Organometallics **1983,** *2,* 1202–1207

the temperature range 188–303 K.

The above assignment and hence the proposed pattern of dynamic behavior for I is inconsistent with that reported for the structurally related carbide clusters $\mathrm{Fe_4M(CO)_x(C)}$.[33] In the latter systems however intermetallic exchange is rapid at ambient temperature for basal sites although less facile between basal and apical sites; intrametallic exchange at $\mathrm{M(CO)_3}$ units is also facile.

Possible factors contributing to the slow intermetallic exchange in I may include the rigid stereochemistry at Ru(4) and Ru(5), the presence of a μ-$\mathrm{PPh_2}$ group occupying a site stereochemically equivalent to that of a bridging CO group in one of the proposed intermediates for intermetallic basal ligand exchange in the carbido clusters, and the fact that activation energies for fluxional processes are generally higher for ruthenium than iron clusters. In this regard it is worth noting that whereas the carbonyls bound to the apical atom in the carbido iron clusters appear equivalent at the lowest temperatures attainable,[33] in I rotation of the apical $\mathrm{Ru(CO)_3}$ unit is slow on the NMR time scale at 188 K.

The $^{13}\mathrm{CO}$ spectrum of II (Table VII) did not permit unequivocal assignment of any bands, other than the bridging CO, due to the lack of distinguishing features in the spectrum over the temperature range studied.

Conclusions

The molecule $\mathrm{Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)}$ may be considered as a closed-shell 74-electron cluster according to the EAN rule or as a nido polyhedron with seven skeletal electron pairs in terms of the Wade–Williams–Rudolph–Mingos counting rules.[34] In the former case addition of two electrons to give a 76-electron species should result in a polyhedron with only seven metal–metal bonds. In the latter a conversion from a nido octahedron to an arachno pentagonal bipyramid is predicted. Extensions of the skeletal electron counting scheme to include certain hydrocarbon atoms as verticles[34,35] are not as readily applicable in that, while I can indeed be viewed as a monocapped square pyramid, the CO adduct II does not readily fit into the nido category.

Rearrangements of the type encountered here are fundamental to cluster chemistry. There are, for example, increasing indications that associative interactions may be responsible for ligand exchange and substitution in cluster systems.[3] Clearly, cluster metal–metal bond cleavage creating additional coordination sites may play a similar role to the generation of coordinatively unsaturated species in mononuclear chemistry. Exploitation of this behavior in cluster catalysis may be possible.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for a grant (A.J.C.) and a scholarship (S.A.M.).

Registry No. I, 85957-32-0; II, 85957-33-1; $\mathrm{Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)(MeCN)}$, 85957-34-2; $\mathrm{Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)(Pr\text{-}\mathit{i}\text{-}NH_2)}$, 85957-35-3; $\mathrm{Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)(\mathit{sec}\text{-}BuNH_2)}$, 85957-36-4; $\mathrm{Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)(C_5H_5N)}$, 85957-37-5; $\mathrm{Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)(PhCN)}$, 85957-38-6.

Supplementary Material Available: Table S1, anisotropic thermal parameters for $\mathrm{Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)}$, Table S2, anisotropic thermal parameters for $\mathrm{Ru_5(CO)_{14}(\mu_5\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)}$, Table S3, additional bond angles and bond lengths for $\mathrm{Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)}$, and Table S4, additional bond angles and bond lengths for $\mathrm{Ru_5(CO)_{14}(\mu_5\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)}$, and tables of observed and calculated structure factors for $\mathrm{Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)}$ and $\mathrm{Ru_5(CO)_{14}(\mu_5\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)}$ (43 pages). Ordering information is given on any current masthead page.

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Reactions of 2-Alkoxyfurans with Nonacarbonyldiiron or Dodecacarbonyltriruthenium Giving Binuclear Vinylcarbene Complexes and a 2-Pyrone Complex. A Novel Precursor for α,β-Unsaturated Alkylidene Ligands and an Unusual Carbonylation of the Furans

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2-Methoxyfuran reacted with nonacarbonyldiiron in diethyl ether at 35 °C for 4 h to give a binuclear α,β-unsaturated alkylidene complex, hexacarbonyl(μ-3-η^1-*anti*-(methoxycarbonyl)-η^3:η^1-allyl)diiron(*Fe–Fe*)(**5a**) and a 2-pyrone derivative, tricarbonyl(3–6-η-6-methoxy-2-pyrone)iron (**6a**). 2-Methoxyfuran also reacted with dodecacarbonyltriruthenium in benzene under an atmosphere of carbon monoxide at 150 °C for 4 h to give a corresponding binuclear α,β-unsaturated alkylidene complex, hexacarbonyl(μ-3-η^1-*anti*-(methoxycarbonyl)-η^3:η^1-allyl)diruthenium(*Ru–Ru*) (**10**), 6-methoxy-2-pyrone (**11**), and dimethyl glutaconate (**12**). Both reactions could be explained by assuming mononuclear η^3-vinylcarbene complexes as reaction intermediates.

Much attention has been focused on the chemistry of alkylidene–transition-metal complexes; mono- (**1**)[1] and binuclear (**2**)[2] alkylidene complexes have been well investigated especially concerning the mechanism for

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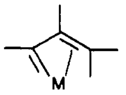
Fischer–Tropsch reactions and the metatheses of olefins. Furthermore, mono- (**3**)[3,4] and binuclear (**4**)[5] 1–3-η α,β-unsaturated alkylidene or vinylcarbene complexes have been prepared; the structures have been determined by X-ray analyses and the large contribution of the structure (**3′**)[4,6] or (**4′**)[5,7] has been revealed. Although it has been pointed out that these complexes are the key intermediates in the characteristic carbon–carbon bond formation on metal complexes such as double carbonylation[5] or metathetical polymerization of acetylenes,[8] there have been only a few method to prepare these complexes.[7-19] We now report (i) that 2-alkoxyfurans are novel precursors of α,β-unsaturated alkylidene ligands and (ii) that an unusual carbonylation of 2-alkoxyfuran gives 6-alkoxy-2-pyrone derivatives.



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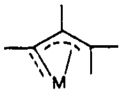

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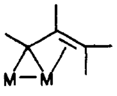

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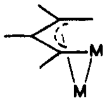

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Results and Discussion

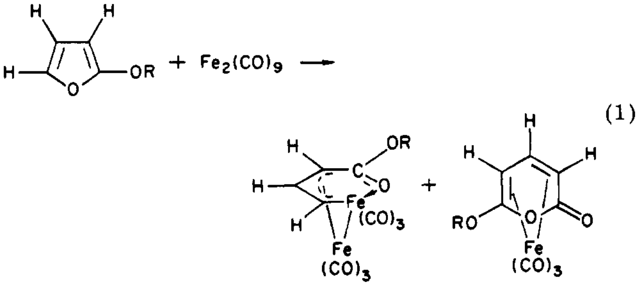
Reactions of 2-Alkoxyfurans with Nonacarbonyldiiron. 2-Methoxyfuran (0.27 g, 2.8 mmol) readily reacted with $Fe_2(CO)_9$ (1.5 g, 4.1 mmol) in diethyl ether at 35 °C for 4 h under an argon atmosphere to give reddish brown crystals of **5a** and yellow crystals of **6a** in yields of 9 and 41% (based on the furan), respectively (eq 1). The products were isolated by column chromatography on silica gel. Analytical data and IR and ^1H and ^{13}C NMR spectral data of **5a** and **6a** are summarized in Tables I–IV. The structures of **5a** and **6a** were deduced to be hexacarbonyl(μ-3-η^1-*anti*-(methoxycarbonyl)-η^3:η^1-allyl)diiron-(*Fe–Fe*) and tricarbonyl(3–6-η-6-methoxy-2-pyrone)iron, respectively, by comparing the spectral data of these complexes with those of the derivatives **7**[5] and **8**[20] prepared by the reaction of tricarbonyl(η^3-vinylcarbene)iron (**9**) with $Fe_2(CO)_9$ (eq 2) or with carbon monoxide (eq 3). The structures of **7**[5] and **8**[20] have been determined by X-ray analyses. The spectral data of **5a** were also in fair agreement with those of other binuclear vinylcarbene complexes reported in the literatures.[10,19]

Table I. Infrared Spectral Data (cm^{-1}, KBr)[a]

complex	metal carbonyl			ester
5a	2077 vs	2028 vs	2012 vs	1600 s, ν(C=O—Fe)
	1981 vs	1965 vs	1948 vs	
5b	2086 s	2015 vs	1997 vs	1603 s, ν(C=O—Fe)
	1989 vs	1976 s	1945 vs	
	1936 vs			
10	2083 vs	2042 vs	2018 vs	1596 s, ν(C=O—Fe)
	1988 vs	1978 vs	1970 vs	
6a	2072 vs	2011 vs	1993 vs	1747 s
	1982 vs			

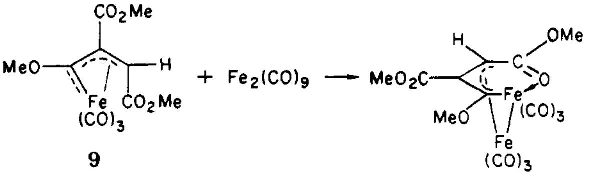
(carbonyl bands: metal carbonyl; ester)

[a] s = strong, vs = very strong.

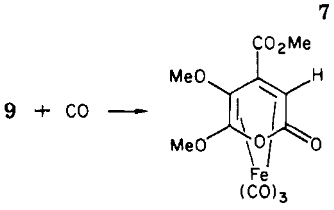


(1)

5a, R = Me **6a**, R = Me
b, R = *t*-Bu **b**, R = *t*-Bu



9 **7** (2)



8 (3)

The IR spectrum of **5a** (Table I) exhibited six strong absorptions of terminal ν(C≡O) in the 1948–2077 cm^{-1} region and ester ν(C=O) coordinated to the iron atom at

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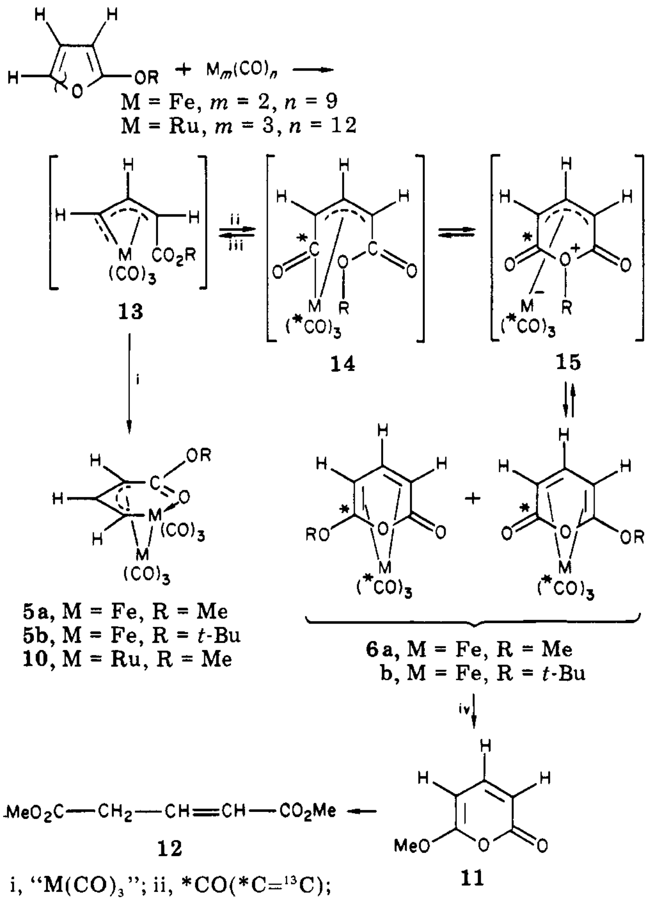
Table II. Hydrogen NMR Spectral Data (δ Relative to $SiMe_4$, J (Hz))[a]

complex	H^1	H^2	H^3	others
5a[c]	9.16 (dd, 6.8, 1.7, 1 H)	6.20 (dd, 6.8, 5.6, 1 H)	3.05 (dd, 5.6, 1.7, 1 H)	3.46 (s, 3 H, OCH_3)
5b	9.15 (dd, 7.0, 1.8, 1 H)	6.14 (dd, 7.0, 5.7, 1 H)	3.00 (dd, 5.7, 1.8, 1 H)	1.26 (s, 9 H, $OC(CH_3)_3$)
10	8.53 (dd, 7.1, 1.6, 1 H)	6.36 (dd, 7.1, 5.6, 1 H)	3.17 (dd, 5.6, 1.6, 1 H)	3.50 (s, 3 H, OCH_3)
6a[b]	2.92 (dd, 6.1, 1.5, H^3)	6.04 (dd, 6.1, 4.4, H^4)	5.40 (dd, 4.4, 1.5, H^5)	3.68 (s, 3 H, OCH_3)

[a] s = singlet, d = doublet, recorded at 100 MHz; solvent $CDCl_3$. [b] Assignment of signals are shown in the parentheses. [c] See Table III for structures.

Scheme I



i, "$M(CO)_3$"; ii, *CO(*C=^{13}C); iii, –*CO; iv, M = Ru, R = Me, –"$M(CO)_3$".

1600 cm^{-1} strongly suggesting that **5a** is a derivative of **7**. The ^1H NMR signal of the H^1 proton at low field (δ 9.16) (see Table II) and the ^{13}C NMR signal of C^1 carbon at δ 158.4 (dd, J(CH) = 158.2 and 9.8 Hz) (see Table III) showed the presence of a σ bond between C^1 and Fe^2. The upfield shift of the C^1 carbon of **5a** compared with that of **7** is due to the substituent effect at the 1-position, the hydrogen atom in **5a** and the methoxy group in **7**. Taking into account these substituents effects, the spectral data of **5a** showed that the complex is a derivative of **7**.

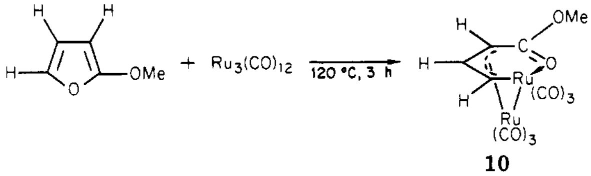
The IR spectrum of **6a** (Table I) showed ν(C=O) at 1747 cm^{-1} which exhibited the existence of a lactone ring as well as the absorptions of terminal ν(C≡O) at 2072, 2011, 1993, and 1982 cm^{-1}. The ^1H NMR signals of three olefinic protons (δ 2.92, 5.40, and 6.04) (see Table II) and the ^{13}C NMR signals of four olefinic carbons (δ 47.6, 65.3, 85.9, and 130.2) (see Table III) showed the presence of a butadiene moiety coordinated to the iron atom. These spectral data for **6a** showed that **6a** is a derivative of **8**.

The yields of **5a** and **6a** depend upon the molar ratio of $Fe_2(CO)_9$/2-methoxyfuran, the solvent, and the atmospheres (Table V). When the ratio was 11 (run 3), **5a** was selectively formed in 30% yield. On the contrary, when the ratio was 0.4 (run 4), **6a** was obtained selectively. In the reaction under an atmosphere of carbon monoxide (the molar ratio = 0.5, run 5), both selectivity and yield of **6a** increased. The reaction carried out in benzene gave **6a** in higher yield than that in ether (the molar ratio = 1.0, runs 2 and 6). In the reaction in benzene under an atmosphere of carbon monoxide (the molar ratio = 0.9, run 7), **6a** was selectively obtained in 58% yield.

2-*tert*-Butoxyfuran also gave the corresponding binuclear vinylcarbene complex **5b** in 19% yield, but only a trace of **6b** was detected by spectroscopy.

Other furans, furan, 2-methylfuran and methyl furoate did not react with $Fe_2(CO)_9$ under similar conditions.

Reaction of 2-Methoxyfuran with Dodecacarbonyltriruthenium. The reaction of 2-methoxyfuran with $Ru_3(CO)_{12}$ requires somewhat higher temperature; the furan (40 mg, 0.4 mmol) reacted with $Ru_3(CO)_{12}$ (130 mg, 0.2 mmol) at 120 °C in benzene for 3 h affording hexacarbonyl(μ-3-η^1-*anti*-(methoxycarbonyl)-η^3:η^1-allyl)diruthenium(*Ru–Ru*) (**10**) in 55% (based on $Ru_3(CO)_{12}$) yield (eq 4). When the reaction was carried out at 150 °C for 4 h in the presence of excess amount of 2-methoxyfuran under a pressure of carbon monoxide at 65 atm, **10** was obtained in 67% yield accompanied by the formation of ca. 50% of 6-methoxy-2-pyrone (**11**) and 74% of dimethyl glutaconate (**12**) (eq 5). In these reaction solutions, the formation of tricarbonyl(6-methoxy-2-pyrone)ruthenium was not observed.



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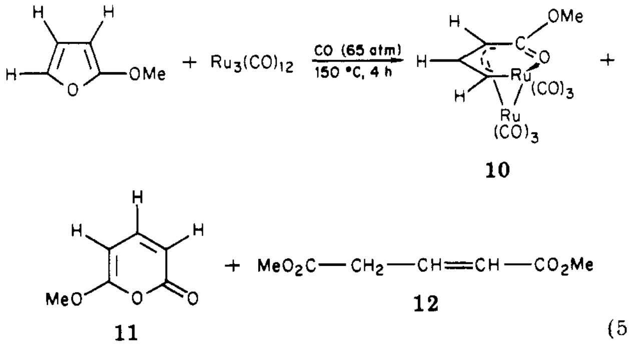


(5)

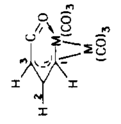
Analytical data and IR and ^1H and ^{13}C NMR spectral data of **10** are summarized in Tables I–IV. These spectral data for **10** apparently showed that **10** is an analogue of **5a**.

The IR spectrum of **11** showed the characteristic absorptions due to ν(C=C) of a pyrone ring at 1630 and 1535 cm^{-1} in addition to that of ν(C=O) at 1735 cm^{-1}. The ^1H NMR spectrum of **11** showed three olefinic protons at δ 5.37, 5.86, and 7.39, and the ^{13}C NMR spectrum of **11** showed four olefinic carbons at δ 81.3, 104.5, 147.6, and 165.2, which exhibited the existence of a pyrone ring. Although **11** was not obtained in analytically pure form, **11** was deduced to be 6-methoxy-2-pyrone on the basis of

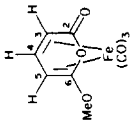
Table III. Carbon-13 NMR Spectral Data (δ, $SiMe_4$, Internal Reference, $J(^{13}C\text{-}H)$ (Hz))[a]

complex	C^1	C^2	C^3	C=O	FeC=O	others
5a[c]	158.4 (dd, 158.2, 9.8)	91.5 (d, 169.9)	45.5 (ddd, 162.1, 9.8, 3.9)	184.5 (s)	212.9 (s)	54.1 (q, 148.4, OCH_3)
5b	158.7 (dd, 156.3, 9.8)	91.3 (d, 169.9)	48.0 (ddd, 162.1, 9.8, 3.9)	183.7 (d, 3.9)	213.2 (s)	28.1 (qhept, 127.0, 3.9, $OC(CH_3)_3$) 84.8 (s, $OC(CH_3)_3$)
10	148.0 (dd, 156.3, 9.8)	90.1 (d, 169.9)	39.7 (ddd, 159.2, 9.8, 5.9)	185.9 (s)	198.3 (s) 206.2 (s) 211.6 (s)	54.0 (q, 147.8, OCH_3)
6a[b]	168.7 (s, C^2)	47.6 (d, 169.9, C^3)	85.9 (d, 181.6, C^4)	65.3 (d, 179.7, C^5), 130.2 (s, C^6)	207.5 (FeC=O)	58.7 (q, 146.5, OCH_3)

[a] s = singlet, d = doublet, q = quartet, hept = heptet; solvent $CDCl_3$. [b] Assignment of signals are shown in the parentheses. [c]



5a,b, 10



6a

spectral data described above and GC–mass spectral data (M^+ = 126).

12 was identified to be dimethyl glutaconate by comparing the spectral data with those of the authentic sample.

When 2-methoxyfuran (5.0 mmol) reacted with $Ru_3(CO)_{12}$ (0.2 mmol) at 180 °C for 12 h under a pressure of carbon monoxide at 73 atm, **12** was formed in 157% yield (based on Ru atom and determined by means of GLC analyses). Therefore the present reaction apparently proceeded catalytically.

Mechanisms of the Formation of 5, 6, 10, and 11. Taking into account the reactions of mononuclear tricarbonyl(η^3-vinylcarbene)iron (**9**) with $Fe_2(CO)_9$ and with carbon monoxide affording **7** and **8**, respectively (eq 1 and 2), the present reaction could be explained by assuming the formation of a reactive mononuclear (η^3-3-(alkoxycarbonyl)prop-2-enylidene)tricarbonylmetal complex (**13**) derived by the fission of C(5)–O bond of 2-alkoxyfuran.[21] Complexes **5** and **10** would be formed by the "coordination" of **13** to the $Fe(CO)_3$ moiety as a bidentate ligand through the carbon–iron double bond and the ester group in a similar manner to the reaction of complex **9** with $Fe_2(CO)_9$. Concerning the reaction path of the formation of **6**, the following facts have been observed. Complex **5** was not converted into **6** under an atmosphere of carbon monoxide, which ruled out the possibility that **6** is derived from the binuclear complex **5**. When the reaction of 2-methoxyfuran with $Fe_2(CO)_9$ was carried out under an atmosphere of 90% ^{13}C-enriched carbon monoxide at 35 °C for 4 h, 5.2 and 5.0% of ^{13}C was introduced into both 2- and 6-positions of the pyrone ligand in complex **6a**. On the basis of these observations, the mechanism of this unusual carbonylation reaction of 2-alkoxyfurans can be rationalized as follows (Scheme I). First, the η^3-vinylcarbene complex **13** is formed as described above. The carbonylation of complex **13** gives a η^4-vinylketene complex (**14**).[20,22] Then, although there is no evidence now, the nucleophilic attack of the alkoxy group of the ester on the acyl carbon of the ketene group would give a π-allyloxonium complex (**15**). Then alkyl transfer to either of the two carbonyl oxygens occur to give the η^4-2-pyrone complex **6**. This possible mechanism is consistent with the fact that the equal amounts of ^{13}C were introduced into the 2- and 6-positions of the pyrone ligand. When complex **6a** labeled with ^{13}C obtained by the above reaction was treated under an atmosphere of ^{12}CO for 72 h, 1.7% (2-position) and 1.6% (6-position) of ^{13}C was exchanged by ^{12}C. When **6a** was treated with $Fe_2(CO)_9$ at 70 °C in 1,2-dichloroethane, the binuclear vinylcarbene complex **5a** was obtained in 19% yield. These observations show the presence of a reversible process from **6** to **13** in the reaction, and the latter one strongly suggests the mechanism that the binuclear vinylcarbene complexes **5** and **10** are formed via the mononuclear complexes **13**.

In the reaction of 2-methoxyfuran with $Ru_3(CO)_{12}$, a pyrone ligand eliminated to form 6-methoxy-2-pyrone (**11**).

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[21] Although there is no evidence now, the mechanism of the formation of **13** could be explained as follows. First, 2-alkoxyfuran coordinated to "$M(CO)_3$". Then, the oxidative addition occurs to form **16** followed by the electronic change to give **13**.

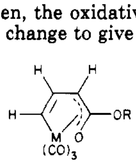

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Table IV. Analytical Data

complex	color	mass m/e (M^+)	mp, °C	% C calcd	% C found	% H calcd	% H found
5a	reddish brown	378	85 dec	34.97	34.52	1.60	1.64
5b	reddish brown	420	85	40.04	40.00	2.88	2.87
10	yellow	468	98	28.21	28.43	1.29	1.54
6a	yellow	266	98 dec	40.64	40.53	2.27	2.51

Table V. Reaction of 2-Methoxyfuran with $Fe_2(CO)_9$

run	2-methoxyfuran, mmol	$Fe_2(CO)_9$, mmol	mole ratio of $Fe_2(CO)_9$/2-methoxyfuran	solvent	atmosphere	yield,[a] % 5a	yield,[a] % 6a
1	2.8	4.1	1.5	ether	Ar	9	41
2	1.0	1.0	1.0	ether	Ar	7	26
3	0.9	9.5	11	ether	Ar	30	0
4	5.9	2.5	0.4	ether	Ar	2[b]	51[b]
5	4.7	2.4	0.5	ether	CO	2[b]	66[b]
6	2.4	2.5	1.0	benzene	Ar	5	49
7	11	10	0.9	benzene	CO	~0	58

[a] Based on the amount of 2-methoxyfuran. [b] Based on the amount of $Fe_2(CO)_9$.

Although the mechanism of the formation of dimethyl glutaconate (**12**) is not yet clear, methanol may be formed by the cleavage of 2-methoxyfuran and **12** would be formed by the methanolysis of η^4-2-pyrone complex or 6-methoxy-2-pyrone. This mechanism is supported by the fact that the reaction of the η^4-2-pyrone complex **6a** with methanol under a pressure of carbon monoxide gives dimethyl glutaconate (**12**) in 62% yield (determined by means of GLC analysis).

Conclusion

As described above, the reactions of 2-alkoxyfurans with $Fe_2(CO)_9$ or $Ru_3(CO)_{12}$ gave binuclear α,β-unsaturated alkylidene complexes and 2-pyrone derivatives.

Several methods to prepare binuclear α,β-unsaturated alkylidene complexes have been reported: reactions of μ-alkylidene complexes with acetylenes;[8,10] reactions of cyclopropenes with metal carbonyls;[11,12] and miscellaneous methods.[7,9,13-19] The present reaction provides a novel and facile method to prepare these complexes.

The carbonylation of cyclic ethers such as tetrahydrofuran giving lactones by cobalt catalysts[23] has been well investigated, and the mechanism involving hydroxyalkanoyl species derived by the insertion of carbon monoxide into a carbon–metal single bond has been proposed.[24] In contrast, the formation of 2-pyrone derivatives from 2-alkoxyfurans would involve the carbonylation of mononuclear vinylcarbene complexes. The reaction would be a novel carbonylation reaction of heterocycles which has been first proposed in the isomerization of (2-pyrone)Fe$(CO)_3$ complexes.[20] It would be worthwhile to note that much attention has been given to the insertion of carbon monoxide into carbon–metal double bond concerning the mechanisms for Fischer–Tropsch synthesis or double carbonylation of acetylene.

Experimental Section

Unless indicated otherwise, all of experimentals were performed in an atmosphere of argon. Infrared spectra were recorded on a JASCO A-302 grating spectrometer, ^1H NMR spectra on a JEOL JNM-FX-100 spectrometer, and ^{13}C NMR spectra on a JEOL JNM-FX-100 spectrometer at 25.05 MHz. Mass spectra were recorded on a JMS-O1SG mass spectrometer or Hitachi M-80 GC/MS spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. GLC analyses were carried out on a Shimadzu gas chromatograph GC-8A equipped with a 3 m × 3 mm column packed with 2% OV-17 on Chromosorb W. Solvents were dried by published techniques and were distilled in an atmosphere of argon before use. 2-Methoxyfuran,[25] 2-*tert*-butoxyfuran,[26] nonacarbonyldiiron,[27] dodecacarbonyltriruthenium[28] were prepared by the methods described in the literture.

Reaction of 2-Methoxyfuran with $Fe_2(CO)_9$. To a suspension of $Fe_2(CO)_9$ (1.5 g, 4.1 mmol) in diethyl ether (10 mL) was added 2-methoxyfuran (272 mg, 2.8 mmol), and the mixture was stirred for 4 h at 35 °C. After the evaporation of solvent, the residual oil was chromatographed on silica gel to give reddish brown crystals of **5a** (93 mg, 9%) and yellow crystals of **6a** (303 mg, 41%).

Reaction of 2-*tert*-Butoxyfuran with $Fe_2(CO)_9$. To a suspension of $Fe_2(CO)_9$ (1.8 g, 5.0 mmol) in diethyl ether (10 mL) was added 2-*tert*-butoxyfuran (353 mg, 2.5 mmol) at 30 °C. After 19 h, the solvent was distilled off in vacuo, and the residual oil was chromatographed on alumina (Merk, deactivated by 10% of water) to give reddish brown crystals of **5b** (202 mg, 19%).

Reaction of 2-Methoxyfuran with $Ru_3(CO)_{12}$ under an Argon Atmosphere. $Ru_3(CO)_{12}$ (130 mg, 0.2 mmol), 2-methoxyfuran (43 mg, 0.44 mmol), and benzene (5 mL) were placed in an ampule, which had been flushed with argon, and the mixture was heated at 120 °C for 3 h. After the evaporation of solvent, the residual solid was chromatographed on silica gel to give yellow crystals of **10** (40 mg, 25%).

Reaction of 2-Methoxyfuran with $Ru_3(CO)_{12}$ under a Pressure of Carbon Monoxide. $Ru_3(CO)_{12}$ (130 mg, 0.2 mmol), 2-methoxyfuran (478 mg, 4.9 mmol), and benzene (5 mL) were placed in an autoclave under an argon atmosphere. The autoclave was charged with 65 atm of carbon monoxide and was heated at 150 °C for 4 h. After the solvent was distilled off in vacuo, the residual oil was chromatographed on silaca gel to give **10** (64 mg, 67%), **11** (ca. 50%), and **12** (24 mg, 74%).

Reaction of 5a with Carbon Monoxide. The solution of **5a** (99 mg, 0.26 mmol) in benzene (5 mL) was stirred under an atmosphere of carbon monoxide (1 atm) at 50 °C for 8.5 h. After the solvent was distilled off in vacuo, **5a** was recovered unchanged.

Reaction of 2-Methoxyfuran with $Fe_2(CO)_9$ under an Atmosphere of ^{13}CO. $Fe_2(CO)_9$ (1.1 g, 3.0 mmol), 2-methoxyfuran (323 mg, 3.3 mmol), and benzene (5 mL) were placed in an autoclave under an argon atmosphere. After argon was replaced

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with 90% ^{13}C-enriched carbon monoxide, the autoclave was kept at 35 °C for 4 h. Then the solvent was distilled off in vacuo, and the residual solid was washed with *n*-hexane to give **6a** in 61% yield. The ^{13}C NMR of the complex showed that the 5.2% and 5.0% of ^{13}C was introduced into the 2- and 6-positions.

Reaction of 6a Labeled with ^{13}C with ^{12}CO. The benzene solution of the labeled (**6a**), which was obtained from the reaction of 2-methoxyfuran with $Fe_2(CO)_9$ under an atmosphere of 90% ^{13}C-enriched carbon monoxide, was stirred under an atmosphere of carbon monoxide (1 atm) at 35 °C for 72 h.

Reaction of 6a with $Fe_2(CO)_9$. The mixture of **6a** (133 mg, 0.5 mmol) and $Fe_2(CO)_9$ (364 mg, 1.0 mmol) in 1,2-dichloroethane (5 mL) was stirred at 70 °C for 6 h. After the evaporation of solvent, the residual oil was chromatographed on silica gel to give **5a** (36 mg, 19%) and unreacted **6a** (27 mg, 20%).

Reaction of 6a with Methanol. Complex **6a** (266 mg, 1.0 mmol) and methanol (5 mL) were placed in an autoclave under an argon atmosphere. The autoclave was charged with 50 atm of carbon monoxide and was heated at 150 °C for 4 h. Then the reaction mixture was subjected to GLC analysis, which showed the presence of 62% of **12** (based on the amount of **6a**).

Acknowledgment. We thank Prof. Y. Takegami and Dr. T. Suzuki for helpful discussions and also Prof. H. Fukami and Dr. T. Ueno for taking the GC–MS spectra.

Registry No. **5a**, 84474-43-1; **5b**, 84474-44-2; **10**, 84462-69-1; **6a**, 84462-70-4; **11**, 84507-41-5; **12**, 5164-76-1; $Fe_2(CO)_9$, 15321-51-4; $Ru_3(CO)_{12}$, 15243-33-1; 2-methoxyfuran, 25414-22-6; 2-*tert*-butoxyfuran, 32460-41-6.

Proximity-Assisted Formation of Bridged Iron and Ruthenium Carbonyl Complexes of μ-Polymethylene-Bis(1,3-pentadiene). Preparation and Molecular Structure of $Ru(CO)[(\mu\text{-}(CH_2)_3)(\eta^4\text{-}C_5H_7)_2]$ and $(\mu\text{-}(CH_2)_3)[Ru(CO)_3(\eta^4\text{-}C_5H_5)][Ru(CO)(\eta^4\text{-}C_5H_7)]$ (Ru–Ru)

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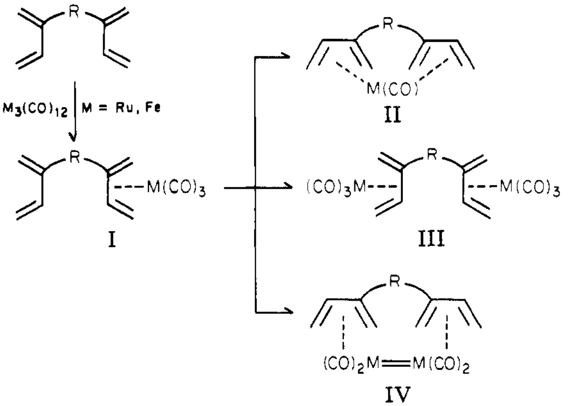
The 4:1 reaction of 3,7-divinyl-1,8-nonadiene (**1**) with $Ru_3(CO)_{12}$ gave mononuclear $Ru(CO)[(\mu\text{-}C_3H_6)(\eta^4\text{-}C_5H_7)_2]$ (**7a**) and binuclear $(\mu\text{-}C_3H_6)[Ru(CO)_3(\eta^4\text{-}C_5H_5)][Ru(CO)(\eta^4\text{-}C_5H_7)]$ (**8a**) in an 8:2 ratio by the proximity effect of two adjacent diene groups. Higher analogues, 3,8-divinyl-1,9-decadiene (**2**) and 3,9-divinyl-1,10-undecadiene (**3**), preferred the formation of $(\mu\text{-polymethylene})[Ru(CO)_3(\eta^4\text{-}C_5H_7)]_2$, while a linear tetraene, 1,3,7,9-decatetraene (**4**), gave $Ru(CO)_3$(bicyclo[4.2.0]2,4-octadiene) by a valence isomerization reaction with $Ru_3(CO)_{12}$. Corresponding reactions with iron carbonyls always gave the complexes $(\mu\text{-polymethylene})[Fe(CO)_3(\eta^4\text{-}C_5H_7)]_2$, irrespective of the type of tetraene ligands. The X-ray structure analysis of (3,3′-μ-trimethylene)bis(η^4-1,3-pentadiene)carbonylruthenium (**7a**) and (3,3′-μ-trimethylene)(η^4-2-methyl-1,1,1-tricarbonylruthenacyclopenta-2,4-diene)(η^4-1,3-pentadiene)monocarbonylruthenium(*Ru–Ru*) (**8a**) suggests that the former is converted to the latter through dehydrogenative metallacyclization. Crystal data for **7a**: triclinic, space group $P\bar{1}$ with $Z = 2$, $a = 7.563$ (1) Å, $b = 13.132$ (1) Å, $c = 7.276$ (1) Å, $\alpha = 98.21$ (1)°, $\beta = 112.74$ (1)°, $\gamma = 81.37$ (1)°, $R_1 = 0.031$, and $R_2 = 0.042$ from the 2251 reflections. Crystal data for **8a**: monoclinic, space group $P2_1/a$ with $Z = 4$, $a = 19.265$ (3) Å, $b = 13.182$ (2) Å, $c = 7.624$ (1) Å, $\beta = 119.10$ (1)°, $R_1 = 0.051$, and $R_2 = 0.051$ from the 2140 reflections.

Multidentate ligands with chalcogen or pnicogen donor atoms in linear or cyclic arrays have played important roles in coordination chemistry. Polyolefinic carbon ligands have so far been limited to mostly cyclic ones, e.g., cyclooctatetraene,[1] bis(cyclooctatetraene),[2] etc. We have been interested in linear polyolefines because of their potential as bridging ligands between two or more metal atoms and have examined the complex formation of d^8 metals with a series of compounds containing two conjugated diene moieties connected by a polymethylene chain. Consideration of the stability of the products has led us to bind $M(CO)_3$ fragments (M = Fe, Ru) with the diene parts. The possible products are shown in eq 1.



(1)

Much interest rests in how the product distribution (I–IV) depends on the number of methylene (R) between vinylidene groups, since mutual steric dispositions of the two diene units is of critical importance. In some favorable cases, the resulting polynuclear complexes may provide novel electronic or magnetic materials. The bifunctionality

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