffraction, and reactions with phosphines and $(NH_4)_2[Ce(NO_3)_6]$ of complexes **2**.

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of N_2 or Ar by using standard procedures.[9] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Melting points were measured on a Thomas–Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283B spectrophotometer and were calibrated with polystyrene. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker AC-200, AM-250, AC-300, or AM-500 spectrometer. IR and ^1H and $^{13}C\{^1H\}$ NMR data for all new complexes prepared in this study are given in Table I. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on Kratos MS-30 and VG70-250S spectrometers, respectively, by Dr. C. R. Weisenberger or Mr. David C. Chang. All listed mass peaks are those of ions containing ^{187}Re.

Materials. All solvents were dried, distilled under an Ar atmosphere, and degassed before use. Tetrahydrofuran (THF) was distilled from potassium and benzophenone, CH_2Cl_2 from CaH_2, hexane and pentane from potassium, and diethyl ether from Na/K alloy.

Reagents were obtained from various chemical sources and used as received except trimethylamine *N*-oxide, from Aldrich, which was sublimed. Merck silica gel (grade 60, 230–240 mesh) was used for column chromatography.

A solution of $Na[Re(CO)_5]$ in THF was prepared as follows from $Re_2(CO)_{10}$ (Strem or Pressure Chemical) and Na (obtained by washing a Na dispersion in mineral oil with pentane, removing the liquid, and pumping to dryness). Metallic Na (ca. 0.4 g, from 0.5 g of a Na dispersion in mineral oil) in THF (45 mL) was treated with solid $Re_2(CO)_{10}$ (0.50 g, 0.77 mmol), and the resulting mixture was stirred for 12 h. Unreacted Na was allowed to settle, and the product $Na[Re(CO)_5]$, characterized by its IR ν(CO) spectrum,[10] was used as a dark orange THF solution without isolation or further purification. (This solution generally contained a small amount of a polynuclear rhenium carbonyl species which proved difficult to remove; however, its presence did not interfere with subsequent reactions.) The calculated concentration of $Na[Re(CO)_5]$ (0.034 M) is based on the assumption of complete reductive cleavage of $Re_2(CO)_{10}$.

$Na[(CO)_4ReC(CO_2Me)C(CO_2Me)C(O)]$ (1a). To 45 mL of a 0.034 M THF solution of $Na[Re(CO)_5]$ (1.5 mmol) was added by syringe 0.18 mL (1.156 g/mL, 1.5 mmol) of $MeO_2CC{\equiv}CCO_2Me$. The color of the solution darkened immediately. After a few minutes THF was removed under vacuum to leave a dark brown oil. Treatment of this oil with 10 mL of 4:1 diethyl ether/THF produced a brown solid, which was filtered off and discarded. The filtrate was concentrated to a maroon oil, which was dissolved in 1.2 mL of 5:1 diethyl ether/THF. Following the addition of hexane, the reaction mixture was kept at room temperature for ca. 24 h. The brown–maroon solid that formed was isolated after decantation of the mother liquor and was dried in vacuo. The yield was 0.66 g (84%) of $(\mathbf{1a})_2\cdot THF$. The analytically pure product was obtained by dissolution of this solid in minimum diethyl ether/THF and addition of hexane to induce crystallization. FAB MS: *m/z* 563 (M^+ + THF − 1), 493 (M^+ + 1), 465 (M^+ − CO + 1), 437 (M^+ − 2CO + 1), 409 (M^+ − 3CO + 1), M = **1a**. Anal. Calcd for $C_{26}H_{20}Na_2O_{19}Re_2$ ($(\mathbf{1a})_2\cdot THF$): C, 29.61; H, 1.91. Found: C, 30.01; H, 1.98.

$Na[(CO)_4ReC(Me)C(CO_2Me)C(O)]$ (1b). Methyl 2-butynoate (0.15 mL, 0.981 g/mL, 1.5 mmol) was added to 45 mL of a 0.034 M THF solution of $Na[Re(CO)_5]$ (1.5 mmol), and the resulting mixture was stirred overnight. The solvent was removed in vacuo, the residue was extracted with 15 mL of ca. 1:1 diethyl ether/THF, and the extract was filtered. Solvent was evaporated from the filtrate, and the orange–brown residue was dissolved in 2 mL of ca. 1:1 diethyl ether/THF and treated with hexane to give large yellow crystals. Yields of up to 77% (0.57 g) of $(\mathbf{1b})_3\cdot 2THF$ have been realized. FAB MS: *m/z* 519 (M^+ + THF − 1), 449 (M^+ + 1), 391 (M^+ − 2CO − 1), M = **1b**. Anal. Calcd for $C_{38}H_{34}Na_3O_{23}Re_3$ ($(\mathbf{1b})_3\cdot 2THF$): C, 30.70; H, 2.30. Found: C, 30.68; H, 2.16.

$Na[(CO)_4ReCHC(CO_2Me)C(O)]$ (1c). Methyl propiolate (0.27 mL, 0.945 g/mL, 3.1 mmol) was added to 90 mL of a 0.034 M THF solution of $Na[Re(CO)_5]$ (3.1 mmol), and the resulting reaction mixture was worked up similarly to that of **1a**. The yield of **1c**·*x*THF (*x* ∼ 0.5 by integration of ^1H NMR signals), an orange solid, was 0.80 g (ca. 55%). A satisfactory FAB mass spectrum could not be obtained.

$(CO)_4ReC(CO_2Me)C(CO_2Me)C(OEt)$ (2a). A suspension of $(\mathbf{1a})_2\cdot THF$ (1.58 g, 3.00 mmol of **1a**) in 20 mL of CH_2Cl_2 was treated with Et_3OPF_6 (0.82 g, 3.3 mmol) in 5 mL of CH_2Cl_2, and the resulting mixture was stirred for 1 h. A dark brown solution was separated from a white solid ($NaPF_6$) by cannula, and the solid was washed with hexane. The solvent was removed from the combined hexane wash and brown solution, and the residue was extracted with 10-mL portions of hexane until the extracts became colorless (≥5 times). The extracts were then evaporated to dryness to give a slightly gummy yellow-orange solid (1.0 g, 67% yield). EI MS: *m/z* 498 (M^+), 467 (M^+ − OMe), 441 (M^+ − CO − Et), 413 (M^+ − 2CO − Et), 385 (M^+ − 3CO − Et). Satisfactory elemental analysis could not be obtained.

$(CO)_4ReC(Me)C(CO_2Me)C(OEt)$ (2b). The procedure was similar to that for **2a** and utilized 1.35 g of $(\mathbf{1b})_3\cdot 2THF$ (2.72 mmol of **1b**) and 0.76 g (3.0 mmol) of Et_3OPF_6. Only two extractions with 20-mL portions of hexane were necessary, and evaporation to dryness of the extracts left a yellow solid (1.0 g) in 81% yield. Analytically pure **2b** was obtained by slow evaporation of a saturated hexane solution of **2b** at 10 °C. Anal. Calcd for $C_{12}H_{11}O_7Re$: C, 31.79; H, 2.44. Found: C, 31.63; H, 2.23.

$(CO)_4ReCHC(CO_2Me)C(OEt)$ (2c). The title complex was prepared from **1c**·*x*THF (ca. 3.2 mmol) and a slight excess of Et_3OPF_6 in CH_2Cl_2 solution in a manner similar to that described for **2a**. The yield of a gummy orange solid was 0.98 g (ca. 70%). FAB MS: *m/z* 441 (M^+ + 1), 411 (M^+ − CO − 1), 385 (M^+ − 2CO + 1), 355 (M^+ − 3CO − 1), 327 (M^+ − 4CO − 1).

$(CO)_4ReC(PEt_3)(CO_2Me)C(CO_2Me)C(OEt)$ (3a). To a yellow solution of **2a** (0.20 g, 0.40 mmol) in 20 mL of CH_2Cl_2 was added by syringe 0.060 mL (0.40 mmol) of PEt_3, resulting in a color change to lighter yellow. The mixture was stirred for 1 h, and then the solvent was removed in vacuo to leave a dark yellow oil. The oil was purified by dissolution in diethyl ether, layering with hexane, and cooling this mixture at −23 °C for 2–3 days. The product goes into solution as impurities oil out. The solution was separated from the oil, and the solvent was removed to afford a yellow oil, **3a**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 38.6. FAB MS: *m/z* 589 (M^+ − CO + 1), 557 (M^+ − CO − OMe), 531 (M^+ − 3CO − 1), 503 (M^+ − 4CO − 1).

$(CO)_4ReC(PEt_3)(Me)C(CO_2Me)C(OEt)$ (3b). The title complex was prepared from **2b** (0.26 g, 0.57 mmol) and PEt_3 (0.080 mL, 0.54 mmol) in CH_2Cl_2 solution in a manner analogous to that described for **3a** and was similarly purified to afford a yellow oil. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 41.9. FAB MS: *m/z* 573 (M^+ + 1), 544 (M^+ − CO), 515 (M^+ − 2CO − 1).

$(CO)_4ReC(P(p\text{-}Tol)_3)(CO_2Me)C(CO_2Me)C(OEt)$ (4a). A solution of **2a** (0.20 g, 0.40 mmol) in 20 mL of CH_2Cl_2 at −78 °C was treated with $P(p\text{-}Tol)_3$ (0.12 g, 0.39 mmol) in 5 mL of CH_2Cl_2, and the reaction

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Table I. IR and ^{1}H and ^{13}C NMR Spectral Data for New Complexes

complex	IR, ν(CO)[a] cm^{-1}	^{1}H NMR,[b] δ	^{13}C{^{1}H} NMR,[c] δ
1a	2060 m, 1960 vs, 1916 s, 1715 m, 1692 s, 1608 w	1.79 (m, THF), 3.52 (s, $\mathrm{CO_2CH_3}$), 3.63 (m, THF), 3.72 (s, $\mathrm{CO_2CH_3}$)	26.05 (s, THF), 50.87 (s, $\mathrm{CO_2\mathit{C}H_3}$), 68.01 (s, THF), 159.26 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 160.50 (s, $\mathrm{CO_2}$), 175.91 (s, $\mathrm{CO_2}$), 187.02 (s, $\mathrm{Re\mathit{C}CO_2CH_3}$), 195.55 (s, CO), 196.24 (s, CO), 197.43 (s, trans CO's), 227.87 (s, $\mathrm{Re\mathit{C}OC}$)
1b	2045 w, 1957 vs, 1906 s, 1717 m, 1675 w	1.79 (m, THF), 2.81 (s, $\mathrm{CCH_3}$), 3.57 (s, $\mathrm{CO_2CH_3}$), 3.63 (m, THF)	25.82 (s, THF), 32.53 (s, $\mathrm{C\mathit{C}H_3}$), 49.65 (s, $\mathrm{CO_2\mathit{C}H_3}$), 67.76 (s, THF), 160.85 (s, $\mathrm{CO_2}$), 162.98 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 197.53 (s, CO), 197.74 (s, CO), 199.85 (s, trans CO's), 214.13 (s, $\mathrm{Re\mathit{C}CH_3}$), 224.64 (s, $\mathrm{Re\mathit{C}OC}$)
1c	2054 w, 1953 s, 1910 s, 1688 w	1.79 (m, THF), 3.55 (s, $\mathrm{CO_2CH_3}$), 3.63 (m, THF), 10.37 (s, CH)	26.09 (t, THF), 50.49 (quartet, $\mathrm{CO_2\mathit{C}H_3}$), 68.03 (t, THF), 160.45 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 171.53 (s, $\mathrm{CO_2}$), 191.20 (d, ReCH), 197.07 (s, CO), 197.24 (s, CO), 199.12 (s, trans CO's), 228.75 (s, $\mathrm{Re\mathit{C}OC}$)[d]
2a	2092 w, 1998 vs, 1950 s, 1717 w	1.65 (t, J_{HH} = 7.2 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 3.64 (s, $\mathrm{CO_2CH_3}$), 3.85 (s, $\mathrm{CO_2CH_3}$), 4.99 (quartet, J_{HH} = 7.2 Hz, $\mathrm{OCCH_2}$)	14.87 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 51.50 (s, $\mathrm{CO_2\mathit{C}H_3}$), 51.70 (s, $\mathrm{CO_2\mathit{C}H_3}$), 82.89 (s, $\mathrm{OCH_2}$), 153.99 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 158.16 (s, $\mathrm{CO_2}$), 174.24 (s, $\mathrm{CO_2}$), 189.53 (s, trans CO's), 191.56 (s, CO), 192.20 (s, CO), 210.54 (s, $\mathrm{Re\mathit{C}CO_2CH_3}$), 253.78 (s, $\mathrm{Re\mathit{C}OEt}$)
2b	2082 w, 1991 vs, 1937 s, 1704 w	1.59 (t, J_{HH} = 7.2 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 3.07 (s, $\mathrm{CCH_3}$), 3.70 (s, $\mathrm{CO_2CH_3}$), 4.70 (quartet, J_{HH} = 7.2 Hz, $\mathrm{OCH_2}$)	14.97 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 35.24 (s, $\mathrm{C\mathit{C}H_3}$), 50.60 (s, $\mathrm{CO_2\mathit{C}H_3}$), 81.10 (s, $\mathrm{OCH_2}$), 156.87 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 159.43 (s, $\mathrm{CO_2}$), 191.15 (s, trans CO's), 192.99 (s, CO), 194.46 (s, CO), 243.71 (s, $\mathrm{Re\mathit{C}OEt}$), 246.39 (s, $\mathrm{Re\mathit{C}CH_3}$)
2c	2086 m, 1998 s, 1942 s, 1715 w	1.63 (t, J_{HH} = 7.13 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 3.65 (s, $\mathrm{CO_2CH_3}$), 4.93 (quartet, J_{HH} = 7.15 Hz, $\mathrm{OCH_2}$), 11.50 (s, CH)	14.92 (quartet, $\mathrm{OCH_2\mathit{C}H_3}$), 51.10 (quartet, $\mathrm{CO_2\mathit{C}H_3}$), 82.29 (t, $\mathrm{OCH_2}$), 158.73 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 164.50 (s, $\mathrm{CO_2}$), 190.70 (s, trans CO's), 192.29 (s, CO), 193.87 (s, CO), 219.81 (d, ReCH), 251.89 (s, $\mathrm{Re\mathit{C}OEt}$)[d]
3a[e]	2075 m, 1988 vs, 1957 s, 1930 s, 1655 m	1.30 (m, J_{HH} = 7.35 Hz, $\mathrm{PCH_2C\mathit{H}_3}$), 1.36 (t, J_{HH} = 7.11 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 2.39 (m, $\mathrm{PCH_2}$), 3.52 (s, $\mathrm{CO_2CH_3}$), 3.61 (s, $\mathrm{CO_2CH_3}$), 3.99 (quartet, J_{HH} = 7.04 Hz, $\mathrm{OCH_2}$)	8.10 (d, J_{CP} = 5.47 Hz, $\mathrm{PCH_2\mathit{C}H_3}$), 12.09 (d, J_{CP} = 55.15 Hz, ReCP), 15.59 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 16.84 (d, J_{CP} = 51.82 Hz, $\mathrm{PCH_2}$), 50.59 (s, $\mathrm{CO_2\mathit{C}H_3}$), 50.89 (s, $\mathrm{CO_2\mathit{C}H_3}$), 73.53 (s, $\mathrm{OCH_2}$), 107.11 (s, $\mathrm{ReC\mathit{C}CO_2}$), 165.27 (s, $\mathrm{ReCC\mathit{C}O_2}$), 178.18 (d, J_{CP} = 11.63 Hz, $\mathrm{ReC\mathit{C}O_2}$), 188.61 (s, CO), 190.66 (s, CO), 191.80 (s, CO), 193.05 (s, CO), 193.88 (d, J_{CP} = 12.33 Hz, $\mathrm{Re\mathit{C}OEt}$)
3b[e]	2065 m, 1978 s, 1946 s, 1928 s, 1649 m	1.27 (t, J_{HH} = 7.86 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 1.28 (m, J_{HH} = 7.7 Hz, $\mathrm{PCH_2C\mathit{H}_3}$), 2.16 (d, J_{PH} = 17.6 Hz, $\mathrm{CCH_3}$), 2.26 (m, $\mathrm{PCH_2}$), 3.49 (s, $\mathrm{CO_2CH_3}$), 3.96 (m, J_{HH} = 7.86 Hz, $\mathrm{OCH_2}$)	−2.58 (d, J_{CP} = 28.07 Hz, ReCP), 7.75 (d, J_{CP} = 5.58 Hz, $\mathrm{PCH_2\mathit{C}H_3}$), 15.35 (d, J_{CP} = 49.8 Hz, $\mathrm{PCH_2}$), 15.46 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 28.69 (d, J_{CP} = 4.59 Hz, $\mathrm{C\mathit{C}H_3}$), 50.08 (s, $\mathrm{CO_2\mathit{C}H_3}$), 73.11 (s, $\mathrm{OCH_2}$), 115.83 (d, J_{CP} = 5.74 Hz, $\mathrm{ReC\mathit{C}CO_2}$), 164.87 (s, $\mathrm{ReCC\mathit{C}O_2}$), 190.99 (s, 2CO), 192.62 (d, J_{CP} = 14.6 Hz, $\mathrm{Re\mathit{C}OEt}$), 193.29 (s, CO), 194.33 (s, CO)
4a[e]	2079 m, 1988 s, 1965 s, 1928 s, 1690 w, 1661 m	1.34 (t, J_{HH} = 7.1 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 2.38 (s, $\mathrm{C_6H_4C\mathit{H}_3}$), 2.42 (s, $\mathrm{C_6H_4C\mathit{H}_3}$), 2.46 (s, $\mathrm{C_6H_4C\mathit{H}_3}$), 3.12 (s, $\mathrm{CO_2CH_3}$), 3.53 (s, br, $\mathrm{CO_2CH_3}$), 4.05 (quartet, J_{HH} = 7.1 Hz, $\mathrm{OCH_2}$), 7.2–7.7 (m, $\mathrm{C_6H_4}$)	15.56 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 21.22 (s, $\mathrm{2C_6H_4\mathit{C}H_3}$), 21.36 (s, $\mathrm{C_6H_4\mathit{C}H_3}$), 49.51 (s, $\mathrm{CO_2\mathit{C}H_3}$), 50.56 (s br, $\mathrm{CO_2\mathit{C}H_3}$), 72.77 (s, $\mathrm{OCH_2}$), 108.07 (s, $\mathrm{ReC\mathit{C}CO_2CH_3}$), 118–144 (m, $\mathrm{C_6H_4}$), 122.50 (d br, J_{CP} = 81.45 Hz, ReCP), 164.01 (s, $\mathrm{ReCC\mathit{C}O_2CH_3}$), 177.48 (s br, $\mathrm{ReC\mathit{C}O_2}$), 188.40 (s, CO), 190.71 (s, CO), 192.13 (s, CO), 192.52 (s, CO), 196.64 (d, J_{CP} = 13.14 Hz, $\mathrm{Re\mathit{C}OEt}$)
5b[e]	2003 vs, 1925 s, 1894 s, 1694 w	1.32 (t, J_{HH} = 7.2 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 2.38 (s, $\mathrm{C_6H_4C\mathit{H}_3}$), 2.64 (d, J_{HP} = 1.6 Hz, $\mathrm{CCH_3}$), 3.51 (s, $\mathrm{CO_2CH_3}$), 4.20 (m, $^2J_{\mathrm{HH}}$ = 10.68 Hz, $^3J_{\mathrm{HH}}$ = 7.16 Hz, OCH), 4.22 (m, $^2J_{\mathrm{HH}}$ = 10.67 Hz, $^3J_{\mathrm{HH}}$ = 7.16 Hz, OCH), 7.2–7.7 (m, $\mathrm{C_6H_4}$)	14.19 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 20.92 (s, $\mathrm{C_6H_4\mathit{C}H_3}$), 34.05 (s, $\mathrm{CH_3}$), 49.58 (s, $\mathrm{CO_2\mathit{C}H_3}$), 73.13 (s, $\mathrm{OCH_2}$), 128–141 (m, $\mathrm{C_6H_4}$), 153.31 (d, J_{CP} = 6.8 Hz, $\mathrm{\mathit{C}CO_2CH_3}$), 158.79 (d, J_{CP} = 2.7 Hz, $\mathrm{CO_2}$), 196.76 (d, J_{CP} = 59.3 Hz, CO trans to P), 199.75 (d, J_{CP} = 7.6 Hz, CO cis to P), 201.56 (d, J_{CP} = 8.7 Hz, CO cis to P), 227.94 (d, J_{CP} = 11.5 Hz, $\mathrm{\mathit{C}OEt}$), 231.95 (d, J_{CP} = 10.6 Hz, $\mathrm{Re\mathit{C}CH_3}$)
6b[e]	2000 vs, 1922 s, 1892 s, 1695 m	1.05 (m, $\mathrm{PCH_2C\mathit{H}_3}$), 1.54 (t, J_{HH} = 7.13 Hz, $\mathrm{OCCH_2C\mathit{H}_3}$), 1.79 (m, $\mathrm{PCH_2}$), 2.93 (d, J_{HP} = 1.71 Hz, $\mathrm{CCH_3}$), 3.62 (s, $\mathrm{CO_2CH_3}$), 4.63 (M, $^2J_{\mathrm{HH}}$ = 10.37 Hz, $^3J_{\mathrm{HH}}$ = 7.19 Hz, OCH), 4.79 (m, $^2J_{\mathrm{HH}}$ = 10.38 Hz, $^3J_{\mathrm{HH}}$ = 7.19 Hz, OCH)	7.60 (d, J_{CP} = 2.3 Hz, $\mathrm{PCH_2\mathit{C}H_3}$), 14.78 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 18.73 (d, J_{CP} = 27.28 Hz, $\mathrm{PCH_2}$), 34.74 (s, $\mathrm{C\mathit{C}H_3}$), 49.95 (s, $\mathrm{CO_2\mathit{C}H_3}$), 79.54 (s, $\mathrm{OCH_2}$), 153.89 (d, J_{CP} = 4.65 Hz, $\mathrm{\mathit{C}CO_2CH_3}$), 159.15 (d, J_{CP} = 2.7 Hz, $\mathrm{CO_2}$), 197.99 (d, J_{CP} = 56.11 Hz, CO trans to P), 199.82 (d, J_{CP} = 7.38 Hz, CO cis to P), 201.92 (d, J_{CP} = 8.17 Hz, CO cis to P), 253.21 (d, J_{CP} = 11.74 Hz, $\mathrm{\mathit{C}OEt}$), 255.32 (d, J_{CP} = 11.70 Hz, $\mathrm{Re\mathit{C}CH_3}$)
7b[e]	2062 vw, 2002 m, 1988 s, 1888 vs, 1702 m, 1665 m, 1635 m	1.04–1.3 (m, both $\mathrm{PCH_2C\mathit{H}_3}$ and $\mathrm{OCH_2C\mathit{H}_3}$), 1.84 (d, $\mathrm{CH_3}$ overlap with $\mathrm{CPCH_2}$), 1.91 (m, $\mathrm{PCH_2}$ overlap with $\mathrm{CH_3}$), 2.21 (m, $\mathrm{RePCH_2}$), 3.47 (s, $\mathrm{CO_2CH_3}$), 4.00 (m, $\mathrm{OCH_2}$)	−2.52 (dd, $^2J_{\mathrm{CP}}$ = 25.18 Hz, $^3J_{\mathrm{CP}}$ = 7.38 Hz, ReCP), 7.37 (d, J_{CP} = 6.09 Hz, $\mathrm{PCH_2\mathit{C}H_3}$), 8.02 (d, J_{CP} = 3.11 Hz, $\mathrm{PCH_2\mathit{C}H_3}$), 15.79 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 15.27 (d, J_{CP} = 48.79 Hz, $\mathrm{PCH_2}$), 18.68 (d, J_{CP} = 23.76 Hz, $\mathrm{RePCH_2}$), 25.69 (dd, $^2J_{\mathrm{CP}}$ = 3.70 Hz, $^3J_{\mathrm{CP}}$ = 3.58 Hz, $\mathrm{C\mathit{C}H_3}$), 49.31 (s, $\mathrm{CO_2\mathit{C}H_3}$), 71.98 (s, $\mathrm{OCH_2}$), 112.40 (dd, $^2J_{\mathrm{CP}}$ = 6.98 Hz, $^3J_{\mathrm{CP}}$ = 6.81 Hz, $\mathrm{\mathit{C}CO_2CH_3}$), 164.87 (s, $\mathrm{CO_2}$), 198.73 (d, J_{CP} = 56.96 Hz, CO trans to P), 197.60 (d, J_{CP} = 8.80 Hz, CO cis to P), 200.57 (d, J_{CP} = 8.17 Hz, CO cis to P), 206.94 (dd, $^2J_{\mathrm{CP}}$ = 13.49 Hz, $^3J_{\mathrm{CP}}$ = 13.42 Hz, $\mathrm{Re\mathit{C}OEt}$)
8a	2105 w, 2001 vs, 1948 s, 1756 w, 1737 w, 1698 w	1.51 (t, J_{HH} = 7.11 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 3.65 (s, $\mathrm{CO_2CH_3}$), 3.83 (s, $\mathrm{CO_2CH_3}$), 4.62 (quartet, J_{HH} = 7.12 Hz, $\mathrm{OCH_2}$)	15.09 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 51.50 (s, $\mathrm{CO_2\mathit{C}H_3}$), 52.79 (s, $\mathrm{CO_2\mathit{C}H_3}$), 79.71 (s, $\mathrm{OCH_2}$), 126.51 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 163.19 (s, $\mathrm{CO_2}$), 163.29 (s, $\mathrm{CO_2}$), 184.10 (s, trans CO's), 189.15 (s, CO), 190.09 (s, CO), 196.37 (s, $\mathrm{ReO\mathit{C}CO_2CH_3}$), 268.31 (s, $\mathrm{Re\mathit{C}OEt}$)
8b	2101 w, 1999 vs, 1942 s, 1727 w, 1703 w	1.50 (t, J_{HH} = 7.07 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 2.38 (s, $\mathrm{CCH_3}$), 3.75 (s, $\mathrm{CO_2CH_3}$), 4.53 (quartet, J_{HH} = 7.07 Hz, $\mathrm{OCH_2}$)	15.23 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 26.00 (s, $\mathrm{C\mathit{C}H_3}$), 51.25 (s, $\mathrm{CO_2\mathit{C}H_3}$), 78.15 (s, $\mathrm{OCH_2}$), 127.53 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 165.64 (s, $\mathrm{CO_2}$), 185.19 (s, trans CO's), 189.97 (s, CO), 191.10 (s, CO), 211.81 (s, $\mathrm{ReO\mathit{C}CH_3}$), 258.53 (s, $\mathrm{Re\mathit{C}OEt}$)
8c	2106 w, 2004 vs, 1947 s, 1717 w, 1684 w	1.59 (t, J_{HH} = 7.12 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 3.72 (s, $\mathrm{CO_2CH_3}$), 4.66 (quartet, J_{HH} = 7.12 Hz, $\mathrm{OCH_2}$), 9.44 (s, CH)	15.14 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 50.83 (s, $\mathrm{CO_2\mathit{C}H_3}$), 79.75 (s, $\mathrm{OCH_2}$), 127.28 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 162.63 (s, $\mathrm{CO_2}$), 184.83 (s, trans CO's), 189.58 (s, CO), 190.41 (s, CO), 204.37 (s, ReOCH), 266.71 (s, $\mathrm{Re\mathit{C}OEt}$)
9a	*f*	1.38 (t, J_{HH} = 7.14 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 3.69 (s, $\mathrm{CO_2CH_3}$), 3.84 (s, $\mathrm{CO_2CH_3}$), 4.47 (quartet, J_{HH} = 7.14 Hz, $\mathrm{OCH_2}$)	13.98 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 51.58 (s, $\mathrm{CO_2\mathit{C}H_3}$), 52.03 (s, $\mathrm{CO_2\mathit{C}H_3}$), 65.58 (s, $\mathrm{OCH_2}$), 125.83 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 161.20 (s, $\mathrm{CO_2}$), 174.94 (s, $\mathrm{ReC\mathit{C}O_2}$), 184.36 (s, $\mathrm{ReO\mathit{C}OEt}$), 185.36 (s, trans CO's), 188.96 (s, CO), 190.60 (s, CO), 219.69 (s, $\mathrm{Re\mathit{C}CO_2CH_3}$)
9b	*f*	1.35 (t, J_{HH} = 7.12 Hz, $\mathrm{OCH_2C\mathit{H}_3}$), 2.91 (s, $\mathrm{CCH_3}$), 3.78 (s, $\mathrm{CO_2CH_3}$), 4.39 (quartet, J_{HH} = 7.10 Hz, $\mathrm{OCH_2}$)	14.05 (s, $\mathrm{OCH_2\mathit{C}H_3}$), 34.13 (s, $\mathrm{C\mathit{C}H_3}$), 51.60 (s, $\mathrm{CO_2\mathit{C}H_3}$), 64.32 (s, $\mathrm{OCH_2}$), 128.62 (s, $\mathrm{C\mathit{C}O_2CH_3}$), 165.25 (s, $\mathrm{CO_2}$), 184.60 (s, $\mathrm{ReO\mathit{C}OEt}$), 187.55 (s, trans CO's), 191.29 (s, CO), 191.56 (s, CO), 233.70 (s, $\mathrm{Re\mathit{C}CH_3}$)

[a] In $\mathrm{CH_2Cl_2}$ for **3a**,**b**,**4a**,**5b**,**6b**, and **7b**; THF for all other compounds. Abbreviations: vs, very strong; s, strong; m, medium; w, weak. [b] In $\mathrm{CD_2Cl_2}$ for **4a**, **5b**, and **6b**; in $\mathrm{CDCl_3}$ for **8a–c** and **9a**,**b**; all other compounds in $\mathrm{(CD_3)_2CO}$. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. In $\mathrm{CD_2Cl_2}$ for **3a**,**b**, **4a**, and **5b**; in $\mathrm{CDCl_3}$ for **8a–c** and **9a**,**b**; all other compounds in $\mathrm{(CD_3)_2CO}$. [d] DEPT experiments. [e] For ^{31}P NMR data, see the Experimental Section. [f] Indistinguishable from that of **8a**,**b** (see the Experimental Section).

Table II. Crystal Data and Collection and Refinement Parameters

	(1a)$_2$·THF	**2b**	**4a**	**8b**
	crystal data			
formula	$C_{26}H_{20}Na_2O_{19}Re_2$	$C_{12}H_{11}O_7Re$	$C_{34}H_{32}O_9PRe$	$C_{12}H_{11}O_8Re$
fw	1054.83	453.42	801.80	469.42
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2/c$
a, Å	12.642(2)	7.265(2)	11.549(2)	15.288(2)
b, Å	12.986(2)	27.695(2)	12.802(2)	6.466(1)
c, Å	11.179(1)	7.378(3)	23.784(2)	16.680(2)
α, deg	104.81(1)			
β, deg	98.00(1)	95.86(3)	103.53(1)	112.920(6)
γ, deg	88.06(1)			
V, Å^3	1757.0(8)	1477(1)	3419(2)	1518.7(7)
Z	2	4	4	4
D_{calcd}, g cm^{-3}	1.99	2.04	1.56	2.05
cryst size, mm	0.15 × 0.27 × 0.50	0.04 × 0.19 × 0.35	0.15 × 0.31 × 0.38	0.07 × 0.21 × 0.35
	data collection and refinement			
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
λ(Mo K$\bar{\alpha}$), Å	0.710 69	0.710 69	0.710 69	0.710 73
μ, cm^{-1}	70.75	83.64	36.96	81.40
transm factors	0.211–0.356	0.464–1.0	0.438–0.616	0.207–0.567
temp, K	296	296	296	296
2θ limits, deg	$4 \leq 2\theta \leq 55$	$4 \leq 2\theta \leq 55$	$4 \leq 2\theta \leq 55$	$4 \leq 2\theta \leq 55$
scan speed, deg min^{-1} (in ω with max 4 scans/refln)	8	8	4	4
scan type	ω–2θ	ω	ω	ω–2θ
scan range, deg in ω	$1.35 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$	$1.05 + 0.35 \tan\theta$
data collected	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of variables	445	181	416	190
no. of unique data	8087	3486	8204	3804
no. of unique data used in refinement	4927 ($I > 3\sigma(I)$)	1574 ($I > 3\sigma(I)$)	4207 ($I > 2\sigma(I)$)	2165 ($I > 3\sigma(I)$)
$R(F)$,[a] $R_w(F)$[b]	0.033, 0.035	0.041, 0.041	0.048, 0.044	0.033, 0.036
goodness of fit, e	1.17	1.20	1.23	1.16

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

mixture was first stirred for 1 h and then allowed to warm to room temperature in 2–4 h. The solvent was removed in vacuo, and the residue was washed with hexane and recrystallized from CH_2Cl_2/hexane at –23 °C to yield pale yellow crystals (0.20 g, 62%), mp 164–166 °C. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 35.3. Anal. Calcd for $C_{34}H_{32}O_9PRe$: C, 50.90; H, 4.02. Found: C, 50.70; H, 4.12.

(CO)$_3$(P(*p*-Tol)$_3$)ReC(Me)C(CO$_2$Me)C(OEt) (5b). The title complex was obtained in 72% yield (0.216 g) as a yellow solid by reaction of **2b** (0.186 g, 0.41 mmol) with P(*p*-Tol)$_3$ (0.125 g, 0.41 mmol) in CH_2Cl_2 (15 mL) for 45 min at room temperature, followed by recrystallization from CH_2Cl_2/hexane at –23 °C, mp 150 °C dec. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 12.8. FAB MS: *m/z* 730 (M$^+$), 702 (M$^+$ – CO), 674 (M$^+$ – 2CO), 646 (M$^+$ – 3CO). Anal. Calcd for $C_{32}H_{32}O_6PRe$: C, 52.67; H, 4.42. Found: C, 52.40; H, 4.31.

(CO)$_3$(PEt$_3$)ReC(Me)C(CO$_2$Me)C(OEt) (6b). A solution of **3b** (0.06 mmol) in hexane (15 mL) was maintained at reflux for 2 h, and the solvent was evaporated from the reaction mixture. The resultant yellow oil solidified when kept under reduced pressure for several days. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ –6.8. FAB MS: *m/z* 545 (M$^+$ + 1), 517 (M$^+$ – CO + 1), 487 (M$^+$ – 2CO – 1), 459 (M$^+$ – 3CO – 1).

(CO)$_3$(PEt$_3$)ReC(PEt$_3$)(Me)C(CO$_2$Me)C(OEt) (7b). A hexane solution of **6b** (7.0 mL, 0.124 M, 0.87 mmol) was treated with PEt$_3$ (0.14 mL, 0.95 mmol), and the reaction mixture was stirred for 30 min at room temperature as its color changed from orange to yellow. Removal of the volatiles left an orange-yellow oil. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 41.0 (s, CP), –15.4 (s, ReP). FAB MS: *m/z* 662 (M$^+$), 634 (M$^+$ – CO), 617 (M$^+$ – OEt), 608 (M$^+$ – 2CO + 2).

(CO)$_4$ReOC(CO$_2$Me)C(CO$_2$Me)C(OEt) (8a) and (CO)$_4$ReC(CO$_2$Me)C(CO$_2$Me)C(OEt)O (9a). A solution of $(NH_4)_2[Ce(NO_3)_6]$ (1.5 g, 2.7 mmol) in 60 mL of acetone was added to **2a** (0.40 g, 0.80 mmol), and the reaction mixture was stirred for 1 h, resulting in a color change from orange to yellow. (All subsequent manipulations were carried out in air.) Acetone was evaporated in vacuo, the residue was treated with CH_2Cl_2, and the resulting suspension was filtered to remove an insoluble yellow solid. A ^1H NMR spectrum of the filtrate revealed a 3:1 mixture of two products, which could not be distinguished by IR spectroscopy. The filtrate was concentrated and chromatographed on a column of silica gel eluting with 24% diethyl ether/pentane to remove a yellow band. (It may be necessary to repeat this chromatography to ensure isolation of a pure product.) The solvent was evaporated to leave a pale yellow oil, **8a**. The minor product **9a** could not be readily eluted off the column. It was characterized by NMR spectroscopies as an impurity in a sample of **8a**. FAB MS (for **8a**): *m/z* 513 (M$^+$ – 1), 483 (M$^+$ – OMe), 455 (M$^+$ – CO – OMe).

(CO)$_4$ReOC(Me)C(CO$_2$Me)C(OEt) (8b) and (CO)$_4$ReC(Me)C(CO$_2$Me)C(OEt)O (9b). These complexes were prepared similarly to **8a** and **9a** by reaction of **2b** (0.33 g, 0.73 mmol) with $(NH_4)_2[Ce(NO_3)_6]$ (1.5 g, 2.7 mmol) in acetone (60 mL). Again, a mixture of two products in an approximate ratio of 3:1 was indicated by ^1H NMR spectroscopy. The major product **8b** was obtained (0.11 g, 32%) after chromatography, eluting with 12% diethyl ether/pentane and evaporation to dryness of the collected solution. The off-white residue was recrystallized by slow evaporation of a saturated diethyl ether solution of **8b** at –23 °C. The minor product **9b** could not be eluted off the column and was therefore characterized by NMR spectroscopies as an impurity in a sample of **8b**, mp 62–64 °C. FAB MS: *m/z* 471 (M$^+$ + 1), 443 (M$^+$ – CO + 1), 413 (M$^+$ – 2CO – 1).

(CO)$_4$ReOCHC(CO$_2$Me)C(OEt) (8c). The title complex was obtained as a pale yellow oil from **2c** (0.31 g, 0.71 mmol) and $(NH_4)_2[Ce(NO_3)_6]$ (1.17 g, 2.13 mmol) in acetone (60 mL) by a procedure analogous to that for **8a** and **9a**. The product was eluted off the silica gel column with 13% diethyl ether/hexane. FAB MS: *m/z* 457 (M$^+$ + 1), 429 (M$^+$ – CO + 1), 399 (M$^+$ – 2CO – 1).

Crystallographic Analyses. Crystals of **(1a)$_2$·THF**, **2b**, **4a**, and **8b** for X-ray examination were obtained as described in the synthesis of these complexes. The cell constants were determined by a least-squares fit of the diffractometer (Rigaku AFC5S) setting angles for 25 reflections in the 2θ ranges 27–30, 23–30, 24–30, and 21–30°, respectively, for the four complexes with Mo Kα radiation. The crystal data are given in Table II.

Six standard reflections were measured after every 150 reflections during data collection; the crystal of **4a** was stable whereas the other three crystals displayed various amounts of decomposition. For **(1a)$_2$·THF**, the average decrease in intensity for the standards was 12%. For **2b**, the average decrease in intensity was 48%. Visual examination of this crystal at the end of data collection indicated that it had decreased in size, so that the decrease in intensity may have been the result of sublimation.

For **8b**, the intensities of the standards decreased by an average of 21%. Data reduction included linear decay corrections of $(\mathbf{1a})_2$·THF, **2b**, and **8b**. Data reduction and all subsequent calculations were done with the TEXSAN package of crystallographic programs[11] for all four complexes. For $(\mathbf{1a})_2$·THF, **4a**, and **8b**, the data were corrected for absorption by the analytical method;[12] for **2b**, the empirical ψ-scan method was used.[13]

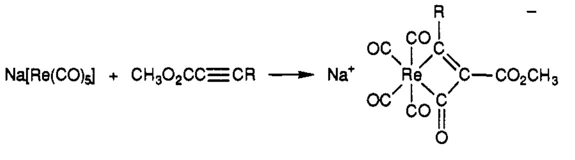
The positions of the Re atoms were located on Patterson maps. The remainder of each structure was obtained by a combination of the DIRDIF procedure[14] and standard Fourier methods. Full-matrix least-squares refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The $(\mathbf{1a})_2$·THF, there are four Na^+ ions in the unit cell: one is located at a general position from which the second ion gets generated by an inversion operation, and the third and fourth ions are each located at inversion centers. There are two Re anionic complexes and a THF solvent molecule present in the asymmetric unit. For **4a**, the methyl carbon atom of the OEt group is disordered over two positions, and these are labeled as C(13A) and C(13B). The occupancy factor (α) of C(13A) was allowed to refine and converged to 0.57(2). The occupancy factor for C(13B) was constrained to be $1 - \alpha$.

For all four structures, after a cycle of anisotropic refinement, H atoms were added to the model as fixed contributions in calculated positions with the assumption C–H = 0.95 Å for $(\mathbf{1a})_2$·THF and **2b** and C–H = 0.98 Å for **4a** and **8b**. The methyl hydrogens were idealized to sp^3 geometry on the basis of their positions in various difference electron density maps. The maximum and minimum peaks in the final difference electron density maps are as follows: for $(\mathbf{1a})_2$·THF, 1.55 and −1.25 e/Å^3; for **2b**, 0.90 and −0.80 e/Å^3; for **4a**, 0.82 and −0.67 e/Å^3; for **8b**, 0.60 and −1.06 e/Å^3. For **8b**, three reflections with F_o values significantly smaller than F_c values were removed from the data set for the final least-squares cycles: $(20\bar{2})$, (200), and $(10\bar{4})$. Scattering factors for neutral atoms were used along with anomalous dispersion terms.[15]

Further crystallographic details are provided in Table II. Lists of final positional and equivalent isotropic thermal parameters, anisotropic thermal parameters, and complete bond distances and angles for $(\mathbf{1a})_2$·THF, **2b**, **4a**, and **8b** are available as supplementary material.[16]

Results and Discussion

Anionic Rhenacyclobutenone Complexes. Sodium pentacarbonylrhenate(1-) reacts at ambient temperature with the activated acetylenes dimethylacetylenedicarboxylate (DMAD), methyl 2-butynoate, and methyl propiolate to afford the anionic metallacyclobutenone complexes **1a–c** (eq 1). The formation of **1a,c** takes place rapidly (within minutes of addition of the acetylene), whereas that of **1b** requires at least 12 h. **1a,b**, isolated as THF solvates, are stable for months under an inert atmosphere. **1c**, also a THF solvate, shows lower stability than **1a,b** in the solid under these conditions.



(1)

1a R = CO_2CH_3
1b R = CH_3
1c R = H

The addition of the acetylene to the metal and a cis CO of $[Re(CO)_5]^-$ to generate a rhenacyclobutenone ring is consistent with the spectroscopic data of **1** (vide infra) and has been confirmed by a single-crystal X-ray analysis of **1a**. The latter revealed the composition of solid **1a** as 2Na[Re(CO)$_5$]·2DMAD·THF ($(\mathbf{1a})_2$·THF), in agreement with the elemental analysis. The crystal structure contains two kinds of a $[Re(CO)_5]^-$ anion and three unique six-coordinate Na^+ cations. The former are rendered inequivalent by the manner in which the Na^+ ions are positioned around their periphery. This results in two different orientations of one of the CO_2Me groups. As can be seen in the ORTEP drawing in Figure 1, each Na^+ ion is surrounded by six oxygen atoms from the ligands of the $[(CO)_4\overline{ReC(CO_2Me)C(CO_2Me)C}(O)]^-$ anions and from the THF molecules. The ketonic oxygens (O(1), O(10)) and carbonyl oxygens of the central ester groups (O(8), O(17)) of the two drawn $[(CO)_4\overline{ReC(CO_2Me)C(CO_2Me)C}(O)]^-$ anions, along with an additional O(1) and a terminal CO oxygen (O(12)) from other rhenium-containing anions, are coordinated to Na(1). Four terminal CO oxygens and two ketonic oxygens bond to Na(2), while four ester carbonyl oxygens and two THF molecules coordinate to Na(3). A list of selected bond distances and angles is furnished in Table III. A mononuclear component of $(\mathbf{1a})_2$·THF (i.e. **1a**) is drawn in Figure 2, with the Na^+ ions omitted for clarity. The geometry around each Re atom is a distorted octahedron (the most acute angle of the cyclobutenone ring, C–Re–C, is 61.2(2)° (average)). The Re–C(O) and Re–C(CO$_2$-

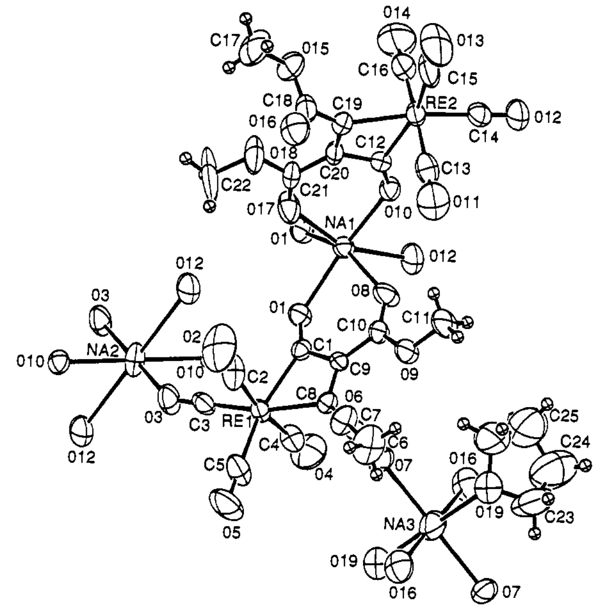


Figure 1. ORTEP drawing of the asymmetric unit of the crystal structure of $(\mathbf{1a})_2$·THF. Some additional symmetry related atoms are included to show the geometry about the Na^+ ions.

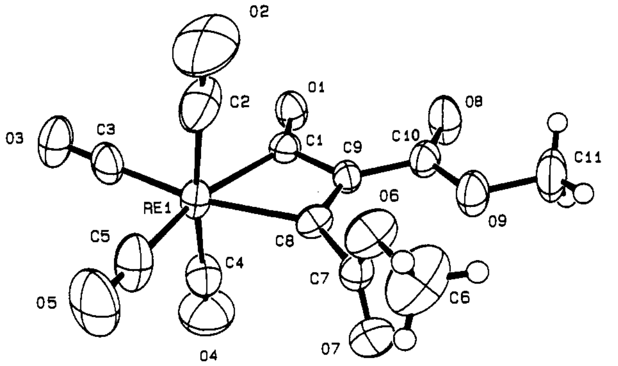


Figure 2. ORTEP drawing of the mononuclear unit **1a** of $(\mathbf{1a})_2$·THF, with the Na^+ ions removed for clarity. The non-hydrogen atoms are represented by 50% probability thermal ellipoids. The hydrogen atoms are drawn with an artificial radius.

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[11] TEXSAN, TEXRAY Structure Analysis Package, Version 2.1. Molecular Structure Corp., College Station, TX, 1987.

[12] de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

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[14] Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures – An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands, 1984.

[15] Scattering factors for the non-hydrogen atoms, including terms for anomalous dispersion, are from the *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71, 148. The scattering factor for the hydrogen atom is from Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

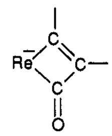
[16] See paragraph at end of paper regarding supplementary material.

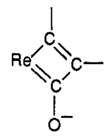
Table III. Selected Bond Distances (Å) and Angles (deg) for (**1a**)$_2$·THF

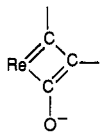
Re(1)–C(1)	2.193(7)	O(17)–C(21)	1.188(9)
Re(1)–C(8)	2.200(6)	O(18)–C(21)	1.331(9)
Re(2)–C(12)	2.197(7)	O(18)–C(22)	1.440(10)
Re(2)–C(19)	2.191(7)	C(1)–C(9)	1.491(9)
O(1)–C(1)	1.222(8)	C(7)–C(8)	1.488(9)
O(6)–C(6)	1.442(10)	C(8)–C(9)	1.342(9)
O(6)–C(7)	1.331(9)	C(9)–C(10)	1.479(9)
O(7)–C(7)	1.196(8)	C(12)–C(20)	1.488(9)
O(8)–C(10)	1.203(8)	C(18)–C(19)	1.503(10)
O(9)–C(10)	1.334(8)	C(19)–C(20)	1.361(10)
O(9)–C(11)	1.443(9)	C(20)–C(21)	1.472(10)
O(10)–C(12)	1.237(8)	Na(1)–O av	2.378(6)
O(15)–C(17)	1.456(11)	Na(2)–O av	2.627(5)
O(15)–C(18)	1.348(11)	Na(3)–O av	2.512(7)
O(16)–C(18)	1.184(10)		

C(1)–Re(1)–C(2)	83.6(3)	Re(1)–C(1)–C(9)	95.2(4)
C(1)–Re(1)–C(3)	106.0(3)	O(1)–C(1)–C(9)	125.3(6)
C(1)–Re(1)–C(5)	163.7(3)	Re(1)–C(2)–O(2)	175.8(10)
C(1)–Re(1)–C(8)	61.1(2)	O(6)–C(7)–O(7)	123.9(7)
C(2)–Re(1)–C(3)	89.8(3)	O(6)–C(7)–C(8)	111.7(6)
C(2)–Re(1)–C(4)	169.4(4)	O(7)–C(7)–C(8)	124.3(7)
C(2)–Re(1)–C(5)	97.0(4)	Re(1)–C(8)–C(7)	135.2(5)
C(2)–Re(1)–C(8)	86.7(3)	Re(1)–C(8)–C(9)	99.6(4)
C(3)–Re(1)–C(8)	166.9(3)	C(7)–C(8)–C(9)	125.2(6)
C(5)–Re(1)–C(8)	102.6(3)	C(1)–C(9)–C(8)	104.0(5)
C(12)–Re(2)–C(14)	105.5(3)	C(1)–C(9)–C(10)	126.0(6)
C(12)–Re(2)–C(15)	162.6(3)	C(8)–C(9)–C(10)	130.1(6)
C(12)–Re(2)–C(16)	86.5(4)	Re(2)–C(12)–O(10)	139.0(5)
C(12)–Re(2)–C(19)	61.2(3)	Re(2)–C(12)–C(20)	95.6(4)
C(13)–Re(2)–C(15)	93.7(5)	O(10)–C(12)–C(20)	125.4(6)
C(13)–Re(2)–C(16)	171.4(4)	Re(2)–C(19)–C(18)	136.0(5)
C(14)–Re(2)–C(16)	89.0(4)	Re(2)–C(19)–C(20)	99.9(5)
C(14)–Re(2)–C(19)	166.7(3)	C(18)–C(19)–C(20)	123.8(6)
C(15)–Re(2)–C(16)	94.8(5)	C(12)–C(20)–C(19)	103.2(6)
C(15)–Re(2)–C(19)	101.5(3)	C(12)–C(20)–C(21)	125.9(7)
C(16)–Re(2)–C(19)	89.1(3)	C(19)–C(20)–C(21)	130.9(7)
Re(1)–C(1)–O(1)	139.5(5)		

Me) average bond distances are equal (2.195(7) Å), and the carbon–carbon bond distances (O)C–C(CO_2Me) and (MeO_2C)C–C(CO_2Me) measure 1.490(9) and 1.352(9) Å (average), respectively, corresponding to a single and a double bond. The ketonic carbon–oxygen bond length of 1.230(8) Å (average) is close to that of a normal C═O double bond (1.20 Å).[17] The foregoing data support the metallacyclobutenone (III) formulation


III

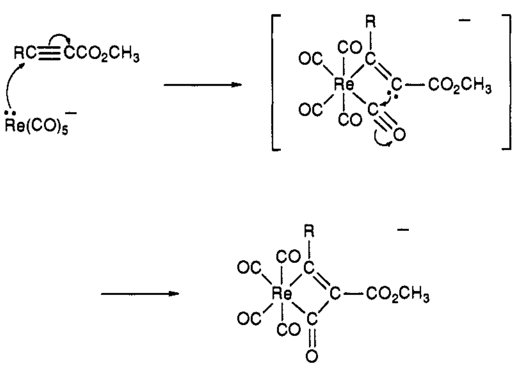

IV


V

of **1a**, with the resonance structures IV and V making lesser contributions. The rhenacyclobutenone ring is very nearly planar (the dihedral angle between the Re-C(O)-C(CO_2Me) and Re-C(CO_2Me)-C(CO_2Me) planes is 176.1° (average)).

The reactions of Na[Re(CO)$_5$] with the unsymmetrical acetylenes MeC≡CCO$_2$Me and HC≡CCO$_2$Me were investigated to elucidate the regiochemistry of this [2 + 2] cycloaddition. The products **1b,c** are also assigned rhenacyclobutenone structures on the basis of the similarlity of their spectroscopic data to those of **1a** (Table I). Accordingly, ^{13}C resonances of the ring carbons, listed in the order ReC(O), ReC═*C*, and Re*C*(R)═C, occur at δ 227.9, 159.3, and 187.0 for **1a**, δ 224.6, 163.0, and 214.3 for **1b**, and δ 228.8, 160.4, and 191.2 for **1c**. These assignments were aided by long-range C–H coupling experiments, which showed that the two kinds of CO_2Me protons of **1a** are coupled to the

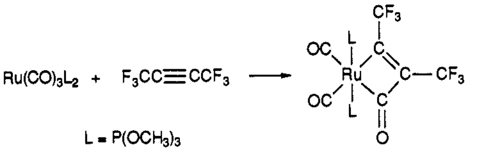
Scheme I



carbon atoms resonating at δ 175.9 and 160.5 (two *C*O$_2$Me). After that, the ^{13}C signals at δ 187.0 and 159.3 are assigned straightforwardly. For **1b**, the ReCMe protons are long-range coupled to the carbon atoms resonating at δ 214.1 (Re*C*Me) and 163.0 (ReC(Me)*C*), whereas the CO_2Me protons are long-range coupled to the carbon atom resonating at δ 160.8 (*C*O$_2$Me). Furthermore, a ^{13}C DEPT experiment showed that the signal at δ 191.2 for **1c** is that of the ReCH carbon. The foregoing results for **1b,c** implicate the ReC(R)C(CO$_2$Me)C(O) rather than the alternative ReC(CO$_2$Me)C(R)C(O) ring structure for these [2 + 2] cycloaddition products. The former type of structure was unequivocally established by an X-ray analysis of **2b**, obtained through derivatization of **1b** (vide infra).

The formation of **1** proceeds regiospecifically by nucleophilic attack of [Re(CO)$_5$]$^-$ at the R*C* acetylenic carbon atom. As depicted in Scheme I, this attack places the developing negative charge on the acetylenic carbon bearing the ester group, and leads to ring closure by nucleophilic interaction of this carbon with a cis CO ligand.

Although, to our knowledge, anionic metallacyclobutenone complexes had not been previously synthesized, examples of related neutral compounds, both mononuclear (eq 2)[18] and binuclear,[19-22]



(2)

have been reported. Furthermore, an anionic nitrogen-containing metallacyclic compound, Na[(CO)$_4$ReC(═CPh$_2$)N(Ph)C(O)], analogous to **1**, has been obtained by reaction of Na[Re(CO)$_5$] with Ph$_2$C═C═NPh.[23]

Rhenacyclobutadiene Complexes. Complexes **1a–c** undergo facile ethylation at the ketonic oxygen with Et$_3$OPF$_6$ in CH$_2$Cl$_2$ solution to afford the neutral rhenacyclobutadienes **2a–c** (eq 3) as stable yellow to orange solids in good yield. No reaction was observed between **1a–c** and the weaker alkylating reagent MeI under similar conditions.

The molecular structure of **2b** was elucidated by X-ray diffraction techniques, and an ORTEP drawing is presented in Figure 3 whereas selected bond distances and angles are given in Table IV. The structure confirms the proposed regiochemistry

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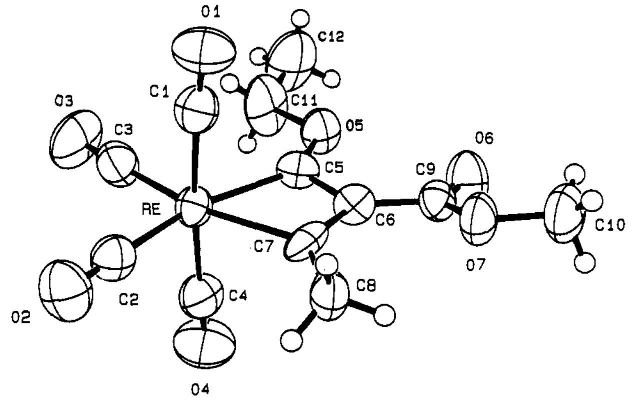
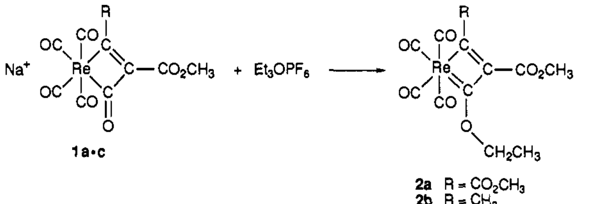


Figure 3. ORTEP drawing of **2b**. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

Table IV. Selected Bond Distances (Å) and Angles (deg) for **2b**

Re–C(5)	2.13(1)	O(7)–C(10)	1.44(2)
Re–C(7)	2.18(1)	C(5)–C(6)	1.45(2)
O(5)–C(5)	1.30(1)	C(6)–C(7)	1.36(2)
O(5)–C(11)	1.46(1)	C(6)–C(9)	1.46(2)
O(6)–C(9)	1.19(1)	C(7)–C(8)	1.49(2)
O(7)–C(9)	1.34(1)		
C(1)–Re–C(2)	91.4(6)	Re–C(5)–O(5)	141(1)
C(1)–Re–C(3)	92.4(6)	Re–C(5)–C(6)	99.8(8)
C(1)–Re–C(4)	175.0(5)	O(5)–C(5)–C(6)	119(1)
C(1)–Re–C(5)	87.6(5)	C(5)–C(6)–C(7)	100(1)
C(1)–Re–C(7)	87.2(5)	C(5)–C(6)–C(9)	128(1)
C(2)–Re–C(5)	162.0(5)	C(7)–C(6)–C(9)	132(1)
C(2)–Re–C(7)	102.2(5)	Re–C(7)–C(6)	100.5(8)
C(3)–Re–C(5)	105.6(5)	Re–C(7)–C(8)	132(1)
C(3)–Re–C(7)	165.4(6)	C(6)–C(7)–C(8)	128(1)
C(5)–Re–C(7)	59.8(5)		

of the cycloaddition of $MeC{\equiv}CCO_2Me$ to $[Re(CO)_5]^-$ in the formation of the precursor complex **1b**, i.e. addition of $Me\mathit{C}{\equiv}$ to Re and of $\equiv\mathit{C}CO_2Me$ to cis CO. The dihedral angle of 179.1° between the Re–C(5)–C(6) and Re–C(7)–C(6) planes of **2b** shows the rhenacyclobutadiene ring to be planar, as it is in the related complex $(CO)_4Re(\eta^2\text{-}C_3Ph_3)$.[6] However, unlike the ring in the latter rhenacyclobutadiene, which is symmetrical, the ring in **2b** displays a noticeable lack of symmetry. The two Re–C_α bond lengths are only slightly different (Re–C(5) = 2.13(1) Å and Re–C(7) = 2.18(1) Å), but the two C–C bond distances differ considerably more (C(5)–C(6) = 1.45(2) Å and C(6)–C(7) = 1.36(2) Å). The O(5)–C(5) bond distance of 1.30(1) Å is longer than the corresponding C═O bond in the rhenacyclobutenone $(\mathbf{1a})_2\cdot$THF; however, it is considerably shorter than the O(5)–C(11) bond distance of 1.46(1) Å of **2b**, a typical C–O single bond.[17] The transannular distances Re···C(6) of 2.77 Å and C(5)···C(7) of 2.15 Å indicate no bonding interaction between these two pairs of opposite atoms. The most acute bond angle in the four-membered ring is C(5)–Re–C(7) (59.8(5)°), whereas the angle C(5)–C(6)–C(7) measures 100(1)°. These bond angles and the average Re–C_α bond length are remarkably close to the corresponding values for $(CO)_4Re(\eta^2\text{-}C_3Ph_3)$.[6]

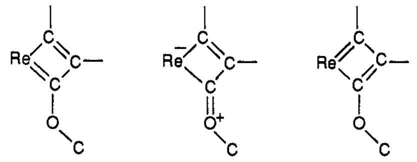


(3)

1a-c

2a R = CO₂CH₃
2b R = CH₃
2c R = H

The foregoing bond distances support a bonding description of **2b** in terms of the resonance structures VI and VII. This representation corresponds to a metallacyclic structure that incorporates a metal–(Fischer) carbene bond and a metal–vinyl bond. Resonance structure VIII, in contrast, appears to be making a smaller contribution on the basis of the values of the aforementioned bond distances of **2b**. Interestingly, however, as will be shown later, C(7) shows a more pronounced Fischer carbene reactivity than does C(5).



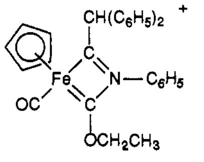
VI VII VIII

Spectroscopic data for **2a–c**, set out in Table I, support similar structural features of the three complexes. In the $^{13}C\{^1H\}$ NMR spectra, two downfield signals are observed in the region δ 254–210 for each complex and are assigned to the C_α atoms of the ring. For **2c**, a ^{13}C DEPT experiment showed the resonance at δ 219.8 as belonging to CH; the one at δ 251.9 is then assigned to *C*OEt. On the basis of the foregoing correspondence, the assignments of δ 253.8 to *C*OEt and of δ 210.5 to *C*CO₂Me for **2a** would appear probable. With the help of long-range C–H coupling experiments, the closely separated signals at δ 246.4 and 243.7 for **2b** are attributed to *C*Me and *C*OEt, respectively.

The downfield resonances in the $^{13}C\{^1H\}$ NMR spectra of **2** are characteristic of Fischer carbene complexes. Typical chemical shifts of carbene carbon atoms of the latter range from δ 400 to 200.[24] The observed values for **2** lend support to contribution of each of the resonance structures VI and VIII.

The static structure noted by ^{13}C NMR spectroscopy at ambient temperature for the Fischer-type rhenacyclobutadiene complexes **2a–c** contrasts with a dynamic behavior of the related compound $(CO)_4Re(\eta^2\text{-}C_3Ph_3)$.[6] For that complex, the ^{13}C NMR spectrum at −50 °C is consistent with the X-ray structure; however, at higher temperatures a dynamic process occurs which is thought to involve rapid interconversion between rhenacyclobutadiene and rhenium-η^3-cyclopropenyl structures. A similar dynamic behavior has been proposed for high-valent rhenium metallacycle complexes.[11]

Complexes **2** represent unique examples of metallacyclobutadienes or metallacycles incorporating two carbene–vinyl ambifunctional groups that are stabilized by the presence of a heteroatom attached to one of the C_α carbon atoms. A structurally related ring in a cationic complex, IX was reported by Fehlhammer;[25] however, its complete characterization by X-ray diffraction techniques and ^{13}C NMR spectroscopy is apparently lacking.



IX

Reactions of Rhenacyclobutadiene Complexes with Tertiary Phosphines. Addition of nucleophiles to the carbene carbon atom is an important class of reactions of Fischer carbene complexes.[8,24] To investigate the electrophilic character of the rhenacyclobutadiene complexes **2a,b**, we examined their reactions with tertiary phosphines.

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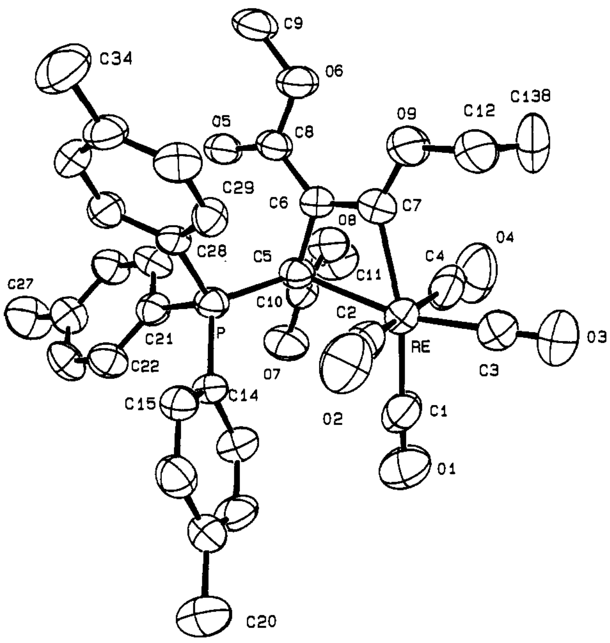
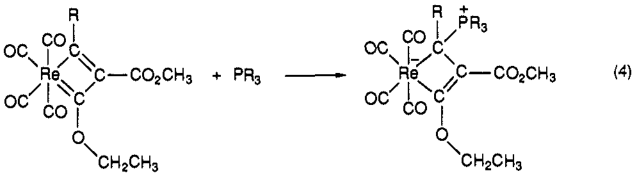


Figure 4. ORTEP drawing of **4a**. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are omitted. Only one of the disordered positions for C(13) is shown.

Complex **2a** reacts with each of PEt_3 and $P(p\text{-Tol})_3$ to yield the addition products **3a** and **4a**, respectively, whereas **2b** reacts with PEt_3 at ambient temperatures to give the adduct **3b** (eq 4). In all three cases, the phosphine adds to the carbene carbon atom bearing group R (CO_2Me or Me).


(4)

2a-b

3a R = CO_2CH_3, PR_3 = $P(C_2H_5)_3$
3b R = CH_3, PR_3 = $P(C_2H_5)_3$
4a R = CO_2CH_3, PR_3 = $P(p\text{-}C_6H_4CH_3)_3$

The regiochemistry of the foregoing nucleophilic addition reaction was established by an X-ray diffraction analysis of the structure of the $P(p\text{-Tol})_3$ adduct of **2a** (**4a**). An ORTEP drawing of **4a** is presented in Figure 4, whereas selected bond distances and angles are given in Table V. The added $P(p\text{-Tol})_3$ is attached to the α-carbon atom (C(5)) that also carries the CO_2Me substituent in a new zwitterionic rhenacyclobutene structure. This four-membered ring is puckered, with the dihedral angle between the Re–C(7)–C(6) and Re–C(5)–C(6) planes being equal to 173.8°. The Re–C(5) bond (2.377(7) Å) is longer than the Re–(C(7) bond (2.153(8) Å), and the C(6)–C(7) distance of 1.352(10) Å reflects a C═C double bond while the C(5)–C(6) distance of 1.497(9) Å measures close to that of a C—C single bond.

The ORTEP drawing also shows the bulkiness of the $P(p\text{-Tol})_3$ moiety, which might be expected to hinder rotation around the P–C(5) bond. Such restricted rotation has been confirmed by NMR spectroscopy (Table I). In the ^1H NMR spectrum of **4a**, a barrier to rotation is evidenced by the appearance of three resonances for the Me protons of $P(p\text{-Tol})_3$ and by the extremely broad resonance of the Me protons of the CO_2Me group geminal to $P(p\text{-Tol})_3$. The $^{31}P\{^1H\}$ NMR spectrum of **4a** likewise shows a broad signal. In the $^{13}C\{^1H\}$ NMR spectrum the resonances assigned to the three carbon atoms of $PCCO_2Me$ also experience broadening. By way of contrast, the NMR spectra of the PEt_3 adducts of **2a** and **3a**, i.e. **3a** and **3b**, respectively, do not show a signal broadening presumably because of the lesser steric requirements of this phosphine.

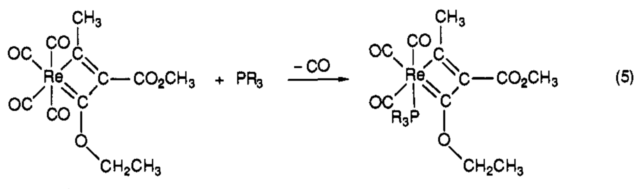
Table V. Selected Bond Distances (Å) and Angles (deg) for **4a**

Re–C(5)	2.377(7)	O(8)–C(11)	1.454(10)
Re–C(7)	2.153(8)	O(9)–C(7)	1.357(9)
P–C(5)	1.820(7)	O(9)–C(12)	1.439(10)
O(5)–C(8)	1.213(8)	C(5)–C(6)	1.497(9)
O(6)–C(8)	1.352(8)	C(5)–C(10)	1.500(10)
O(6)–C(9)	1.433(8)	C(6)–C(7)	1.352(10)
O(7)–C(10)	1.198(8)	C(6)–C(8)	1.454(9)
O(8)–C(10)	1.361(9)		
C(1)–Re–C(2)	91.8(4)	C(5)–P–C(21)	114.1(4)
C(1)–Re–C(3)	89.8(3)	C(5)–P–C(28)	108.5(3)
C(1)–Re–C(4)	91.5(4)	C(10)–O(8)–C(11)	114.8(7)
C(1)–Re–C(5)	103.4(3)	C(7)–O(9)–C(12)	118.8(7)
C(1)–Re–C(7)	164.1(3)	Re–C(5)–P	120.0(4)
C(2)–Re–C(3)	85.8(4)	Re–C(5)–C(6)	88.6(4)
C(2)–Re–C(4)	173.2(4)	Re–C(5)–C(10)	104.5(4)
C(2)–Re–C(5)	96.3(3)	P–C(5)–C(6)	115.5(5)
C(2)–Re–C(7)	92.7(4)	P–C(5)–C(10)	106.6(5)
C(3)–Re–C(4)	88.2(4)	C(6)–C(5)–C(10)	121.1(7)
C(3)–Re–C(5)	166.5(3)	C(5)–C(6)–C(7)	107.7(6)
C(3)–Re–C(7)	105.8(3)	C(5)–C(6)–C(8)	121.4(7)
C(4)–Re–C(5)	88.7(3)	C(7)–C(6)–C(8)	130.8(7)
C(4)–Re–C(7)	85.8(4)	Re–C(7)–O(9)	137.2(6)
C(5)–Re–C(7)	60.9(3)	Re–C(7)–C(6)	102.5(5)
C(5)–P–C(14)	115.1(3)	O(9)–C(7)–C(6)	120.1(7)

Complexes **3a,b** are assigned structures analogous to that of **4a** on the basis of similarities of their NMR spectra to those of **4a**. The $^{13}C\{^1H\}$ NMR spectra are particularly revealing, as they show a dramatic upfield shift of the resonance of the *C*R α-carbon atom of the four-membered ring upon the addition of the phosphine. Accordingly, this signal moves from δ 210.5 for **2a** to δ 12.1 for **3a** and δ 122.5 for **4a**, and from δ 246.4 for **2b** to δ −2.6 for **3b**. Similar upfield shifts have been noted upon addition of PR_3 to the α-carbon atom of Fischer carbene complexes of tungsten.[26] Complexes **3a,b** and **4b** show metal carbonyl stretching bands at lower frequencies than the parent rhenacyclobutadienes (cf. Table I), consistent with their zwitterionic nature (positive charge at P and negative charge at Re).

It is somewhat surprising that the addition of PR_3 occurs at the carbene carbon *C*R rather than *C*OEt, since the latter carbon atom of **2a** shows a more pronounced electropositive or Fischer carbene character by ^{13}C NMR. It is unlikely that steric factors are of any major consequence in these additions, as neither CO_2Me/Me nor OEt exerts much more steric influence than the other. Thus, in all probability, nucleophilic attack of PR_3 is orbital rather than charge controlled, as proposed for simple carbene complexes.[27-29]

Unlike **2a**, **2b** reacts with $P(p\text{-Tol})_3$ at ambient temperature to give the CO-substitution product **5b** (eq 5). The pattern of three strong IR ν(CO) bands for **5b** is diagnostic of a six-coordinate *fac*-tricarbonyl structure.[30] In the $^{13}C\{^1H\}$ NMR spectrum, two ReC signals at δ 232.0 and 227.9 and three equal intensity ReCO


(5)

2b

5b PR_3 = $P(p\text{-}C_6H_4CH_3)_3$

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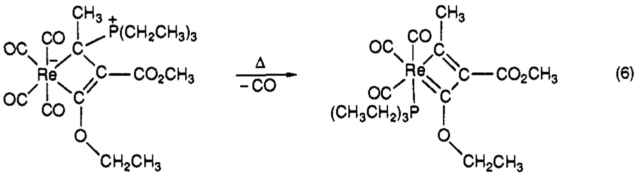
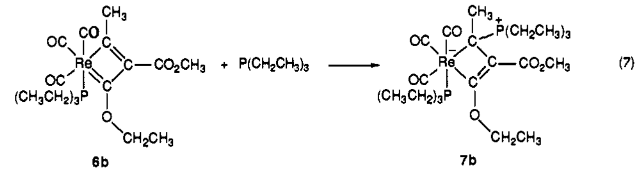
signals at δ 201.6, 199.8, and 196.8 lend support to the assigned structure. The last signal occurs with a substantial phosphorus–carbon coupling constant, J_{CP} = 59.3 Hz, and is attributed to the CO trans to P(p-Tol)$_3$. The other four signals have values of J_{CP} in the range 7.6–11.5 Hz (Table I). Interestingly, the CH$_2$ protons of the OEt group appear inequivalent in the ^{1}H NMR spectrum, presumably owing to the presence of a chiral rhenium center, and are seen as two overlapping quartets. All ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR signals of **5b** are quite sharp, in contrast to those in the spectra of **4a**.

The reactions of **1a** and **2b** with P(p-Tol)$_3$ demonstrate that the nature of substituent (CO$_2$Me or Me) at the α-carbon atom of the rhenacyclobutadiene complex can have a considerable effect in determining whether addition or substitution will occur. In an attempt to prepare an addition product of **2b** and P(p-Tol)$_3$ that would be analogous to **4a**, the two reactants were allowed to interact at −78 °C and then warmed to room temperature. Monitoring by ^{31}P NMR spectroscopy revealed the formation of a product with a resonance at δ 27.7, in addition to **5b** (δ 12.8). The product underwent conversion to **5b** in the course of attempted isolation and could not be completely characterized. While it is possible that this species represents the desired adduct of **2b** and P(p-Tol)$_3$, the observed instability of the intermediate makes such an assignment tenuous.

Rhenacyclobutadiene–phosphine adducts can undergo conversion to the corresponding CO-substitution products on heating. Thus, complex **3b** loses 1 equiv of CO in hexane at reflux to afford a quantitative yield of the CO-substituted **6b** (eq 6). The ^{13}C{^{1}H} NMR spectrum of **6b** reveals two carbene carbon signals at δ 255.3 and 253.2 and three CO signals at δ 201.9–198.0 with the coupling constants J_{CP} similar to those for **5b**. The phosphine-substituted rhenacyclobutadiene **6b** reacts with another equivalent of PEt$_3$ to give the addition product **7b**, which incorporates two molecules of the phosphine (eq 7). As do the related complexes **3a**,**b**, and **4a**, complex **7b** shows a ^{13}C{^{1}H} NMR spectrum in which one of the α-carbon atom resonances has shifted dramatically upfield to δ-2.5 while the other one is still observed downfield at δ 206.9. The ^{31}P{^{1}H} NMR spectrum of **7b** consists of two singlets at δ 41.0 and −15.4, in the regions expected for CPR$_3$ and RePR$_3$ phosphine attachments, respectively. Complex **7b** does not react further by PEt$_3$ substitution under reflux conditions.



3b **6b**

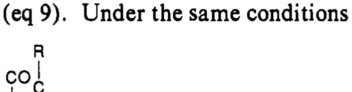


6b **7b**

Attempts were made also to convert **3a** and **4a** to phosphine-substituted rhenacyclobutadiene complexes analogous to **5b** and **6b**, however, without success. No reaction was observed when **3a** was heated at reflux in hexane for 40 h. When **4a** was maintained in toluene at reflux or treated with Me$_3$NO in an attempt to remove a CO ligand, only uncharacterized decomposition products were obtained.

Reactions of chromium and tungsten carbene complexes (CO)$_5$M=C(R)OMe (M = Cr, W) with secondary and tertiary phosphines have been investigated by Fischer and co-workers.[26,31–33] It was observed that at low temperatures reversible addition of the phosphine occurred at the carbene carbon, whereas at the higher temperatures carbon monoxide substitution took place instead. Heating the adduct of the carbene complex and phosphine led to the appropriate substitution at the metal center. Reactions of the methyl-substituted rhenacyclobutadiene complexes **2b** and **6b** with PR$_3$ in general follow a similar pattern. In contrast, the MeO$_2$C-substituted complex **2a** was found only to form the addition compounds, there being no evidence for substitution at rhenium. Fischer and co-workers[33] concluded that the value of the equilibrium constant for the reversible addition of phosphines to (CO)$_5$M=C(Me)OMe (M = Cr, W) depends on M, phosphine, and the solvent. Since only methoxy-substituted carbene complexes were used, the effect of a substituent at the α-carbon atom on K_{eq} was not determined. Our results appear to indicate that the presence of CO$_2$Me at the α-carbon stabilizes the adducts of metal carbene complexes and PR$_3$.

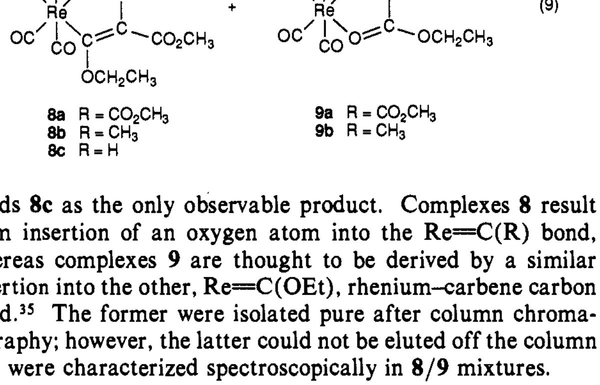
Oxidation of Rhenacyclobutadiene Complexes. Fischer carbene complexes can be oxidized, with an oxygen atom replacing the metal in the released oxidized organic ligand, as illustrated in eq 8.[7,34] A similar reaction of the rhenacyclobutadienes **2** was



$$(CO)_5Cr{=}C(OR^2)R^1 \xrightarrow{[O]} O{=}C(OR^2)R^1 + \cdots \qquad (8)$$

considered as a possible means of detaching a modified carbene ligand from the rhenium center and making it available in organic synthesis.

Treatment of complexes **2a** and **2b** with an excess of (NH$_4$)$_2$[Ce(NO$_3$)$_6$] at ambient temperatures affords the oxygen atom insertion products **8a**/**9a** and **8b**/**9b**, respectively, in a ratio of ca. 3:1 **8**/**9** (eq 9). Under the same conditions for the oxidation, **2c** yields **8c** as the only observable product. Complexes **8** result from insertion of an oxygen atom into the Re=C(R) bond, whereas complexes **9** are thought to be derived by a similar insertion into the other, Re=C(OEt), rhenium–carbene carbon bond.[35] The former were isolated pure after column chromatography; however, the latter could not be eluted off the column and were characterized spectroscopically in **8**/**9** mixtures.



2a-c

8a R = CO$_2$CH$_3$
8b R = CH$_3$
8c R = H

9a R = CO$_2$CH$_3$
9b R = CH$_3$

The structure of **8b** was determined by single-crystal X-ray diffraction analysis and is shown in Figure 5. Selected bond distances and angles are listed in Table VI. The five-membered oxametallacyclic ring adopts an envelope conformation with the O(5), C(5), C(6), and C(7) atoms in a plane. The Re atom is 0.16 Å from this plane and is the flap atom of the envelope. The

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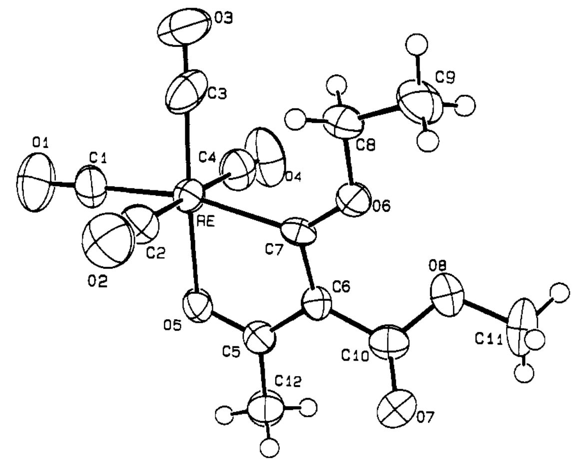
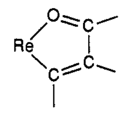


Figure 5. ORTEP drawing of **8b**. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

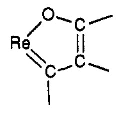
Table VI. Selected Bond Distances (Å) and Angles (deg) for **8b**

Re–O(5)	2.153(5)	O(8)–C(10)	1.364(10)
Re–C(7)	2.165(8)	O(8)–C(11)	1.457(10)
O(5)–C(5)	1.287(9)	C(5)–C(6)	1.415(11)
O(6)–C(7)	1.317(9)	C(5)–C(12)	1.490(11)
O(6)–C(8)	1.451(9)	C(6)–C(7)	1.413(11)
O(7)–C(10)	1.200(10)	C(6)–C(10)	1.484(11)
O(5)–Re–C(1)	91.6(3)	C(3)–Re–C(7)	102.1(3)
O(5)–Re–C(2)	92.9(3)	C(4)–Re–C(7)	88.0(3)
O(5)–Re–C(3)	176.3(3)	Re–O(5)–C(5)	116.2(5)
O(5)–Re–C(4)	87.6(3)	O(5)–C(5)–C(6)	119.3(7)
O(5)–Re–C(7)	75.7(2)	O(5)–C(5)–C(12)	116.1(7)
C(1)–Re–C(2)	90.0(4)	C(6)–C(5)–C(12)	124.6(7)
C(1)–Re–C(3)	90.6(4)	C(5)–C(6)–C(7)	115.1(7)
C(1)–Re–C(4)	92.5(4)	C(5)–C(6)–C(10)	119.9(7)
C(1)–Re–C(7)	167.3(3)	C(7)–C(6)–C(10)	124.8(8)
C(2)–Re–C(3)	90.1(4)	Re–C(7)–O(6)	132.4(5)
C(2)–Re–C(4)	177.5(4)	Re–C(7)–C(6)	113.2(6)
C(2)–Re–C(7)	89.7(3)	O(6)–C(7)–C(6)	114.3(7)
C(3)–Re–C(4)	89.4(4)		

Re–C(7) bond distance of 2.165(8) Å may be compared to the corresponding distance of 2.13(1) Å in **2b** and to the Re–C(CH_2SiMe_3) distance of 2.162(4) Å in *fac*-$(CO)_3(PPh_3)ReOC(OEt)CHC(CH_2SiMe_3)$, reported recently by Bergman and Heathcock.[36] In both rhenium oxametallacyclic complexes, this bond length is midway between Re–C_{sp2} single (ca. 2.22 Å) and double (ca. 2.09 Å) bonds.[37–39] A substantial amount of carbenoid character reflected by these distances is also indicated by the ^{13}C NMR data[24] (vide infra). The C(5)–C(6) and C(6)–C(7) bond distances of 1.415(11) and 1.413(11) Å show extensive delocalization in the chelate ring (resonance structures X and XI), in



X



XI

contrast to the corresponding distances in the Bergman–Heathcock compound, which measure 1.418(5) and 1.351(6) Å, respectively[36] (resonance structure X). Both patterns of carbon–carbon bond lengths have been noted in related oxametallacyclic compounds of manganese,[40] tungsten,[41–43] and osmium.[44]

The spectroscopic data presented in Table I reveal that complexes **8a–c** all adopt a similar structure, which is related to the structure of the respective precursor rhenacyclobutadienes **2a–c**. The $^{13}C\{^1H\}$ NMR data are particularly informative in the elucidation of the site of oxygen atom insertion. Following the oxidation, the resonance of the carbene carbon involved in the insertion shifts upfield by ca. 15 ppm for each of the R = CO_2Me and H derivatives (δ 210.5 to 196.4 and δ 219.8 to 204.4), and by ca. 30 ppm for the R = Me derivative (δ 246.4 to 211.8). The resonances of the carbon (when R = CO_2Me or Me) and hydrogen (when R = H) atoms bonded to these carbon atoms also experience upfield shifts. In contrast, the carbene carbon atom still bonded to rhenium in **8a–c** (i.e. *C*OEt) shows a ca. 15-ppm downfield shift of its resonance upon oxidation of the parent **2**.

Complexes **9a** and **9b** have been assigned oxametallacyclic structures derived by oxygen atom insertion into the Re=C(OEt) bond of **2a** and **2b**, respectively, from ^1H and $^{13}C\{^1H\}$ NMR data. The resonances of the *C*OEt carbon atom of **2a** at δ 253.8 and of **2b** at δ 243.7 move upfield to δ 184.4 and 184.6, respectively, upon oxidation to the appropriate **9**. The signals of the *C*R carbon atom, in contrast, experience much smaller shifts. Furthermore, for the OEt group, the position of the CH_2 carbon resonance in **2a** and **2b**, which remains virtually unaffected by the insertion of oxygen into the Re=C(R) bond, shifts upfield by ca. 15 ppm when oxygen inserts into the Re=C(OEt) bond to give **9a** and **9b**, respectively. Likewise, the CH_2 proton resonances of **2a** (δ 4.99) and **2b** (δ 4.70) move farther upfield in the formation of **9** (δ 4.47 and 4.39, respectively) than in the formation of **8** (δ 4.62 and 4.53, respectively).

Five-membered oxametallacyclic complexes structurally related to **8** and **9** have been synthesized for rhenium and other transition metals but, with one exception,[6] not by oxidation of metallacyclobutadienes. Instead such complexes have been obtained by insertion of appropriate alkynes into metal–carbon (acyl or enolate) and metal–hydrogen bonds.[40–44] The method described here is experimentally straightforward and provides an alternative approach to these five-membered ring compounds for rhenium when the corresponding metallacyclobutadiene can be prepared.

Conclusions

Novel Fischer-type metallacyclobutadiene complexes $(CO)_4ReC(R)C(CO_2Me)C(OEt)$ (R = CO_2Me, Me, H), in which one α-carbon atom of the ring is bonded to a heteroatom, have been obtained by treatment of $[Re(CO)_5]^-$ with $RC{\equiv}CCO_2Me$ followed by akylation with Et_3OPF_6. These complexes show metal carbene character of both ring α-carbon atoms by the values of their Re=C_α bond distances and by the downfield positions of their ^{13}C α-carbon resonances. Their reactivity toward the tertiary phosphines PEt_3 and $P(p\text{-}Tol)_3$ and toward $(NH_4)_2[Ce(NO_3)_6]$

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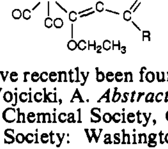
[35] Alternatively, the minor products may result from insertion of oxygen into the Re=C(R) bond followed by replacement of RC=O with $MeCO_2$ in the coordination sphere of Re to give



Related rearrangements have recently been found to occur in other reactions of **2**, see: Plantevin, V.; Wojcicki, A. *Abstracts of Papers*, 206th National Meeting of the American Chemical Society, Chicago, IL, August 22–27, 1993; American Chemical Society: Washington, DC, 1993. Although we favor structure **9** from spectroscopic data, we cannot rule out the alternative structure.

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further reflects the Fischer-type carbenoid character of these rhenacyclobutadienes. In general, the phosphines add to the Re*C*(R) carbon atom at low temperatures, and replace one CO on rhenium at the higher temperatures. $(NH_4)_2[Ce(NO_4)_6]$ oxidizes the rhenacyclobutadienes by oxygen atom insertion into the M=C bonds to give five-membered oxametallacyclic compounds. Both nucleophilic addition/substitution and oxidation reactions find precedence in the chemistry of simple Fischer metal carbene complexes.

Acknowledgment. We gratefully acknowledge financial support of this investigation by the National Science Foundation and The Ohio State University. High-field NMR and mass spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019). L.L.P. thanks the Phillips Petroleum Foundation for a graduate fellowship. We acknowledge helpful discussions of this chemistry with Ms. Véronique Plantevin.

Supplementary Material Available: Tables of final positional and equivalent isotropic thermal parameters, anisotropic thermal parameters, and complete bond distances and angles for complexes $(\mathbf{1a})_2$·THF, **2b**, **4a**, and **8b** (28 pages). Ordering information is given on any current masthead page.