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Synthesis of bimetallic carbonyl complexes of manganese, rhodium, and ruthenium from 1,4-bis(cyclopentadienylthallium)-1,4-butadione

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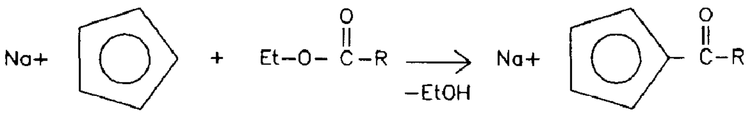
Abstract

1,4-Bis(cyclopentadienylsodium)-1,4-butadione was prepared from reaction of sodium cyclopentadienide and diethylsuccinate and converted into its thallium analog by metal exchange using thallium ethoxide. Reaction of the thallium reagent with $BrMn(CO)_5$ yielded 1,4-bis(cymantrenyl)-1,4-butadione, while reaction with $[ClRh(CO)_2]_2$ gave both a bis(cyclopentadienylrhodiumdicarbonyl) complex and a small amount of a bis(cyclopentadienylrhodiumcarbonyl)-μ-carbonyl species. This latter material was found to undergo slow exchange on the NMR time scale which is believed to involve a side-to-side movement of both the μ-carbonyl and interring bridge. A complete variable temperature analysis of this motion was carried out. Reaction of the thallium reagent with $[Cl_2Ru(CO)_3]_2$ resulted in the formation of a bis(cyclopentadienylrutheniumdicarbonyl) complex and small quantities of two other materials which have not yet been characterized. With the exception of these last two, all transition metal compounds have been fully characterized with IR, ^1H and ^{13}C NMR, mass spectroscopy and elemental analysis.

Bimetallic complexes in which two cyclopentadienylmetal moieties are linked through the cyclopentadienyl rings have the potential of exhibiting a high degree of metal cooperativity because of the proximity of the two metal atoms. Several classes of compounds with the general formula MCp–X–CpM have been reported including those in which $X = CH_2$ [1], $SiMe_2$ [2], and $(CH_2)_3$ [3]. Both cyclopentadienyl and tetramethylcyclopentadienyl rings are represented among the reported compounds. Fulvalene complexes in which the cyclopentadienyl rings are directly coupled constitute a special class of these bimetallic compounds which are being examined by several groups [4].

We have been concerned with the preparation of cyclopentadienylthallium synthons which can be used for the formation of several kinds of cyclopentadienylmetal complexes [1a,5]. Rausch and coworkers have reported that formyl, acetyl and



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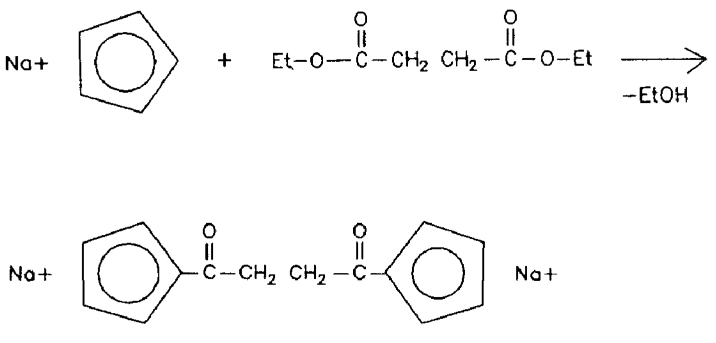


(2)

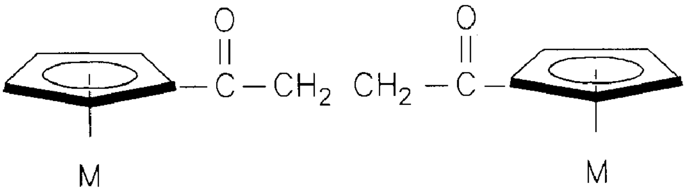
I

carboalkoxycyclopentadienylsodium salts can be prepared by reaction of sodium cyclopentadienide and $RCO_2C_2H_5$, where $R = H, CH_3, OCH_3$, or OC_2H_5, respectively [6]. Arthur has prepared the analogous thallium salts of these compounds and used them for the synthesis of rhodium and iridium complexes [7]. Recently, Bitterwolf, Rausch and Jones have reported improved routes to formyl, acetyl, carboalkoxy, and benzoylcyclopentadienylthallium reagents and have employed them in the preparation of manganese, rhenium, and rhodium complexes [8]. In this paper we wish to report the expansion of these techniques for the preparation of 1,4-bis(cyclopentadienylsodium)-1,4-butadione (I) and its conversion to 1,4-bis(cyclopentadienyl thallium)-1,4-butadione (II). II has been used as a starting point for the synthesis of a series of bimetallic complexes which constitute the first examples of complexes with a four carbon atom bridge between the cyclopentadienyl rings.

Results and discussion

Reactions of sodium cyclopentadienide with esters (eq. 1) give carbonyl substituted cyclopentadienyl products as their sodium salts. These sodium salts can be used directly in the synthesis of transition metal complexes, or can be converted to thallium salts which are generally more air stable and readily handled then their sodium counterparts. We have found that the analogous reaction of an excess of sodium cyclopentadienide with diethylsuccinate (eq. 2) yields 1,4-bis(cyclopentadienyl-sodium)-1,4-butadione, I, as a white to light grey powder in excellent yield. This sodium salt can be readily converted to the corresponding thallium salt, II, by reaction with thallium ethoxide in ethanol. After washing, the thallium salt is recovered as an analytically pure off white solid which is stable to air and can be stored indefinitely under nitrogen without decomposition.

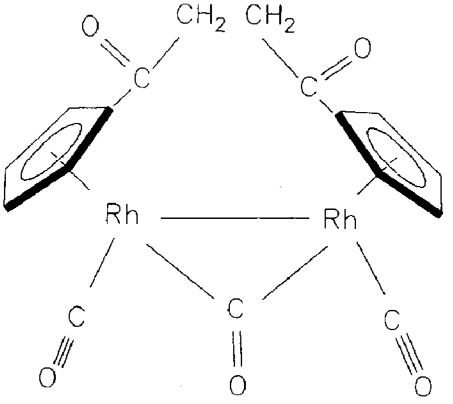
Reaction of II with $BrMn(CO)_5$ in refluxing benzene gives the previously unreported bis(cymantrene) complex III in good yield. A similar reaction with $[ClRh(CO)_2]_2$ gave compounds IV and a small quantity of V. Efforts to prepare V by thermolysis of IV in refluxing xylene or by reaction of IV with trimethylamine oxide have been unsuccessful. $[Cl_2Ru(CO)_3]_2$ reacts with II to give VI in low yield along with small amounts of two other products. These products have complex ^1H NMR and IR spectra and seem to be polymeric products. It has not thus far been possible to characterize these materials.



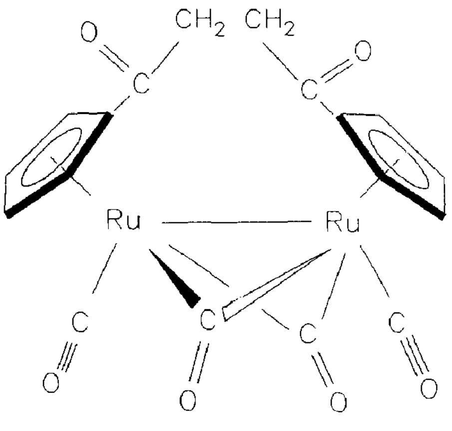
II M = Tl
III M = $Mn(CO)_3$
IV M = $Rh(CO)_2$

Compounds III–VI have been fully characterized by IR, ^1H and ^{13}C NMR as well as by mass spectroscopy and elemental analysis. The relatively simple proton spectra of compounds III, and IV consist of an A_2B_2 triplet for the cyclopentadienyl rings and a singlet for the bridge protons. The proton resonances for the manganese compound are broadened due to the 5/2 spin of ^{55}Mn. The ^{13}C NMR spectra of III and IV contain resonances for all ring, bridge and metal-carbonyl resonances. Rhodium coupling is observed for both the metal carbonyl carbons and the ring carbons.

Surprisingly, the ^1H NMR spectrum for VI consists of a sharp singlet for both the cyclopentadienyl ring protons and the bridge protons. Presumably accidental overlap of the ring hydrogen resonances is contributing to the observed ring singlet as the ^{13}C NMR spectrum of the ring is quite normal showing three lines in the



V



VI

expected intensity ratio for the ring carbons. The ruthenium carbonyl resonances could not be located, even after extended acquisition time.

These NMR observations suggest that the coupled rings and bridges in III, IV, and VI are undergoing substantial, rapid movement which averages the magnetic environments of the ring and bridge protons on the NMR time scale. This averaging is particularly surprising in the case of VI in which the Ru–Ru bond might be expected to contort the molecule so as to create a substantial barrier to oscillation. Indeed, Dreiding models of VI suggest that the bridge must be severely cramped to accommodate the molecule in the *cis* orientation which is indicated by the IR spectrum (vide infra).

Compound V underwent significant decomposition in $CDCl_3$, but its NMR spectra were recorded without difficulty in rigorously degassed benzene-d_6 or toluene-d_8. The room temperature proton NMR spectrum of this compound in benzene-d_6 consisted of four ill-resolved resonances for the cyclopentadienyl protons and a broad doublet for the ethylene protons of the bridge. These features suggested that dynamic processes were occurring on the NMR time scale. The motion which is being observed is believed to involve a side to side switch of the four atom bridge between the rings and the μ-CO between the metals as illustrated in Fig. 1 [9]. A similar movement of the bridging carbonyl is known for

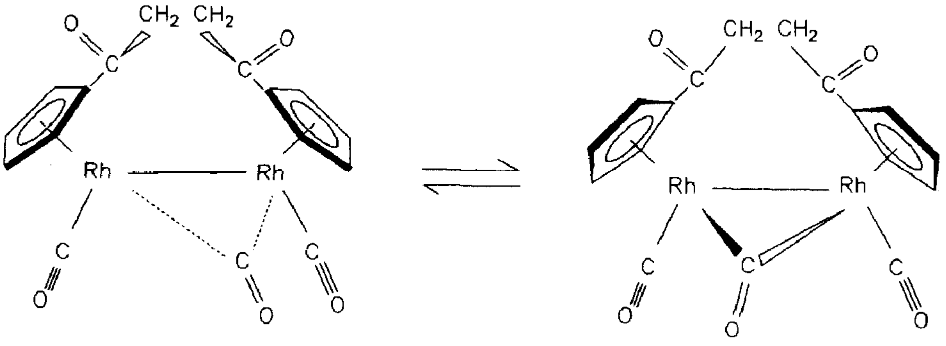


Fig. 1. Proposed oscillation for side-to-side flip of V.

Table 1

Spectral and thermodynamic data for variable temperature study of V

Limiting spectrum: 190 K (in ppm)		T_c	$\Delta G^{\neq}$ (kJ)
5.51 4.45	Protons 2 and 5	299 K	56.9
4.64 4.54	Protons 3 and 4	297 K	62.3
2.93 2.02	Bridge protons, J 6.0 Hz	306 K	58.7

$[CpRh(CO)]_2$-μ-CO [9] and has also been observed by us for $CH_2[(C_5H_4)Rh(CO)]_2$-μ-CO and $CH_2[(C_5H_4)Ir(CO)]_2$-μ-CO [10].

A variable temperature NMR study of V was carried out in an effort to determine the magnitude of this barrier. A variable temperature study conducted in benzene-d_6 provided a manifold of clean, well-resolved spectra at 1°C intervals about the coalescence points giving T_c values with an accuracy of $+/-1$°C. Unfortunately, a low temperature limiting spectrum could not be obtained in benzene. A second study carried out in toluene-d_8 provided an excellent set of low temperature limiting spectra at 190 K, but the spectra in the region of resonance coalescence were not as well resolved as those in benzene. T_c values are estimated to be accurate to at least $+/-2$°C in toluene. The low temperature limiting spectrum of V at 190 K was found to consist of four sharp ring proton resonances and two well-defined doublets for the bridge ethylene protons. The spectral data for V along with coalescence and Free Energy values are presented in Table 1. The observed $\Delta G^{\neq}$ values are in the range of 57–62 kJ/mole. By comparison, we have found that $CH_2[(C_5H_4)Rh(CO)]_2$-μ-CO and $CH_2[(C_5H_4)Ir(CO)]_2$-μ-CO undergo a similar motion with $\Delta G^{\neq}$ values of 54 and 70 kJ/mole, respectively [10].

Concurrent with the variable temperature ^1H NMR study carried out on V, it was found that the room temperature ^{13}C spectrum of V contained a sharp resonance for the 3 and 4 carbons and two broad resonances for the 2 and 5 carbons. At 230 K the two broad resonances were found to have merged to a single broad resonance. At 270 K the resonance for the 2 and 5 carbons appeared as a sharp singlet. Overnight heating of the sample at 270 K resulted in the appearance of new resonances which were presumed to be from a small amount of a thermal decomposition product.

The metal carbonyl stretching frequencies of compounds I–VI are consistent with those of the analogous acetylcyclopentadienyl compounds [8]. The terminal carbonyl stretching bands for both V and VI have a “strong-weak” pattern characteristic of a *cis* ring configuration. The ketone carbonyl stretching frequencies of compounds III and IV (1685 and 1666 cm^{-1}, respectively) are very similar to those of their acetyl analogous (1685 and 1667 cm^{-1}), whereas the ketonic stretching frequencies of the metal–metal bonded complexes V and VI (1653 and 1673 cm^{-1}, respectively) have shifted substantially down in energy compared to their acetyl counterparts (1669 and 1681 cm^{-1}). We attribute this shift to lower energies to strain imposed on the bridge by coupling the metals which produces an eight atom, dimetal ring.

The ketonic stretching frequencies are also indicative of the electron donor abilities of the cyclopentadienylmetal complexes. The stretching frequencies decrease in the order Mn > Ru > Rh which is the anticipated order of increasing electron donation. This same order is seen in the acetylcyclopentadienyl series as well.

The mass spectra of compounds III–VI have been recorded using both electron impact and chemical ionization techniques. In all cases, the parent mass was weak or not observed with electron impact techniques, but was easily observed with chemical ionization. All compounds exhibit the expected cascade loss of carbonyl groups which has been previously reported for the bis(cyclopentadienyl)methane series of compounds. In addition, it would appear that bridge fragmentation is also occurring since fragments are observed which can be attributed to loss of bridge carbonyl and/or C_2H_4 fragments in addition to the loss of metal carbonyl groups. As might be anticipated, the mass spectrum of V is essentially identical to that of IV except for the M^+ fragment. In all cases a major fragment is observed which would correspond to a metal–metal multiple bonded species, i.e., $Cp'_2Mn_2(CO)_3{}^+$, $Cp'_2Rh_2(CO)_2{}^+$, and $Cp'_2Ru_2(CO)_3{}^+$, where Cp'_2 is 1,4-bis(cyclopentadienyl)-1,4-butadione. The ruthenium and rhodium compounds also fragment to give a metallocenophane, Cp'_2M^+, as a major species.

The ease with which two cyclopentadienyl groups are introduced onto the organic diester suggests that it should be possible to prepare bis(cyclopentadienyl) reagents with interring tethers of varying lengths. Alternately, it may be possible to use the reaction of cyclopentadienyl anions with esters to introduce the cyclopentadienyl functionality into appropriate polymers containing ester groups. We are presently examining these approaches to dinuclear complexes and polymer supported complexes, as well as conducting detailed investigations of the chemistry of the ring functionality itself.

Experimental

Diethylsuccinate was purchased from Aldrich and pentacarbonylmanganese bromide was purchased from Strem. These materials were used as received. Thallium ethoxide [11], $[ClRh(CO)_2]_2$ [12] and $[Cl_2Ru(CO)_3]_2$ [13] were prepared by standard literature routes. *Note*: Thallium compounds are highly toxic and must be handled with rigorous safety precautions. All solvents were dried and distilled under nitrogen. Preparative chromatography was conducted using nitrogen flushed solvents and neutral (CAMAG) alumina.

Infrared spectra were recorded on a Bio-Rad Qualimatic FTIR Spectrometer. ^1H and ^{13}C NMR spectra were recorded on an IBM NR-300 MHz NMR spectrometer and were referenced to appropriate solvent resonances. Mass spectroscopy was carried out by Dr. Gary Knerr using both electron impact and chemical ionization modes on a VG 7070-HS GC/MS using direct insertion. Elemental analyses were conducted by Desert Analytics of Tucson, AZ.

Synthesis of 1,4-bis(cyclopentadienylsodium)-1,4-butadione (I)

A 500 ml 3-necked flask equipped with a reflux condenser, addition funnel and a spin bar was charged with 10.2 g (177 mmol) of 40% sodium dispersion in mineral oil. The flask was evacuated and backflushed with argon. Dry THF (200 ml) was added to the flask and the flask was cooled in ice water. An excess of freshly cracked cyclopentadiene (about 16 ml) was added slowly to the sodium dispersion. When all of the cyclopentadiene had been added, the ice water bath was removed and the reaction was allowed to warm to room temperature. Diethylsuccinate, 15.4 g (88.5 mmol), was added rapidly to the solution of sodium cyclopentadienide and the solution refluxed overnight. During this time a white precipitate formed in the reaction mixture. After cooling the mixture to room temperature, solvent was removed under nitrogen by filter stick and the resulting solid washed twice with ethyl ether. Yield 15.5 g (60.3%) of off white, air sensitive solid.

Synthesis of 1,4-bis(cyclopentadienylthallium)-1,4-butadione (II)

I, 6.0 g (23 mmol), was transferred under nitrogen to a 200 ml Schlenk flask equipped with a stir bar. Absolute ethanol (50 ml) was added and thallium ethoxide, 11.45 g (46 mmol), was added dropwise with stirring. A tan solid formed rapidly. After addition of all of the thallium ethoxide, the solution was stirred at room temperature for 2 h. The resulting solid was recovered by vacuum filtration using a Buchner filter and was washed alternately with ethyl alcohol, ethyl ether and pentane. Yield 12.0 g (84.4%) of II as an air stable, tan solid. Analysis: Found: C, 26.40; H, 2.00. $C_{14}H_{12}O_2Tl_2$ calcd.: C, 27.06; H, 1.93%.

Synthesis of 1,4-bis(cyclopentadienylmanganese tricarbonyl)-1,4-butadione (III)

Manganese pentacarbonyl bromide, 4.0 g (14.6 mmol), and II, 4.0 g (6.47 mmol), were taken up in 50 ml of benzene under nitrogen and refluxed overnight under nitrogen. The reaction mixture was filtered through Celite and the filter plug washed with benzene. After removal of solvent the resulting dark brown oil was chromatographed on neutral alumina using dichloromethane as an eluant. A dark brown band was eluted which gave a tan crystalline solid upon removal of solvent. Yield 1.05 g (33%) of a tan crystalline solid, m.p. 134–137 °C. IR (CH_2Cl_2): 2031(s), 1949(s), 1684(m) cm^{-1}. ^1H NMR ($CDCl_3$): 5.48 (broad s, 4H), 4.86 (broad s, 4H), 3.00 (broad s, 4H). ^{13}C NMR ($CDCl_3$): 222.8 (Mn–CO), 195.7 (ketone CO), 91.2 (Cp), 86.7 (Cp), 83.7 (Cp), 32.7 (C_2H_4). MS (chemical ionization): 491 (45.8) $M^+ + 1$; 474 (1.6) – H_2O; 462 (5.2) – CO; 435 (4.7) – 2CO; 406 (100) – 3CO; 379 (13.7) – 4CO; 351 (4.7) – 5CO; 322 (100) – 6CO. Analysis: Found: C, 49.25; H, 2.73. $C_{20}H_{12}O_8Mn_2$ calcd.: C, 48.98; H, 2.45%.

Synthesis of 1,4-bis(cyclopentadienylrhodium dicarbonyl)-1,4-butadione (IV) and 1,4-bis(cyclopentadienylrhodium carbonyl)-1,4-butadione-μ-carbonyl[Rh-Rh] (V)

II, 3.0 g (4.8 mmol) and $[ClRh(CO)_2]_2$, 1.9 g (4.9 mmol), were taken up in benzene and refluxed overnight under nitrogen. After filtration of the reaction mixture and removal of benzene, the oily residue was taken up in 1/1 petroleum ether/dichloromethane and eluted on a neutral alumina column. A broad yellow band was eluted followed by a red band. Additional green and purple bands were observed but were not isolated.

The major yellow band was shown by HPLC to contain a minor, rapidly moving component along with the major component. Careful chromatography of this mixture yielded a small amount of a yellow oil which had infrared bands (CH_2Cl_2) at 2055, 1993, 1728, and 1670 cm^{-1}. This component is believed to be singly metallated and was not further examined. After removal of solvent from the major component, IV, was isolated as a yellow solid, m.p. 132–133 °C. Yield: 0.93 g (36%). IR (CH_2Cl_2): 2055, 1993, 1667 cm^{-1}. ^1H NMR ($CDCl_3$): 5.37 (t, 4H), 4.83 (t, 4H), 2.77 (s, 4H). ^{13}C NMR (CDCl$_3$): 191.3 (ketone CO), 189.4 (d, J 83.5 Hz, Rh–CO), 106.6 (Cp), 91.5 (Cp), 86.4 (Cp), 32.6 (C$_2$H$_4$). MS (chemical ionization): 531 (0.4) $M^+ + 1$, 502 (1.3) – CO, 474 (56.3) – 2CO, 446 (13.3) – 3CO, 417 (7.9) – 4CO, 390 (2.2) – 5CO or 4CO and C$_2$H$_4$, 362 (3.9) – 6CO or 4CO + bridge fragments, 315 (100.0) Cp$'_2$Rh$^+$. Analysis: Found: C, 41.20; H, 2.14. C$_{18}$H$_{12}$O$_6$Rh$_2$ calcd.: C, 40.75; H, 2.26%.

The red band described above yielded V as a red crystalline solid, m.p. 168–169 °C. Yield: 30 mg (1.2%). Ir (CH$_2$Cl$_2$): 2014 (sh), 2004 (s), 1837 (s), 1663 (sh), 1653 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): (297 K) 5.90 (broad s, 4H), 5.59 (broad s, 4H), 3.17 (broad s, 2H), 2.79 (broad s, 2H). ^{13}C (toluene-d_8): (297 K) 192.3 (ketone), 107.7 (ring C(1)), 95.1 and 91.2 (broad s, ring C(2) and C(5)), 89.6 (ring C(3) and C(4)), 35.9 (C$_2$H$_4$). (330 K) 192.1 (ketone), 107.8 (ring C(1)), 93.1 (broad s, ring C(2) and C(5)), 89.6 (ring C(3) and C(4)), 36.0 (C$_2$H$_4$). (370 K) 192.1 (ketone) 107.9 (ring C(1)), 92.9 (sharp s, ring C(2) and C(5)), 89.7 (ring C(3) and C(4)), 36.3 (C$_2$H$_4$). MS (chemical ionization): 502 (3.84) M^+, 474 (38.31) $M^+ -$ CO, 446 (6.93) $M^+ - 2$ CO, 418 (3.74) $M^+ - 3$ CO, 390 (1.07) $M^+ - 4$ CO or 3CO + C$_2$H$_4$, 362 (1.48) $M^+ -$ 5CO or 4CO + bridge fragments, 315 (100.00) Cp$'_2$Rh$^+$. Analysis: Found: C, 40.76; H, 2.51. C$_{17}$H$_{12}$O$_5$Rh$_2$ calcd.: C, 40.63; H, 2.39%.

Synthesis of 1,4-bis(cyclopentadienylruthenium dicarbonyl)-1,4-butadione (VI)

II, 3.63 g (5.86 mmol) and [Cl$_2$Ru(CO)$_3$]$_2$, 3.0 g (5.86 mmol), were taken up in benzene and refluxed overnight under nitrogen. After filtration and removal of the solvent, the resulting brown oil was taken up in dichloromethane and chromatographed on a neutral alumina column using dichloromethane as an eluant. A red band was eluted from which 30 mg of VI was recovered as an orange crystalline solid, m.p. 177–179 °C. Yield 1%. IR (CH$_2$Cl$_2$): 1980 (s), 1952 (m), 1789(s), 1673 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 5.67 (broad s, 8H), 2.80 (broad s, 4H). ^{13}C NMR (CDCl$_3$): 195.0 (ketone CO), 102.3 (Cp), 92.2 (Cp), 89.5 (Cp), 36.1 (C$_2$H$_4$). MS (chemical ionization): 528 $M^+ + 2$; 500 – CO; 471 – 2CO; 441 – 3CO; 416 – 4CO; 388 – 5CO; 358 – 6CO; 314 (C$_5$H$_4$)COC$_2$H$_4$CO(C$_5$H$_4$)Ru. Analysis: Found: C, 41.37; H, 2.45. C$_{18}$H$_{12}$O$_6$Ru$_2$ calcd.: C, 41.06; H, 2.28%.

Continued elution of the column using dichloromethane yielded a yellow band from which 31 mg of a yellow powder was recovered which darkens but does not melt up to 250 °C. IR (CHCl$_3$): 2014.6 (s), 1975.1 (m), 1700.0 (s), 1680 (sh), 1669.4 (m) cm^{-1}. The ^{1}H NMR spectrum of this material in CDCl$_3$ and in acetone-d_6 were complex with apparent olefin resonances in addition to eight distinct ring-hydrogen resonances and an ill-resolved cluster of aliphatic resonances. Further efforts to clarify the structure of this material are underway.

Extraction of the solid residue from the initial filtration using dichloromethane and a soxhlet apparatus yielded 50 mg of a red-orange solid. IR (CH$_2$Cl$_2$): 2065.8 (s), 2016.6 (s), 1962.5 (w), 1785.0 (m), 1684.8 (complex, m) cm^{-1}.

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