Carbon Chain Formation on Metallic Arrays. X-ray Structural Determinations of $[Ru_4(\mu_4\text{-}(CCC(CO_2Me)C(CO_2Me))(\eta\text{-}C_5H_4R)_2(\mu\text{-}CO)(CO)_8]$, $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}CCC(CO_2Me)=C(CO_2Me)C(O)\}]$, and $[\{Ru(CO)_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C=C(CN)_2C=C(CN)_2\}]$ (R = H, Me)

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The open, planar Ru_4C_2 compounds $[Ru_4(\mu_4\text{-}CC)(\eta\text{-}C_5H_4R)_2(\mu\text{-}CO)_2(CO)_8]$ (R = H, Me) react with the activated electron-deficient alkyne dimethyl acetylenedicarboxylate, $(CO_2Me)_2C_2$ (DMAD), to afford a number of products. One of these was found to contain a metallacyclopentadiene ligand ligated at the 1- and 2-positions by $Ru(\eta\text{-}C_5H_4R)$ groups, and another was a new Ru_2 compound resulting from the coupling of DMAD, C_2, and CO to produce a five-carbon chain.

Introduction

We have been interested in modeling the carbon−carbon bond-forming reactions central to the Fischer−Tropsch synthesis.[1−15] This synthesis is typically catalyzed with transition metals and its outcome greatly influenced by the addition of so-called "promoters". Although a tremendous amount of empirical research has provided efficient commercial catalysts, the ability to tailor gas-to-liquid conversion to meet changing needs is lacking. Our aim is to deal with the fundamental aspects of metal-mediated carbon−carbon bond forming reactions and their application to catalysis.

We have recently reported the synthesis of reactive tetranuclear ruthenium carbide complexes, $[Ru_4(\mu_4\text{-}CC)(\eta\text{-}C_5H_4R)_2(\mu\text{-}CO)_2(CO)_8]$ (R = H, Me), which contain an open planar geometry and were found to be reactive, unlike the more condensed pentanuclear complexes we had previously reported.[16,17] We are using these tetranuclear complexes to explore the reactivity of the C_2^{2-} ligand in a metal coordination environment.[18]

Herein we report the reaction of $[Ru_4(\mu_4\text{-}CC)(\eta\text{-}C_5H_4R)_2(\mu\text{-}CO)_2(CO)_8]$ (R = H (**1a**), Me (**1b**)) with the alkyne dimethyl acetylenedicarboxylate (DMAD), together with the reaction of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CC)]$ with DMAD and tetracyanoethylene (TCNE).

Results

Syntheses. Complexes **1**, formed in situ, were found to react readily at ambient temperatures with a slight excess of DMAD, giving three fractions (TLC) (Scheme 1). The products were separated by radial chromatography under argon. The first fraction eluted was identified as $[Ru_3(CO)_{12}]$, retained from the in situ formation of **1**. The second fraction was isolated as a waxy orange material and tentatively assigned as $[Ru_4(C_2C(CO_2Me)C(CO_2Me))(\eta\text{-}C_5H_4R)_2(CO)_9]$ (**2**; yield ca. 20%), on the basis of analytical and spectroscopic data. The final fraction (light orange) band was recrystallized from CH_2Cl_2 and identified as $[Ru_4(\mu_4\text{-}(CCC(CO_2Me)C(CO_2Me))(\eta\text{-}C_5H_4R)_2(\mu\text{-}CO)(CO)_8]$ (**3**; yield ca. 20%), which were both structurally characterized.

On one occasion the reaction of **1** and DMAD yielded another red-brown product, in addition to **2** and **3,** eluting after these two orange bands. This previously

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(1) Gambarotta, S.; Edema, J. J. H.; Minhas, R. K. *Catal. Lett.* **1993**, *22*, 67.
(2) Das, D.; Ravichandran, G.; Chakrabarty, D. K.; Piramanayagam, S. N.; Shringi, S. N. *J. Mol. Catal.* **1994**, *86*, 221.
(3) Bukur, D. B.; Nowicki, L.; Lang, X. S. *Appl. Catal., A: Gen.* **1995**, *128*, 13.
(4) Kim, J. S.; Dai, H. L. *Catal. Today* **1995**, *23*, 17.
(5) Ming, H.; Baker, B. C. *J. Am. Chem. Soc.* **1995**, *117*, 2606.
(6) Boellaard, E.; Vanderkraan, A. M.; Geus, J. W. *Fuel Proc. Technol.* **1996**, *48*, 189.
(7) Herrmann, W. A. *Appl. Homogeneous Catal. Organomet. Compd.* **1996**, *2*, 747.
(8) Hussain, S. T. *Catal. Rev.−Sci. Eng.* **1996**, *38*, 249.
(9) Wohlers, M.; Herzog, B.; Belz, T.; Bauer, A.; Braun, T.; Ruhle, T.; Schlogl, R. *Chem. Commun.* **1996**, *7*, 1.
(10) Xu, L.; Bao, S.; O'Brien, R. J.; Raje, A.; Davis, B. H. *CHEMTECH* **1998**, *28*, 47.
(11) Guczi, L.; Kiricsi, I. *Appl. Catal., A* **1999**, *186*, 375.
(12) Maitlis, P. M.; Quyoum, R.; Long, H. C.; Turner, M. L. *Appl. Catal., A* **1999**, *186*, 363.
(13) Van der Laan, G. P.; Beenackers, A. A. C. M. *Catal. Rev. − Sci. Eng.* **1999**, *41*, 255.
(14) Silva, R.; Schmal, M.; Frety, R.; Dalmon, J. A. *J. Chem. Soc., Chem. Commun.* **1993**, *21*, 1670.
(15) Ganzerla, R.; Lenarda, M.; Storaro, L.; Bertoncello, R. *Stud. Surf. Sci. Catal.* **1998**, *119*, 131.
(16) Byrne, L. T.; Griffith, C. S.; Hos, J. P.; Koutsantonis, G. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 259.
(17) Byrne, L. T.; Hos, J. P.; Koutsantonis, G. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1999**, *592*, 95.
(18) Byrne, L. T.; Hos, J. P.; Koutsantonis, G. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *598*, 28.

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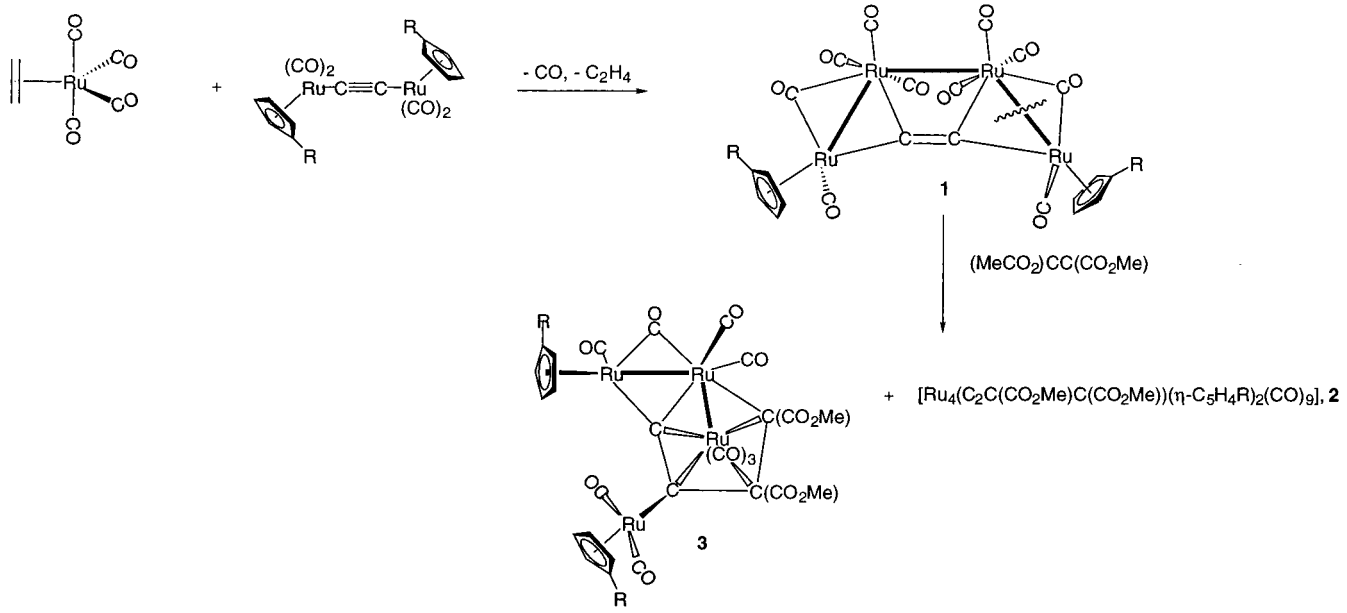
Scheme 1[a]



[a] Legend: **a**, R = H; **b**, R = Me.

unobserved product was recrystallized (CH_2Cl_2/*n*-hexane) and identified by spectroscopic and microanalytical techniques as [{$Ru(CO)_2(\eta$-$C_5H_5)$}$_2${μ-CCC(CO_2Me)=C(CO_2Me)C(O)}] (**4**). It was apparent that complex **4** probably resulted from the reaction of DMAD with unreacted [{$Ru(CO)_2(\eta$-$C_5H_5)$}$_2$(μ-CC)], remaining from the in situ formation of **1**. We probed this possibility with the direct reaction of [{$Ru(CO)_2(\eta$-$C_5H_5)$}$_2$(μ-CC)] and DMAD, which proceeded readily, recognized by a rapid change of color, giving a quantitative yield of **4** (IR, NMR). Given the facility of the reaction with DMAD, we also reacted [{$Ru(CO)_2(\eta$-$C_5H_5)$}$_2$(μ-CC)] with tetracyanoethylene (TCNE). The product of this reaction was very insoluble, giving a very pale yellow precipitate of [{$Ru(CO)_2(\eta$-$C_5H_5)$}$_2${μ-$(CN)_2$C=CC=C-$(CN)_2$}] (**5**), which contained a μ-*trans*-2,3-butadienediyl ligand.

The FAB MS of complexes **2** and **3** both contain a molecular ion, corresponding to [$Ru_4(C_5H_4R)_2(CO)_9C_2C_2$-$(CO_2Me)_2$]$^+$ (R = H, Me), suggestive of their possible isomeric nature. These spectra showed extensive fragmentation, with losses of both OMe and CO groups observed. The solution IR spectra are similar. Absorbances at 1717 and 1722 cm^{-1} are assigned to the ester carbonyl stretches and bridging M−CO bands at 1813 and 1822 cm^{-1} for **2** and **3**, respectively.

The ^{1}H NMR spectra for the complexes **2a** and **3a** each show two sets of methoxy resonances at 3.77, 3.79 ppm and 3.60, 3.80 ppm. The two sets of inequivalent cyclopentadienyl protons are observed with notably broad resonances for **2a** at 5.27 and 5.37 ppm, compared to the sharp signals at 5.20 and 5.57 ppm for **3a**. The η-C_5H_4Me analogues **2b** and **3b** show similar methoxy resonances. The two inequivalent methyl cyclopentadienyl protons are present as a broad singlet at 2.60 ppm in **2b** and as two sharp singlets at 2.12 and 2.17 ppm in **3b**. The resonances for eight CH methylcyclopentadienyl protons for each compound fall in the expected range of 4.7−5.7 ppm and are coupled in the usual fashion.

The ^{13}C NMR spectra of complexes **2** and **3** show significant differences. Omitting the obvious differences between η^5-C_5H_5 and η^5-C_5H_4Me, we assign the spectra of complexes **3** as follows. Resonances for the two inequivalent acetylenic carbon nuclei (−*C*CO_2Me) are assigned to signals at 109.2 and168.2 ppm with the two inequivalent ester carbonyls assigned to singlets at 145.1 and 139.4 ppm, respectively. The previous ethene-like carbides from complex **1b** have significantly different environments in **3b**, with C(1) triply bridging, assigned to 193.6 ppm, and the other doubly bridging, assigned to 174.1 ppm. The five carbonyl signals in the spectra imply some fluxional process in complex **3b**, which contains nine inequivalent CO ligands in the solid state. An intense resonance at 199.6 ppm is assigned to all three carbonyls on Ru(3) and two less intense resonances at 199.8 and 200.6 ppm to the two sets of carbonyls on Ru(4) and Ru(2), respectively. The signals on Ru(2) resonate further downfield, consistent with its more shielded environment, bound to two metal atoms. The remaining terminal carbonyl on Ru(1) is assigned to 196.0 ppm, with the bridging carbonyl assigned the outermost signal at 234.4 ppm.

The assignment of resonances found in the NMR spectra of complex **2b** is difficult without structural information. The resonance at very low field (298.5 ppm) implies a unique mode of coordination, possibly a μ_3 carbonyl, although the infrared spectrum of **2b** does not seems to confirm this hypothesis. This signal at ca. 300 ppm in the carbon spectrum of **2b** appears to be indicative of a cumulenic carbon, possibly a vinylidene or carbyne; it is difficult to compare this with similar structures in the literature due to the lack of reported ^{13}C NMR data.[19−25] A bridging carbonyl is assigned to

(19) Bruce, M. I. *J. Cluster Sci.* **1997**, *8*, 293.
(20) Bruce, M. I. *Organomet. Chem.* **1999**, *27*, 151.
(21) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797−2858.
(22) Bruce, M. I. *Coord. Chem. Rev.* **1997**, *166*, 91.
(23) Sappa, E. *J. Organomet. Chem.* **1999**, *573*, 139.
(24) Bruce, M. I.; Humphrey, P. A.; Miyamae, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *429*, 187.

the signal at 241.6 ppm, and the single strong signal in the carbonyl region at 198.7 ppm must be a result of seven fluxional terminal CO ligands. Six resonances between 96.8 and 172.3 ppm are assigned to the remaining carbide, carboxyl, and acetylenic nuclei, analogous to **3b**.

The ^{1}H and ^{13}C NMR spectra of **4** were uncomplicated, with cyclopentadienyl and carboxymethyl resonances appearing in the expected regions. The three terminal carbonyl ligands are assigned to resonances at 197.0, 197.9, and 200.2 ppm, with the bridging carbonyl assigned to 240.0 ppm. The mass spectrum of **4** showed a molecular ion, with peaks assigned to the loss of two carbonyl ligands and a methoxy group.

The most definitive spectroscopic data obtained for complex **5** was the infrared spectrum, which confirmed the presence of cyano groups with bands at 2215 and 2211 cm^{-1} and the metal bound carbonyls at 2051 and 2003 cm^{-1}. The extreme insolubility of **5** made it difficult to obtain meaningful NMR data, with the solution proton and solid-state ^{13}C NMR spectra confirming only the presence of Ru(η-C_5H_5) groups. Confirmation of the molecular connectivity was only achieved from the results of the structure determination (see below).

Solid-State Structures of $Ru_4(\mu_4$-(CC)C(CO$_2$Me)C-(CO$_2$Me))(η-C_5H_4Me)$_2(\mu$-CO)(CO)$_8$ (3b), [{Ru(CO)$_2$-(η-C_5H_5)}$_2${μ-CCC(CO$_2$Me)=C(CO$_2$Me)C(O)}] (4), and [{Ru(CO)$_2$(η-C_5H_5)}$_2${μ-(CN)$_2$C=CC=C(CN)$_2$}] (5). The results of the room-temperature structure determinations on specimens obtained from CH_2Cl_2/hexanes (**3** and **4**) or dimethyl sulfoxide (**5**) are presented in Figures 1−3; crystal and refinement data are given in Table 1 and relevant interatomic parameters in Tables 2−4. Complexes **3a** and **3b** are isomorphous; the former determination was carried out with inferior material being of lower precision, and therefore, the discussion is conducted in terms of **3b,** the differences between the two being minor.

The results of the room-temperature single-crystal X-ray structure determinations are consistent with the stoichiometries and connectivities implied by the above formulations with one molecule (for **3b** and **4**) and a half-molecule (for **5**) comprising the asymmetric units of their structures.

The essential structural feature of complex **3b** can be described as a substituted ruthenacyclopentadiene unit, defined by the atoms Ru(2), C(1), C(2), C(3), and C(4). The considerably distorted metallacycle bonds through all five members to Ru(3) and has recent precedent in the literature.[26−34] The ring is triply substituted with

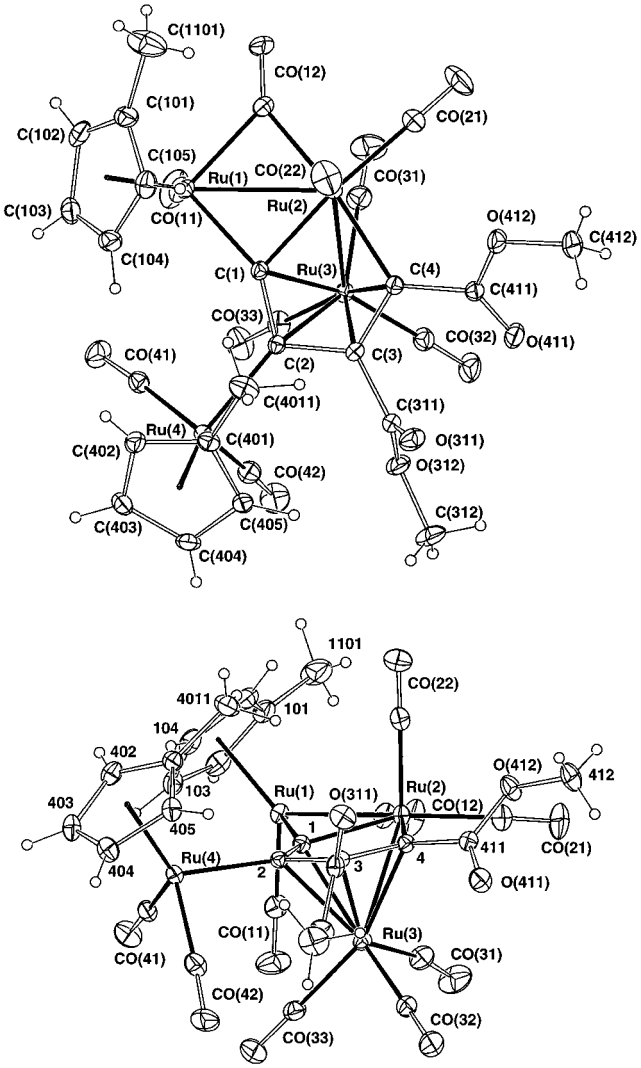


Figure 1. (a, top) Molecular projection of complex **3b**, almost normal to the Ru_2C_4 plane, showing 20% probability ellipsoids for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å. (b) **3b**, projected almost through the Ru_2C_4 plane.

two carboxymethyl substituents at C(3) and C(4) and one Ru(CO)$_2$(η-C_5H_4Me) moiety bound to C(2). The other Ru(CO)$_2$(η-C_5H_4Me) group can be considered to bridge one edge of the metallacyclopentadiene with a bridging carbonyl ligand being found across the metal−metal bond, between Ru(1) and Ru(2). We can draw two extreme forms of the bonding interactions between the bridging C_4 chain and Ru(3) (Figure 4).

Canonical form **A** represents the ruthenacyclopentadiene σ-bound to a Ru(CO)$_3$ fragment, representation **B** being of a metallacycle π-bound to Ru(3). The most relevant literature comparisons can be found in the structures of [$Ru_2(\mu_2$-η^1:η^4-C(C≡CPh)=CPhC(C≡CPh)=CPh}(CO)$_6$][35] (**6**), of adequate precision to provide a meaningful comparison, and [$Ru_4(\mu_2$-η^1:η^4,μ_2-η^1-PhCC-CCPh}(CO)$_8$] (**7**).[36] The Ru−C(σ) bonds comprising the metallacyclic portion of the molecules are comparable

(25) Bruce, M. I.; Humphrey, P. A.; Miyamae, H.; White, A. H. *J. Organomet. Chem.* **1991**, *417*, 431.
(26) Yi, C. S.; Liu, N. H. *Synlett* **1999**, 281.
(27) Zdanovich, V. I.; Lagunova, V. Y.; Dolgushin, F. M.; Yanovsky, A. I.; Ezernitskaya, M. G.; Petrovskii, P. V.; Koridze, A. A. *Russ. Chem. Bull. (Engl. Transl.)* **1998**, *47*, 1789.
(28) Bruce, M. I.; Hinchliffe, J. R.; Humphrey, P. A.; Surynt, R. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *552*, 109.
(29) Tunik, S. P.; Grachova, E. V.; Denisov, V. R.; Starova, G. L.; Nikolskii, A. B.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1997**, *536*, 339.
(30) Braun, T.; Laubender, M.; Gevert, O.; Werner, H. *Chem. Ber.* **1997**, *130*, 559.
(31) Koridze, A. A.; Zdanovich, V. I.; Andrievskaya, N. V.; Siromakhova, Y.; Petrovskii, P. V.; Ezernitskaya, M. G.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T. *Russ. Chem. Bull. (Engl. Transl.)* **1996**, *45*, 1200.
(32) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Tanase, T.; Hidai, M. *Organometallics* **1994**, *13*, 4214.
(33) Burns, R. M.; Hubbard, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9514.
(34) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Morooka, Y. *Organometallics* **1994**, *13*, 1129.
(35) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **1996**, *250*, 129.
(36) Bruce, M. I. *Coord. Chem. Rev.* **1997**, *166*, 91.

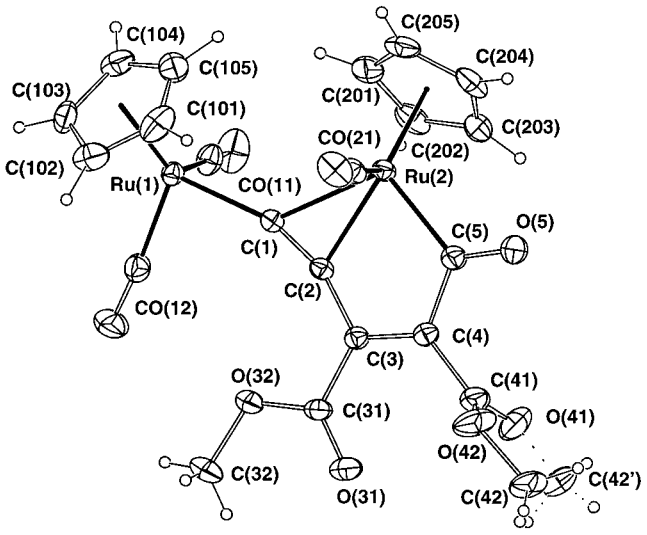


Figure 2. Molecular projection of complex **4**, almost normal to the Ru_2C_5 plane. Disorder in one of the CO_2Me groups is indicated by the dotted lines. Ellipsoids are at the 20% probability level for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

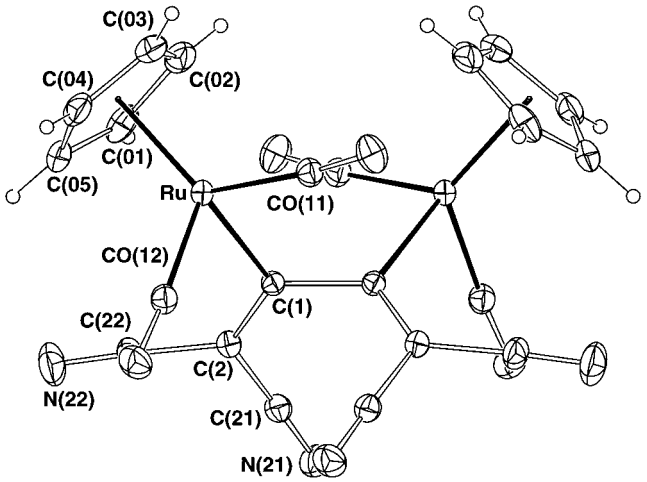


Figure 3. Molecular projection of complex **5**. Ellipsoids are at the 20% probability level for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

in all three structures **3b**, **6**, and **7** (**3b**, 2.034(3) and 2.085(3) Å; **6**, 2.06(2) and 2.07(2) Å; **7**, 2.08(2) and 2.10(2) Å) and lie in the region expected for Ru−C single bonds. The angles about C(1), C(2) and C(3), C(4) are suggestive of a significant deviation from sp^2 hybridization (Ru(2)−C(2)−C(3) = 67.6(1)°, Ru(3)−C(4)−Ru(2) = 79.47(9)°), compared to C(2)−C(3), which has near-ideal sp^2 hybridization (Ru(4)−C(2)−C(3) = 124.0(2)°).

The structure of the dinuclear complex **4** established that one molecule of DMAD had been incorporated into the complex which, interestingly, had coupled with the carbide unit and an additional CO molecule, giving a ruthenium-coordinated acyl ligand. The C(1)−C(2) bond distance has increased marginally (ca. 0.06 Å) from the strictly CC triple bond found in the starting material, [{$Ru(CO)_2(\eta$-$C_5H_5)$}$_2(\mu$-CC)], indicating that significant triple-bond character remains. The resonance structures shown (Figure 5) indicate an alternative interpretation of the η^2-C═C bond to Ru(2). Thus, the ligand found in **4** can be considered as an acyl σ,η^2(3e)-pentadienyl (**C**) or acyl σ,η^2(3e)-enynyl (**D**) moiety, depending on the interpretation of the bond lengths and angles. The most relevant comparison here is the related acyl complex [Ru{C(O)C(Ph)═C(Ph)-η^2-C(Ph)═CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)] (**8**). The ligand in this molecule is an acyl formally derived from penta-2,4-dien-1-one.

The geometry about both C(1) and C(2) in **4** is typical of "bent back" alkyne coordination with close to ideal sp^2 geometries observed at C(3) and C(4). Examination of relevant bond angles reveals an Ru(1)−C(1)−C(2) angle of 160.6(2)° with C(1)−C(2)−C(3) = 161.4(3)°; the acyl portions of the ligands in **4** and **8** are more closely comparable. The Ru−C(O) bonds are similar (**4**, 2.088(4) Å; **8**, 2.040(12) Å) and C(5)−C(4) bonds are also similar (**4**, 1.498(5) Å; **8**, 1.515(15) Å). Thus, the description of the ligand in complex **4** is that of an enyne incorporating a ruthenium-substituted η^2-alkyne (**4′**). The C(3)−C(4) bond distances in **4** and **8** are similar (**4**, 1.352(4) Å; **8**, 1.340(16) Å), with C(1)−C(2) being significantly longer. The C(5)−Ru(2) bond distance in **4** is unremarkable and characteristic of a metal−carbon σ-bond. The distance C(4)−C(5) is long compared to C(3)−C(4), ruling out any resonance along this part of the chain.

The solid-state structure of complex **5** confirmed the incorporation of TCNE into [{$Ru(CO)_2(\eta$-$C_5H_5)$}$_2(\mu$-CC)], giving a *cis*-(μ-tetracyanobutadiene-2,3-diyl)diruthenium complex. There are a number of examples of TCNE reacting with ruthenium alkynyl complexes to give related products, but only one where the reaction of ethynediyl complexes was studied. These diplatinum complexes, [{$PtCl(PMe_3)_3$}$_2${μ-C═C$(CN)_2$C═C$(CN)_2$}] (**9**), exhibit stereoisomerism with both cis and trans isomers with respect to the metal atoms, but complex **5** is clearly cis. The geometry about the ruthenium atom does not appear to be unduly affected by the electron-withdrawing ligand and is similar to that found for other Ru-$(CO)_2(\eta$-$C_5H_5)$ units. However, the tetracyanobutadienyl ligand compares well with the analogous ligand found in **9**. In both complexes **5** and **9** the metal−C bonds are single, lying well within the range for such distances. The *cis*-μ-tetracyanobutadiene-2,3-diyl ligands share many similarities, with C(1)−C(2) (**5**, 1.370(2) Å; **9**, 1.36(1) Å) clearly a double bond and C(1)−C(1′) a single bond (**5**, 1.465(2) Å; **9**, 1.47(1) Å). The geometry about C(1) is clearly sp^2 with M−C(1)−C(2), C(2)−C(1)-C(1′), and M−C(1)−C(1′) approximately 120° (**5**, 123.4(1), 117.5(1), and 119.1(1)°; **9**, 119.2(8), 119.4(10), and 118.1(7)°). The larger M−C(1)−C(2) angle for **5** is most likely a result of the increased steric encumbrance of the $Ru(CO)_2(\eta$-$C_5H_5)$ moiety.

Discussion

Reaction of 1 with DMAD (Scheme 1). The activation of carbon monoxide and its coupling to a hydrocarbon chain is of relevance to FT chemistry. There are a number of examples of this type of migratory insertion reaction in mononuclear chemistry,[37] but examples are less commonly found with cluster-bound hydrocarbons. Some recent examples are the reported insertion of CO into an Ru−C bond, giving the structural fragment **10**,[22]

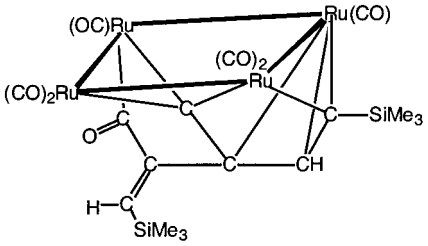
(37) Cavell, K. J. *Coord. Chem. Rev.* **1996**, *155*, 209.

Table 1. Crystal/Refinement Data for Complexes 3−5

	3a	3b	4[a]	5
formula	$C_{27}H_{16}O_{13}Ru_4$	$C_{29}H_{20}O_{13}Ru_4$	$C_{22}H_{16}O_8Ru_2$	$C_{22}H_{10}N_4O_8Ru_2$
M_r	952.7	980.7	610.5	596.5
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/c$ (C_{2h}^5, No. 14)	$P2/n$ (C_{2h}^4, No. 13)
a (Å)	9.786(1)	9.6402(7)	12.270(1)	8.3685(2)
b (Å)	11.209(2)	11.5159(9)	10.107(1)	7.8859(6)
c (Å)	13.945(2)	14.7985(11)	17.521(2)	16.355(1)
α (deg)	81.903(2)	80.740(1)		
β (deg)	72.796(2)	76.015(1)	95.624(2)	101.912(1)
γ (deg)	90.413(3)	89.916(1)		
V (Å^3)	$1444._7$	$1572._2$	$2162._3$	$1056._1$
D_c (g cm^{-3})	2.19_0	2.07_1	1.87_5	1.87_6
μ (cm^{-1})	21.2	19.5	14.4	14.7
specimen (mm)	0.12 × 0.10 × 0.07	0.29 × 0.23 × 0.08	0.45 × 0.13 × 0.07	0.70 × 0.15 × 0.15
"T"$_{min}$, "T"$_{max}$	0.54, 0.80	0.66, 0.84	0.66, 0.85	0.72,0.89
N_t	14346	18268	25129	12173
N (R_{int})	7210(0.045)	7645(0.020)	5483(0.020)	2672(0.019)
N_o	5491	6382	3937	2473
R	0.062	0.026	0.032	0.020
R_w	0.074	0.031	0.039	0.033
n_v	397	496	299	166
$\|\Delta\rho_{max}\|$ (e Å^{-3})	3.5(1)	0.67(3)	0.94(4)	0.68(2)
T (K)	ca. 153	ca. 300	ca. 300	ca. 300

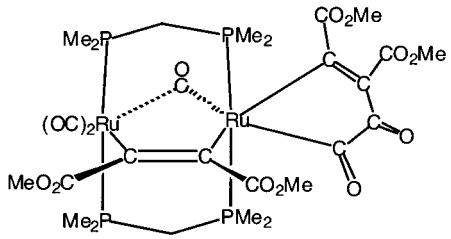
[a] In **4**, the (carboxy-) methyl group was modeled as disordered over two sites, associated with the two oxygen atoms, implying unresolved disorder therein (etc) also; occupancies were refined to 0.57(1) and its complement.

and $[Ru_3(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}AsPh_2)(\mu_2\text{-}OCC_{12}H_{17})]$[38] (**11**; $C_{12}H_{17}$ = 1,6-cyclododecadien-1-yl-3-ylidene).

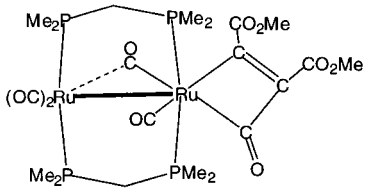


Complex 10

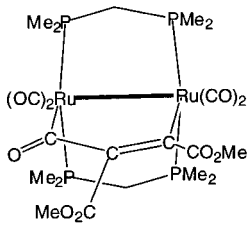
In considering the formation of complexes **3**, we found that there are numerous examples of metallacyclopentadienyl ligands in the literature resulting from the oligomerization of alkynes at group 8 metals.[39] However, there are few examples of this type of ligand where one of the ring carbons is metalated, the most recent examples being derived from the reaction of a cluster-bound allenylidene and internal alkynes, $[Ru_3(CO)_9\{\mu_3\text{-}C(R)C(R)C_2CPh_2\}]$[39] (**12**). It is important to note that DMAD is an activated electron-deficient alkyne and reacts readily in a wide range of organometallic systems. We expected that **1** would experience reactivity at the "long" Ru−Ru bond,[18] which spans the inner two Ru atoms, but it is obvious from the product obtained that one of the Ru(CO)−Ru(η-C_5H_5) bonds is cleaved. It is this observation that suggested to us that the reaction probably proceeds initially by way of reaction at the carbide unit. While DMAD participates readily in cycloaddition reactions, a number of dipolar intermediates can be drawn which rationalize the oligomerization reactions it sometimes undergoes. Gladfelter[40] has proposed a single-electron transfer to DMAD as a possible first step in its reaction with $[Ru_2(dmpm)_2(CO)_5]$; one of the products, **13**, is the result of an unusual double insertion of CO, the others being variants on this theme (**14**−**16**), with **16** being the ultimate thermodynamic product. Recent work[41] has suggested that with the availability of vacant coordination sites, e.g. in $[Ru(CH_3CN)_2(CO)(\eta\text{-}C_5H_5)]^+$, oligomerization of terminal and internal alkynes proceeds through well-accepted coordination and activation pathways, giving ruthenium cyclopentadienone derivatives, **17**.



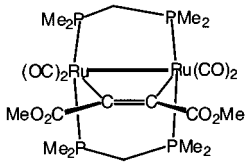
Complex 13



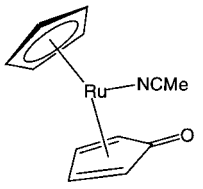
Complex 14



Complex 15



Complex 16



Complex 17

Given these numerous alternatives, it is difficult to a propose a definitive mechanism, but it is clear that Ru-

(38) bin Shawkataly, O.; Puvanesvary, K.; Fun, H. K.; Sivakumar, K. *J. Organomet. Chem.* **1998**, *565*, 267.

(39) Charmant, J. P. H.; King, P. J.; Quesada-Pato, R.; Sappa, E.; Schaefer, C. *J. Chem. Soc., Dalton Trans.* **2001**, *1*, 46.

(40) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1992**, *11*, 2534.

(41) Rueba, E.; Mereiter, K.; Soldouzi, K. M.; Gemel, C.; Schmid, R.; Kirchner, K.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 5384.

Table 2. Selected Geometries for 3a and 3b[a]

Ruthenium Environments[b,c]

(i) Ru(2)

atom	*r*	C(21)	C(22)	C(1)	C(4)
C(12)	2.103(9),2.089(3)	89.1(4), 87.6(1)	101.6(4), 99.4(1)	93.3(4), 94.3(1)	161.9(4), 163.5(1)
C(21)	1.93(1), 1.960(4)		92.1(5), 94.1(2)	163.3(4), 162.8(1)	97.5(4), 98.1(1)
C(22)	1.853(9), 1.856(3)			103.6(4), 102.5(1)	95.0(4), 95.6(1)
C(1)	2.04(1), 2.034(3)				75.6(4), 75.7(1)
C(4)	2.085(9), 2.085(3)				

(ii) Ru(3)

atom	*r*	C(32)	C(33)	C(1)	C(2)	C(3)	C(4)
C(31)	1.92(1), 1.916(3)	96.4(4), 97.2(1)	94.9(4), 94.9(2)	100.9(4), 101.9(1)	136.2(4), 137.5(1)	140.7(4), 140.4(1)	104.2(4), 103.7(1)
C(32)	1.92(1), 1.919(3)		90.7(5), 90.4(1)	158.8(3), 158.2(1)	126.0(4), 124.2(1)	97.1(4), 96.6(1)	96.2(4), 97.7(1)
C(33)	1.90(1), 1.916(4)			99.8(4), 98.2(1)	94.8(4), 94.1(1)	121.6(4), 121.9(1)	158.7(4), 158.6(1)
C(1)	2.315(8), 2.298(3)				35.4(3), 35.60(9)	61.7(3), 61.95(9)	67.8(3), 67.9(1)
C(2)	2.318(8), 2.327(2)					37.1(4), 37.2(1)	64.9(3), 65.0(1)
C(3)	2.220(8), 2.226(2)						37.7(4), 37.6(1)
C(4)	2.215(9), 2.229(3)						

(iii) Ru(1)[d]

atom	*r*	C(12)	C(1)	C(100)
C(11)	1.849(9), 1.858(3)	84.8(4), 85.9(1)	89.5(4), 90.5(1)	$127._6$, $126._6$
C(12)	2.11(1), 2.094(4)		93.9(4), 94.2(1)	$120._6$, $120._9$
C(1)	2.016(9), 2.034(3)			$128._3$, $127._6$
C(100)	1.91_2, 1.91_3			

(iv) Ru(4)[e]

atom	*r*	C(42)	C(2)	C(400)
C(41)	1.88(1), 1.881(3)	91.2(4), 90.1(1)	91.2(4), 91.3(1)	$126._6$, $127._2$
C(42)	1.896(9), 1.873(3)		91.8(4), 91.3(1)	$124._0$, $125._2$
C(2)	2.13(1), 2.125(3)			$122._2$, $121._4$
C(400)	1.89_5, 1.91_3			

(b) Ligand Geometries

Distances (Å)

C(1)−C(2)	1.41(1), 1.414(4)	C(12)−O(12)	1.15(1), 1.174(4)
C(2)−C(3)	1.45(1), 1.457(4)	C(3)−C(311)	1.51(1), 1.513(4)
C(3)−C(4)	1.43(1), 1.436(4)	C(4)−C(411)	1.49(1), 1.494(4)

Angles

O(12)−C(12)−Ru(1)	133.1(9), 134.9(3)	C(1)−C(2)−C(3)	109.2(8), 108.4(3)
O(12)−C(12)−Ru(2)	145.7(9), 143.3(3)	C(2)−C(3)−C(4)	115.6(8), 115.8(2)
Ru(1)−C(12)−Ru(2)	81.1(3), 81.8(1)	C(2)−C(3)−C(311)	122.7(9), 123.1(3)
Ru(1)−C(1)−Ru(2)	84.9(3), 84.6(1)	C(4)−C(3)−C(311)	121.3(9), 120.7(3)
Ru(1)−C(1)−C(2)	150.6(8), 150.3(2)	Ru(3)−C(4)−Ru(2)	79.0(3), 79.47(9)
Ru(2)−C(1)−C(2)	122.8(7), 123.2(2)	C(3)−C(4)−Ru(2)	116.5(7), 116.3(2)
Ru(4)−C(2)−C(1)	126.5(7), 127.4(2)	C(3)−C(4)−C(411)	117.1(8), 116.6(2)
Ru(4)−C(2)−C(3)	124.1(6), 124.0(2)	Ru(2)−C(4)−C(411)	126.0(7), 126.7(2)

[a] C(*n*00) is the centroid of Cp ring C(*n*01−5). [b] *r* is the ruthenium−ligand atom distance (Å), with the first value associated with **3a** and the second with **3b**; the other entries in each matrix comprise the angles (deg) subtended by the associated atoms at the head of each row and column. [c] Ru(2)−Ru(1,3) lengths are 2.737(1), 2.7387(4) Å and 2.738(1), 2.7598(4) Å. Ru(1)−Ru(2)−Ru(3) angles are 90.94(3), 89.96(1)°. [d] Ru(1)−C(10*n*) ranges: 2.21(1)−2.297(9), 2.195(4)−2.313(3) Å. [e] Ru(4)−C(40*n*) ranges: 2.227(9)−2.259(9), 2.236(3)−2.304(3) Å.

(3)−Ru(4) (Scheme 2) is cleaved. This could be promoted by alkyne coordination or a result of the direct reaction of the C_2^{2-} ligand with the electron-poor alkyne. Concomitant with this, cleavage coordination and/or coupling of the DMAD through presumably polar intermediates followed or preceded by CO expulsion and cleavage of Ru(2)−Ru(3) leads to complexes **3**. It should be noted that **1** is rigid in solution, at least on the NMR time scale, and proposing intermediates such as **1′** (Scheme 2) would appear fruitless. Obviously the formation of these compounds is complex, as we have yet to account for the formation of **2.**

Reaction of [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-CC)] with DMAD and TCNE. The observation of complex **4** in the preceding reaction was the stimulus for the further investigation of the reactivity of [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-CC)] with activated substrates. In this case the carbide unit reacted directly with DMAD and TCNE. As mentioned previously, DMAD is thought to react via radical mechanisms,[40] while the cycloaddition of TCNE to transition-metal alkynyl complexes via transient radicals is well-known.[42−51] The alkynyl dianion is electron rich and obviously reacts readily with DMAD,

(42) Onitsuka, K.; Ose, N.; Ozawa, F.; Takahashi, S. *J. Organomet. Chem.* **1999**, *578*, 169.
(43) Stokes, H. L.; Ni, L. M.; Belot, J. A.; Welker, M. E. *J. Organomet. Chem.* **1995**, *487*, 95.
(44) Su, S. R. Thesis, Ohio State University, Columbus, OH, 1971
(45) Su, S. R.; Wojcicki, A. *Inorg. Chim. Acta* **1974**, *8*, 55.
(46) Yamamoto, Y.; Satoh, R.; Tanase, T. *J. Chem. Soc., Dalton Trans.* **1995**, 307.
(47) Kergoat, R.; Kubicki, M. M.; Gomes de Lima, L. C.; Scordia, H.; Guerchais, J. E.; L'Haridon, P. *J. Organomet. Chem.* **1989**, *367*, 143.

Table 3. Selected Geometries for 4[a]

	Distances (Å)		
Ru(1)−C(100)	1.89_8	Ru(2)−C(200)	1.93_7
Ru(1)−C(10*n*) (range)	2.222(4)−2.246(4)	Ru(2)−C(20*n*) (range)	2.228(4)−2.311(5)
Ru(1)−C(11)	1.879(4)	Ru(2)−C(21)	1.838(4)
Ru(1)−C(12)	1.870(4)	Ru(2)−C(1)	2.300(3)
Ru(1)−C(1)	2.029(3)	Ru(2)−C(2)	2.155(3)
C(1)−C(2)	1.250(4)	Ru(2)−C(5)	2.088(4)
C(2)−C(3)	1.421(4)	C(3)−C(31)	1.479(5)
C(3)−C(4)	1.352(4)	C(5)−O(5)	1.216(4)
C(4)−C(5)	1.498(5)		
	Angles (deg)		
C(100)−Ru(1)−C(1)	$125._0$	C(200)−Ru(2)−C(1)	$119._0$
C(100)−Ru(1)−C(11)	$129._0$	C(200)−Ru(2)−C(2)	$134._3$
C(100)−Ru(1)−C(12)	$124._8$	C(200)−Ru(2)−C(21)	$128._6$
C(1)−Ru(1)−C(11)	87.1(2)	C(200)−Ru(2)−C(5)	$118._0$
C(1)−Ru(1)−C(12)	88.5(1)	C(1)−Ru(2)−C(2)	32.4(1)
C(11)−Ru(1)−C(12)	90.0(2)	C(1)−Ru(2)−C(21)	90.6(1)
Ru(1)−C(1)−C(2)	160.6(2)	C(1)−Ru(2)−C(5)	107.9(1)
Ru(1)−C(1)−Ru(2)	131.9(1)	C(2)−Ru(2)−C(21)	93.7(1)
Ru(2)−C(1)−C(2)	67.4(2)	C(2)−Ru(2)−C(5)	76.0(1)
Ru(2)−C(2)−C(1)	80.2(2)	C(21)−Ru(2)−C(5)	86.0(2)
Ru(2)−C(2)−C(3)	116.6(2)	C(2)−C(3)−C(31)	122.6(3)
C(1)−C(2)−C(3)	161.4(3)	C(4)−C(3)−C(31)	121.3(3)
C(2)−C(3)−C(4)	115.9(3)	C(4)−C(5)−O(5)	119.4(3)
C(3)−C(4)−C(5)	115.1(3)	Ru(2)−C(5)−O(5)	124.3(3)
Ru(2)−C(5)−C(4)	116.3(2)		

[a] C(*n*00) is the centroid of Cp ring C(*n*01−5).

Table 4. Selected Geometries for 5[a]

	Distances (Å)		
Ru−C(100)	1.89_5	C(1)−C(1′)	1.465(2)
Ru−C(0*n*) (range)	2.233(2)−2.249(2)	C(2)−C(21)	1.438(2)
Ru−C(11)	1.889(2)	C(2)−C(22)	1.439(3)
Ru−C(12)	1.893(2)	C(21)−N(21)	1.139(3)
Ru−C(1)	2.099(1)	C(22)−N(22)	1.136(3)
C(1)−C(2)	1.370(2)		
	Angles (deg)		
C(100)−Ru−C(1)	$126._9$	Ru−C(1)−C(1′)	119.1(1)
C(100)−Ru−C(11)	$124._3$	C(2)−C(1)−C(1′)	117.5(1)
C(100)−Ru−C(12)	$122._1$	C(1)−C(2)−C(21)	122.9(2)
C(1)−Ru−C(11)	91.73(8)	C(1)−C(2)−C(22)	122.8(2)
C(1)−Ru−C(12)	86.33(7)	C(2)−C(21)−N(21)	178.3(2)
C(11)−Ru−C(12)	95.17(8)	C(2)−C(22)−N(22)	177.6(2)
Ru−C(1)−C(2)	123.4(1)		

[a] C(100) is the centroid of the Cp rings; primed atoms are related by the intramolecular *2*-axis.

but it is impossible to say whether a radical mechanism is operating in this case. However, formally one can speculate (Scheme 3) that the first step involves nucleophilic attack of the dianion at DMAD to form **B** followed by attack at a coordinated carbonyl. It is unlikely that DMAD coordinates a ruthenium, given that our recent work suggests that [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-CC)] is rather inert to substitution. It is noteworthy that acyl pentadienyl complexes similar to **4** are implicated in the formation of ruthenium cyclopentadienone complexes.[41]

While this paper was in preparation, the reaction of group 10 ethynediyl complexes, [{MCl(PR$_3$)$_2$}(μ-C≡C)], with TCNE was reported,[42] these reactions yielding both the *cis*- and *trans*-(μ-tetracyanobutadiene-2,3-diyl)diplatinum complexes **9**. The mechanism operating in this type of reaction is now well understood (Scheme 4). The first step is a [2 + 2] cycloaddition of TCNE to the triple bond of [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-CC)] to give an intermediate cyclobutene-1,2-diyl complex, which then ring-opens to give complex **5**. It was interesting to find that only the cis isomer of **5** was obtained, given that the steric requirements of a Ru(CO)$_2$(η-C$_5$H$_5$) unit should outweigh those of MCl(PR$_3$)$_2$ (M = Pt, Pd) in **9**, where the trans isomer appeared to be the thermodynamic product. Heating a DMSO solution of complex **5** for a prolonged period (weeks) resulted in the formation of several uncharacterized products with ca. 50% of the sample unchanged. There was no conclusive evidence for the formation of a trans isomer.

Summary

We have described the reaction of activated substrates such as the electron-poor DMAD and TCNE with ruthenium complexes containing the alkynyl dianion, C_2^{2-}. In all reactions we have observed the formation of chains containing four, five, or six carbon atoms. In one instance we have also observed the activation of CO and isolated complexes that shed considerable light on well-trodden alkyne oligomerization reactions. It is also clear that the complexes presented here clearly implicate the C_2^{2-} unit in the formation of carbon chains, which could have implications for the mechanism of the Fischer−Tropsch reaction. Maitlis[12] has provided convincing evidence for the implication of vinyl intermediates in FT chemistry which finds support in the CC bond-forming reactions of the permetalated ethene ligand in **1**.

Experimental Section

General Comments. Manipulation of oxygen- and moisture-sensitive compounds was performed under an atmosphere of high-purity argon using standard Schlenk techniques or in a drybox (Miller Howe).

Infrared spectra were recorded using a Bio-Rad FTS 45 or 40 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were acquired using Varian Gemini 200 and Bruker ARX 500 spectrometers. ^{31}P NMR spectra were acquired using a Bruker ARX 500 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced with respect to incompletely deuterated solvent signals.

Mass spectra were obtained on a VG AutoSpec spectrometer employing a fast atom bombardment (FAB) ionization source in all samples, unless otherwise specified.

Elemental analyses were performed by The Research School of Chemistry Microanalytical Unit, Australian National University, Australian Capital Territory, Australia.

Tetrahydrofuran was dried over sodium metal and distilled from potassium benzophenone ketyl under an atmosphere of argon. Hexanes and toluene were dried over sodium metal and distilled under an atmosphere of argon. Distilled solvents were stored over sodium or potassium mirrors until use.

[Ru$_4$(μ_4-CC)(η-C$_5$H$_4$R)$_2$(μ-CO)$_2$(CO)$_8$] (R = H (**1a**), Me (**1b**))[18] and [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-CC)][52] were prepared according to previously reported routes.

Structure Determinations. Full spheres of area-detector diffraction data were measured using a Bruker AXS CCD

(48) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494.
(49) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 501.
(50) Bruce, M. I.; Hambley, T. W.; Rodgers, J. R.; Snow, M. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, *226*, C1.
(51) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, *235*, 105.
(52) Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316.
(53) Hall, S. R.; King, G. S. D.; Stewart, J. M. *The XTAL 3.4 User's Manual*; University of Western Australia: Lamb, Perth, 1995.

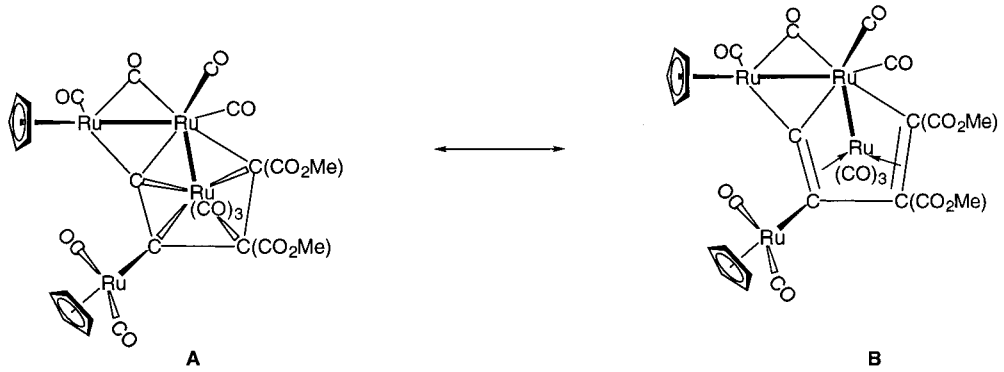


Figure 4. Alternative representations of complex **3a**.

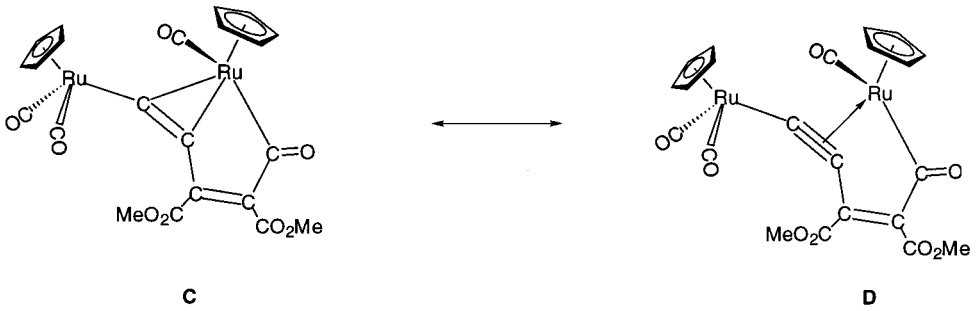
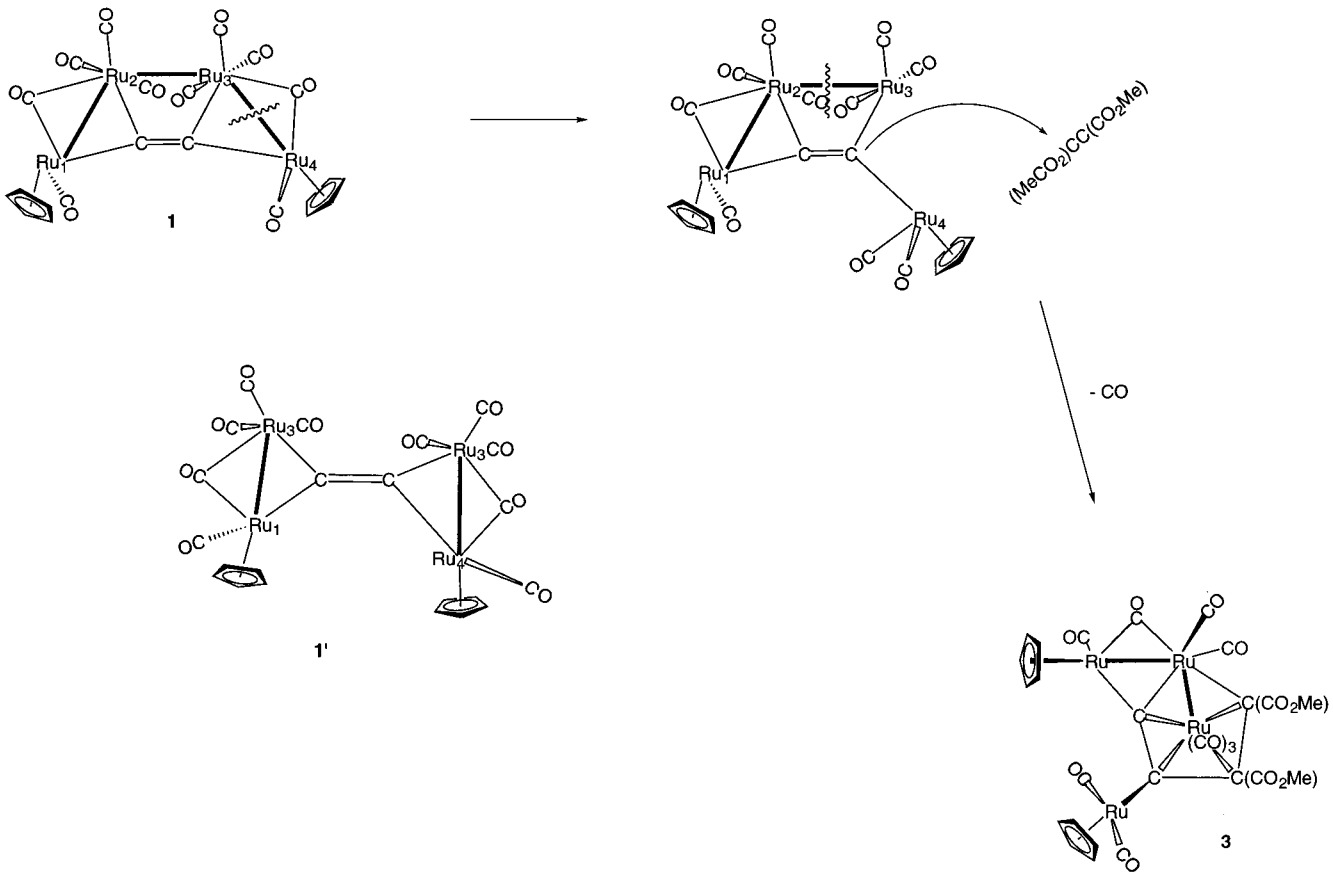


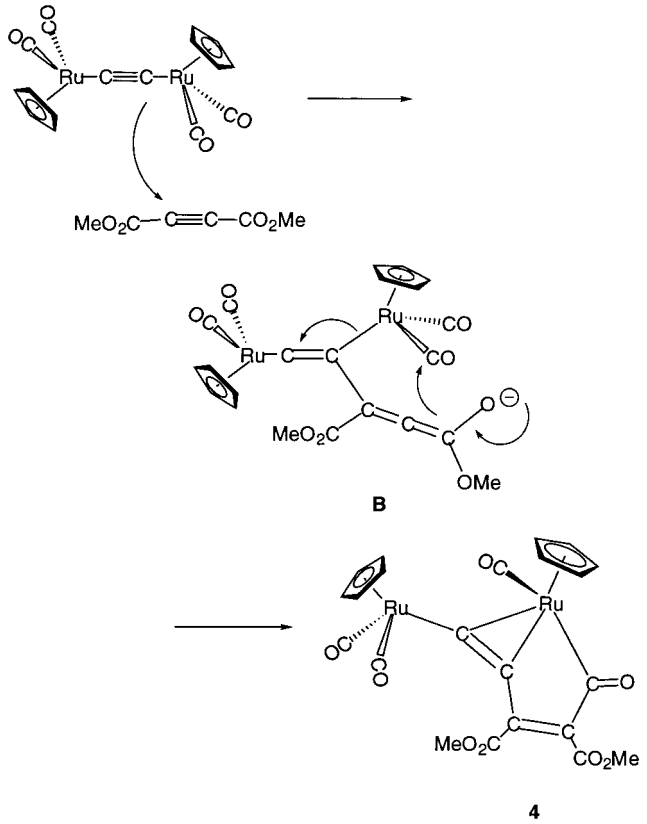
Figure 5. Alternative representations of complex **4**.

Scheme 2

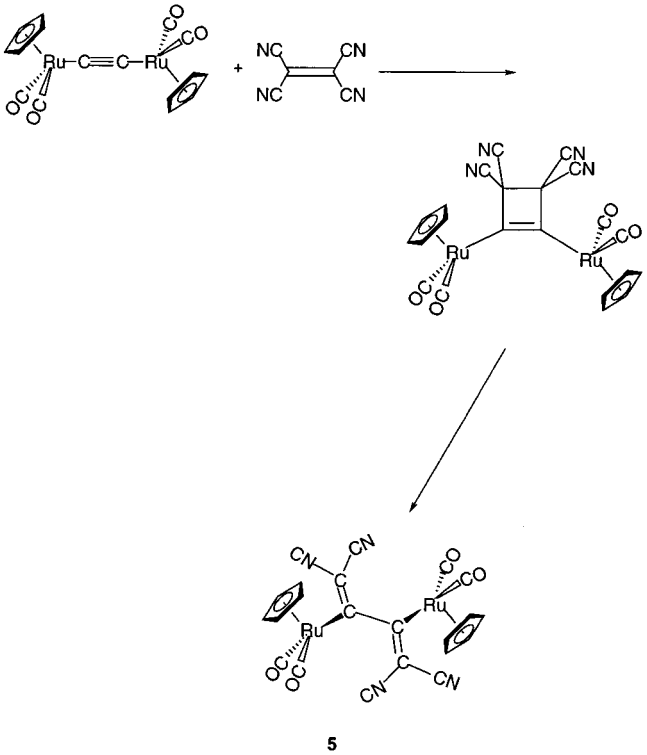


instrument fitted with monochromatic Mo Kα radiation source (λ = 0.7107$_3$ Å) within the limit $2\theta_{max}$ = 58°. $N_{(total)}$ reflections were acquired, reducing to N unique (R_{int} quoted) incorporating "empirical" absorption corrections (proprietary software), N_o of these with $F > 4\sigma(F)$ being used in the full matrix least squares refinements. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being refined for **3b** and **5** and included constrained at estimated values for **3a** and **4**. Conventional residuals on $|F|$, R, R_w (statistical weights) are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the Xtal 3.4 program system.[53] Atomic coordinates are deposited with

Scheme 3



Scheme 4



the Cambridge Crystallographic Data Base (deposition numbers 157509−157512).

Syntheses. [Ru$_4$(μ_4-(CC)C(CO$_2$Me)C(CO$_2$Me))(η-C$_5$H$_5$)$_2$-(μ-CO)(CO)$_8$] (3a). DMAD (20 μL, 0.162 mmol) and **1a** (100 mg, 0.105 mmol) were stirred for ca. 14 h in THF at ambient temperature. The solvent was removed in vacuo, and the residue was applied to a radial chromatography plate which was developed with acetone/*n*-hexane. The first red-orange band was eluted with ca. 10% acetone/hexanes and collected, and the volatiles were removed, giving a waxy red solid (**2a**; 20 mg, 19%), formulated as Ru$_4$(C$_5$H$_5$)$_2$C$_2$C$_2$(CO$_2$Me)$_2$(CO)$_9$. IR (ν(CO)): 2098 w, 2076 m, 2048 vs, 2004 s, 1976 m, 1818 w br, 1710 w br cm^{-1}. ^{1}H NMR (δ; CDCl$_3$): 3.77 (s, 3H, CO$_2$*Me*), 3.79 (s, 3H, CO$_2$*Me*), 5.27 (s br, 5H, C$_5$H$_5$), 5.36 (s br, 5H, C$_5$H$_5$). ^{13}C{^{1}H} NMR (δ; CDCl$_3$): 52.0 (s, CO$_2$*Me*), 52.6 (s, CO$_2$*Me*), 84.1 (s, *C*C), 92.9, 93.3 (s, 2 × *C*$_5$H$_5$), 114.7 (s, *C*−CO$_2$Me), 146.0 (s (br), 2 × *C*O$_2$Me), 166.6 (s, *C*−CO$_2$Me), 172.1 (s, μ_3-*C*C), 198.4 (s, 7 × CO), 237.4 (s, μ-CO), 295.8 (s, Ru−*C*). FAB MS (NOBA/CH$_2$Cl$_2$): *m*/*z* 954 ([M]$^+$, 100%), 923 ([M − OMe]$^+$, 65%), 898, 870, 841, 815, 785 ([M − OMe − *n*CO]$^+$, *n* = 1−5, 40%, 45%, 45%, 55%, 40%). The next light orange band was collected, the volatiles were removed, and the residue was recrystallized (CHCl$_3$/hexanes) to give bright orange crystals of **3a**·CHCl$_3$ (16 mg, 14%). Anal. Calcd for C$_{28}$H$_{17}$Cl$_3$O$_{13}$Ru$_4$: C, 31.36; H, 1.60. Found: C, 31.72; H, 1.53. IR (ν(CO)): 2116 w, 2077 m, 2051 vs, 2003 s, 1976 m, 1818 w br, 1713 w br cm^{-1}. ^{1}H NMR (δ; CDCl$_3$): 3.60 (s, 3H, CO$_2$*Me*), 3.78 (s, 3H, CO$_2$*Me*), 5.20 (s, 5H, C$_5$H$_5$), 5.57 (s, 5H, C$_5$H$_5$). ^{13}C{^{1}H} NMR (δ; CDCl$_3$): 52.2 (s, CO$_2$*Me*), 52.7 (s, CO$_2$*Me*), 88.9 (s, C$_5$H$_5$), 89.0 (s, C$_5$H$_5$), 109.2 (s, Ru−*C*−CO$_2$Me), 139.3 (s, *C*O$_2$Me), 139.4 (s, *C*O$_2$Me), 168.2 (s, μ-*C*−CO$_2$Me), 174.1 (s, μ-*C*C) 193.6 (s, μ_3-*C*C), 196.0 (s, CO), 199.6 (s, 3 × CO), 199.8 (s, 2 × CO), 200.6 (s, 2 × CO), 234.2 (s, μ-CO). FAB MS (NOBA/CH$_2$Cl$_2$): *m*/*z* 954 ([M]$^+$, 100%), 926, 898, 870, 842, 814, 786 ([M − *n*CO]$^+$, *n* = 1−6, 33%, 35%, 22%, 20%, 30%, 20%), 586 ([M − CpRu(CO)$_2$ − 2OMe]$^+$, 35%).

[Ru$_4$(μ_4-(CC)C(CO$_2$Me)C(CO$_2$Me))(η-C$_5$H$_4$Me)$_2$(μ-CO)-(CO)$_8$] (3b). In a manner similar to that for **3a**, DMAD (20 μL, 0.162 mmol) was reacted with **1b** (97 mg, 112 μmol) in THF to yield first a yellow band, eluted with hexane, and identified as Ru$_3$(CO)$_{12}$ (23 mg), presumably from the in situ formation of **1b**. A red band as a waxy red solid (**2b**; 22 mg, 20%) was formulated as Ru$_4$(C$_5$H$_4$Me)$_2$C$_2$C$_2$(CO$_2$Me)$_2$(CO)$_9$. IR (ν(CO)): 2098 w, 2076 m, 2046 vs, 2003 s, 1971 m, 1813 w br, 1717 w br cm^{-1}. ^{1}H NMR (δ; CDCl$_3$): 2.06 (s, 6H), 3.75 (s, 3H, CO$_2$*Me*), 3.80 (s, 3H, CO$_2$*Me*), 4.70−5.40 (m, 8H, 2 × C$_5$*H*$_4$-Me). ^{13}C{^{1}H} NMR (δ; CDCl$_3$): 12.4 (s, 2 × 2 × C$_5$H$_4$*Me*), 52.0 (s, CO$_2$*Me*), 52.6 (s, CO$_2$*Me*), 83.3 (s, *C*C), 88.1, 89.0, 89.5, 91.6, 93.2, 95.5, 96.8 (s, 2 × *C*$_5$H$_4$Me), 114.9 (s, *C*−CO$_2$Me), 145.1 (s (br), 2 × *C*O$_2$Me), 166.8 (s, *C*−CO$_2$Me), 172.3 (s, μ_3-*C*C), 198.7 (s, 7 × CO), 241.6 (s, μ-CO), 298.5 (s, Ru-*C*). FAB MS (NOBA/CH$_2$Cl$_2$): *m*/*z* 982 ([M]$^+$, 65%), 952 ([M − OMe]$^+$, 100%), 927, 898, 869, 843, 814, 785, 756, 729 ([M − OMe − *n*CO]$^+$, *n* = 1−8, 50%, 65%, 70%, 45%, 60%, 35%, 35%, 30%).

The next light orange band was eluted with 30% acetone/hexanes, giving bright orange crystals of **3b** (24 mg, 22%) after recrystallization from CH$_2$Cl$_2$/hexanes. Anal. Calcd for C$_{29}$H$_{20}$O$_{13}$-Ru$_4$: C, 35.50; H, 2.05. Found: C, 35.56; H, 2.08. IR (CH$_2$Cl$_2$; ν(CO)): 2112 w, 2064 m, 2039 vs, 2000 m, 1983 s, 1822 m br, 1722 m br cm^{-1}. ^{1}H NMR (δ; CDCl$_3$): 2.12 (s, 3H, C$_5$H$_4$*Me*), 2.17 (s, 3H, C$_5$H$_4$*Me*), 3.60 (s, 3H, CO$_2$*Me*), 3.79 (s, 3H, CO$_2$*Me*), 4.91 (m, 2H, C$_5$*H*$_4$Me), 4.95 (m, 1H, C$_5$*H*$_4$Me), 5.91 (m, 1H, C$_5$*H*$_4$Me), 5.25 (m, 1H, C$_5$*H*$_4$Me), 5.30 (m, 1H, C$_5$*H*$_4$Me), 5.39 (m, 1H, C$_5$*H*$_4$Me), 5.47 (m, 1H, C$_5$*H*$_4$Me). ^{13}C{^{1}H} NMR (δ; CDCl$_3$): 13.0 (s, C$_5$H$_4$*Me*), 13.6 (s, C$_5$H$_4$*Me*), 51.9 (s, CO$_2$*Me*), 52.4 (s, CO$_2$*Me*), 84.2 (s, 2 × *C*$_5$H$_4$Me), 85.1 (s, 2 × *C*$_5$H$_4$Me), 85.6 (s, 2 × *C*$_5$H$_4$Me), 86.6 (s, 2 × *C*$_5$H$_4$Me), 93.4 (s, *C*$_i$−C$_5$H$_4$-Me), 93.6 (s, *C*$_i$−C$_5$H$_4$Me), 109.2 (s, Ru−*C*−CO$_2$Me), 139.3 (s, *C*O$_2$Me), 139.4 (s, *C*O$_2$Me), 168.2 (s, μ-*C*−CO$_2$Me), 174.1 (s, μ-*C*C) 193.6 (s, μ_3-*C*C), 196.0 (s, CO), 199.6 (s, 3 × CO), 199.8 (s, 2 × CO), 200.6 (s, 2 × CO), 234.4 (s, μ-CO). FABMS (NOBA/CH$_2$Cl$_2$): *m*/*z* 982 ([M]$^+$, 100%), 954, 926, 898 ([M − *n*CO]$^+$, *n* = 1−3, 30%, 35%, 20%), 867 ([M − 3CO − OMe]$^+$, 18%), 843, 815 ([M − *n*CO]$^+$, *n* = 5−6, 12%, 16%).

[Ru$_2$\{μ-CCC(CO$_2$Me)=C(CO$_2$Me)C(O)\}(η-C$_5$H$_5$)$_2$(CO)$_4$] (4). DMAD (5 μL, 45 μmol) was added to [\{Ru(CO)$_2$(η-C$_5$H$_5$)\}$_2$(μ-CC)] (10 mg, 40 μmol) in THF, with stirring. The addition was accompanied by an immediate color change from light brown

to dark brown-red. The solution was filtered through a plug of alumina and recrystallized (CH_2Cl_2/*n*-hexane) as dark brown crystals of **4** (12 mg, 95%). Anal. Calcd for $C_{22}H_{16}O_8Ru_2$: C, 43.27; H, 2.64. Found: C, 42.75; H, 2.39. IR (CH_2Cl_2; ν(CO)): 2052 s, 2000 vs, 1945 m, 1885 w, 1729 m cm^{-1}. ^1H NMR (δ; CD_2Cl_2): 3.76 (s, 3H, CO_2Me), 3.87 (s, 3H, CO_2Me), 5.18 (s, 5H, C_5H_5), 5.56 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (δ; CD_2Cl_2): 52.3 (s, CO_2*Me*), 53.0 (s, CO_2*Me*), 89.5 (s, C_5H_5), 91.3 (s, C_5H_5), 96.8 (s, *C*═C), 98.7 (s, μ-*C*═C), 145.4 (s, *C*CO_2Me), 158.6 (s, *C*CO_2Me), 163.4 (s, *C*O_2Me), 165.3 (s, *C*O_2Me), 197.0 (s, CO), 197.0 (s, CO), 200.2 (s, CO), 240.0 (s, Ru-*C*(O)-C). FABMS (NOBA/CH_2Cl_2): *m*/*z* 612 ($[M]^+$, 100%), 583, 555 ($[M - nCO]^+$, n = 1−2, 25%, 45%), 523 ($[M - 2CO - OMe]^+$, 5%).

[{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2${μ-(CN)$_2$C═CC═C(CN)$_2$}] (5). TCNE (27.3 mg, 0.213 mmol) was added to [{Ru(CO)$_2$(η-C_5H_5)}$_2$(μ-CC)] (100 mg, 0.213 mmol) in THF (10 mL), with stirring. The solution was stirred for 16 h, giving a pale yellow precipitate of **5** (85 mg, 67%). Anal. Calcd for $C_{22}H_{10}N_4O_4Ru_2$: C, 44.28; H, 1.69; N, 9.39. Found: C, 44.90; H, 1.72; N, 9.57. IR (Nujol): ν(CO) 2051 vs, 2003 vs; ν(CN) 2215 s, 2211 s; ν(CC) 1489 m cm^{-1}. ^1H NMR (δ; d_6-DMSO): 5.81 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ CP/MAS NMR (δ) 91.1 (s, C_5H_5).

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Supporting Information Available: Tables of hydrogen and non-hydrogen positional and isotropic displacement parameters, atomic anisotropic displacement parameters, and bond distances and angles, as well as figures giving additional views for complexes **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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