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C−C Coupling of a Permetalated Ethene, (μ_4-C=C)$Ru_2(FeCp^*)_2(CO)_{10}$, with Alkynes, and Isolation of a Labile MeCN Adduct, (μ_4-C=C)$Ru_2(FeCp^*)_2(CO)_8(NCMe)_2$

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A tetranuclear C_2 (dicarbide) cluster complex with a permetallated ethene structure, (μ_4-C=C)$Ru_2(FeCp^*)_2(CO)_{10}$ (**2**), reacts with alkynes in refluxing THF to give a variety of adducts resulting from C−C coupling and oxidative metallacyclization with the C_2 ligand in addition to a unique μ_4-dicarbyne complex with a dimetallacyclobutatriene core, (μ_4-C−C)$Ru_2(FeCp^*)_2(CO)_6$(μ-η^2:η^2-PhC≡CPh). The reactions are initiated by decarbonylation, as confirmed by the reactions of an isolated, labile species lightly stabilized by MeCN, (μ_4-C=C)$Ru_2(FeCp^*)_2(CO)_8(NCMe)_2$, which undergoes the reactions at room temperature and provides the same types of products as those obtained from **2**.

Polymetallic polycarbon species are divergent in their structural motifs, reactivity, and physical properties.[1] Combination of cluster frameworks with polycarbon species, which are always associated with a π system rendering a variety of coordination modes feasible, would lead to a large number of molecular structures featuring different metal−carbon bonding interactions. In comparison to the organometallic chemistry of C_1 species, studied extensively over half a century,[2] polycarbon species containing more than two carbon atoms have been studied less extensively, presumably because of the lack of appropriate starting compounds.[3] Previously we reported that the ethynediyldiiron complex $(OC)_2Cp^*Fe-C\equiv C-FeCp^*(CO)_2$ (**1**; Cp*= η^5-C_5Me_5) served as a versatile starting compound for C_2 (dicarbide) cluster species.[4] In particular, interaction with $Ru_3(CO)_{12}$ resulted in sequential formation of tetranuclear (**2**) and octanuclear cluster compounds (**3**), which were characterized as the unique permetalated ethene and ethane species, respectively (Scheme 1),[5]and, for **2** with a reactive C=C group, we further studied its reactivity. In previous papers, we reported for **2** (1) formal, stepwise hydrogenation of the C_2 ligand[6]and (2) conversion into a unique μ_4-dicarbyne (ethandiylidyne) complex with a dimetallacyclobutatriene core (**4**).[7] In this note we report some derivative chemistry of **2** and **4**.

Results and Discussion

Reaction of the Permetalated Ethene 2 with Alkynes. Transformations reported herein are summarized in Scheme 2.

(i) Reaction of 2 with Internal Alkynes. The reaction of **2** with PhC≡CPh gave the μ_4-dicarbyne complex **4** (1:1 adduct) together with the 1:2 adduct **5**, as reported in the previous communication.[7] Complex **4** turns out to contain the unique dimetallacyclobutatriene core, as characterized by spectroscopy, X-ray crystallography, and EHMO analysis. The other product, **5**, contains a linear 3-oxohepta-1,4-dien-6-yne-1,7-diyl linkage resulting from a 1:2:1 coupling of the C_2, PhC≡CPh, and CO species. It is notable that one of the two Fe parts in **5** is separated from the cluster moiety to form the Fp* group and the alkyne functional group. It is also revealed that the C_2 complex **4** is not a precursor for **5**, as confirmed by a separate reaction of **4** with PhC≡CPh.[8,9]

(ii) Reaction of 4 with 2e Donors (CO, PPh_3). It was expected that 2e donors would add across the unsaturated metal−metal double bond in the C_2 complex **4**, and accordingly, upon exposure to CO the coordinatively saturated starting compound **2** was readily regenerated with liberation of PhC≡CPh, as reported in the earlier communication.[7] On the other hand, **4** did not react with PPh_3 at room temperature but, in refluxing THF, was converted into the unexpected tetranuclear complex **6** (Scheme 2), as characterized by X-ray crystallography.[10] The molecular structure and selected structural parameters of **6** are shown in Figure 1a and Table 1, respectively. Complex **6** contains a spiked triangular metal array, which is apparently formed via Fe migration from Ru2 to Ru1 followed by Fe−Fe bond formation. When the electron counting is taken into account, the longer Fe−Ru interaction (Fe1−Ru1 = 2.8809(7) Å; cf. Fe2−Ru1 = 2.6584(6) Å) should be regarded as a dative bond, as also indicated by the presence of the semibridg-

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[1] Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 231.

[2] See, for example: Davidson, J. L.; Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 4, Chapters 31.5 and 32.6. Akita, M.; Cifuentes, M. P.; Humphrey, M. G. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 7, Chapters 4 and 16. See also ref 1.

[3] For selected works on reactivity of the polyynediyl complexes, see: Low, P. J.; Carty, A. J.; Udachin, K. A.; Enright, G. D. *Chem. Commun.* **2001**, 411. Coat, F.; Guillemot, M.; Paul, F. Lapinte, C. *J. Organomet. Chem.* **1999**, *578*, 76. Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2005**, *690*, 3268. See also ref 1.

[4] (a) Akita, M.; Moro-oka, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420. (b) Akita, M.; Sakurai, A.; Chung, M.-C.; Moro-oka, Y. *J. Organomet. Chem.* **2003**, *670*, 2. For our recent work, see: Akita, M.; Tanaka, Y.; Naitoh, C.; Ozawa, T.; Hayashi, N.; Takeshita, M.; Inagaki, A.; Chung, M.-C. *Organometallics* **2006**, *25*, 5261.

[5] Akita, M.; Sugimoto, S.; Hirakawa, H.; Kato, S.; Terada, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **2001**, *20*, 1555.

[6] Terada, M.; Akita, M. *Organometallics* **2003**, *22*, 355.

[7] Terada, M.; Higashihara, G.; Inagaki, A.; Akita, M. *Chem. Commun.* **2003**, 2984.

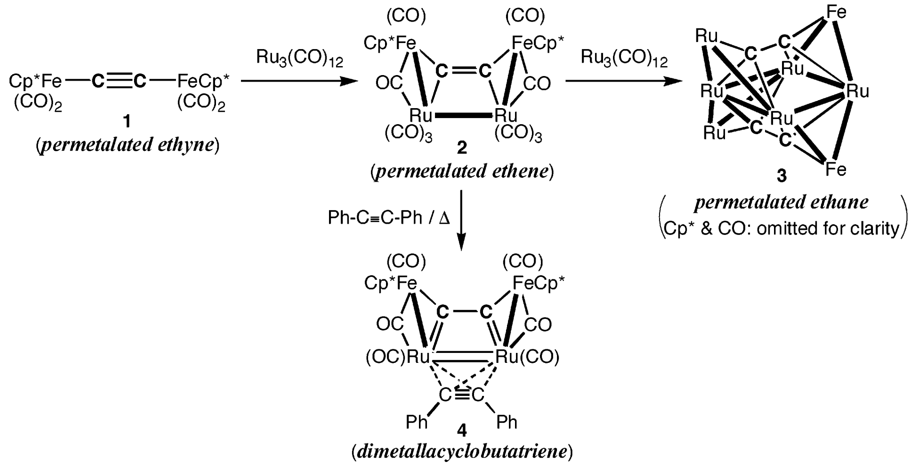
[8] Preparative procedures for **4** and **5** are described in the Experimental Section of this note. For a discussion of their structural features, see ref 7.

[9] A coupling reaction on **4** was attempted but usually resulted in a complex mixture of unidentified products. In the case of the reaction with $Me_3SiC\equiv CH$, FD-MS peaks corresponding to the substituted product (μ_4-C_2)$Ru_2(FeCp^*)_2(CO)_6(Me_3SiC\equiv CH)$ were detected.

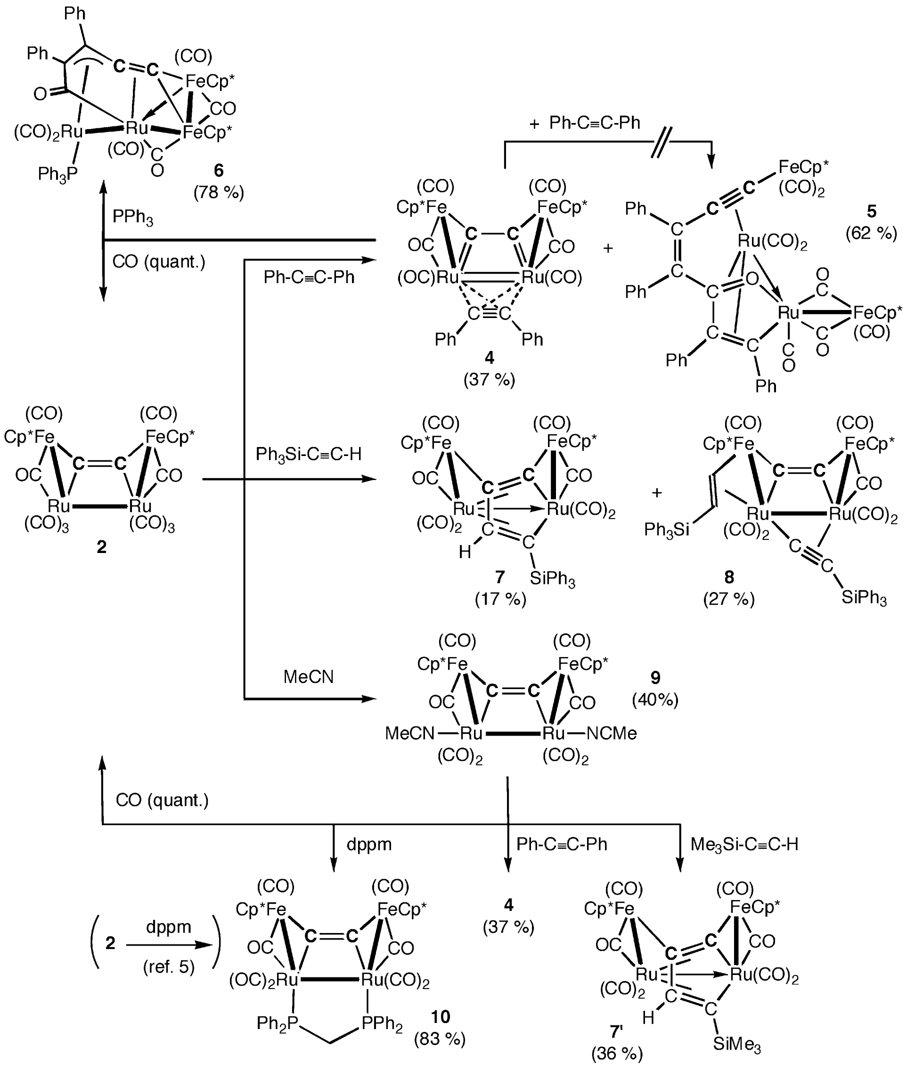
[10] Details of X-ray crystallography are included in the Supporting Information.

10.1021/om0609160 CCC: $37.00

Scheme 1



Scheme 2



ing CO ligand (Fe1−C01−O01 = 157.0(4) Å). The five-carbon linkage is formed via coupling of the C_2 ligand with PhC≡CPh and CO molecules, and the C1−C2−C11 and C2−C11−C12 moieties interact with the metal array as a μ_4-η^1(Fe1):η^1(Fe2):η^2(Ru1):η^2(Ru2)-allenylidene-like ligand[11] and a η^3-allyl ligand, respectively. Because the number of CO groups increases during the transformation (6 (**4**) → 7 (**6**)), some intermolecular process should be operating, but the 1:1 stoichiometry of the C_2 and PhC≡CPh ligands in **6** suggests retention of the tetranuclear structure during the coupling reaction.

(iii) Reactions of 2 with Terminal Alkynes. Reactions of **2** with terminal alkynes gave products of different types. The reaction with $Ph_3SiC≡CH$ afforded a mixture of the metallole

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[11] Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

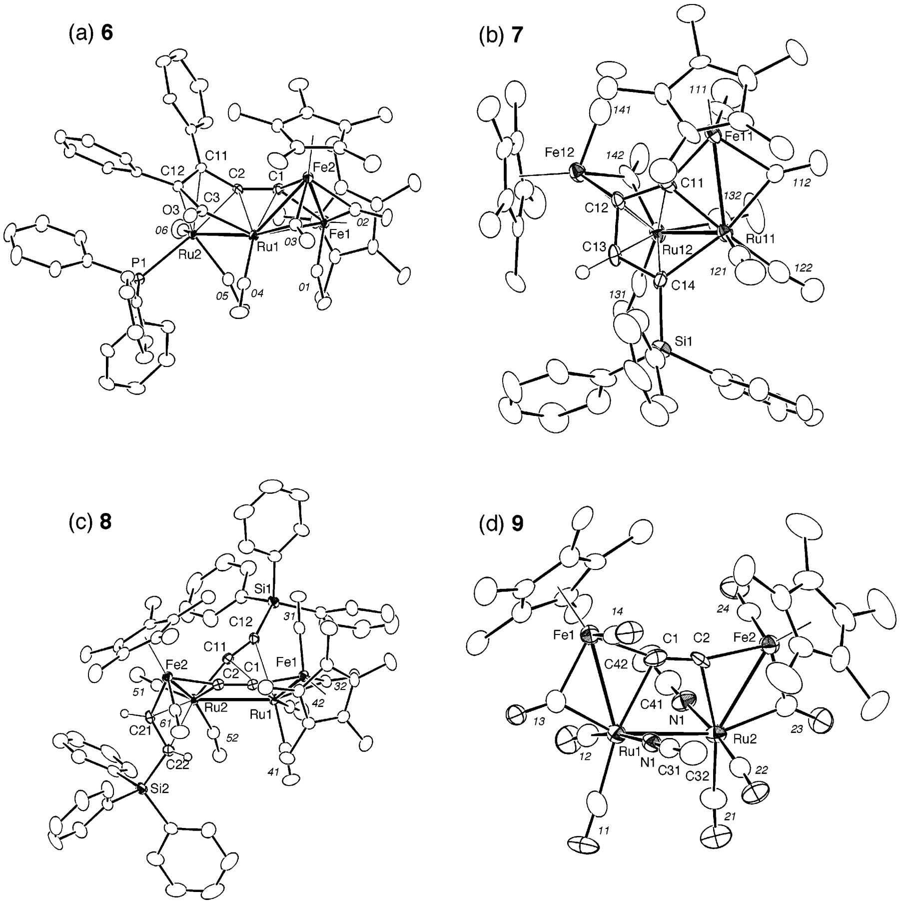


Figure 1. ORTEP views for **6**, **7** (one of two independent molecules), **8**, and **9** with thermal ellipsoids drawn at the 30% probability level. Italic numbers are given for CO ligands.

Table 1. Selected Structural Parameters for 6

Bond Lengths (Å)			
C1−C2	1.358(5)	C3−C12	1.504(5)
C1−Ru1	2.119(3)	C3−O3	1.217(4)
C1−Fe1	1.932(3)	C3−Ru1	2.076(4)
C1−Fe2	1.954(3)	C3···Ru2	2.814(3)
C2−C11	1.442(5)	Ru1−Ru2	2.7405(4)
C2−Ru1	2.176(3)	Ru1−Fe1	2.8809(7)
C2−Ru2	2.145(3)	Ru1−Fe2	2.6584(6)
C11−C12	1.418(5)	Ru2−P1	2.345(1)
C11−Ru2	2.313(3)	Fe1−Fe2	2.5798(7)
C12−Ru2	2.386(3)		
Bond Angles (deg)			
Fe1−C1−C2	138.3(2)	C3−C12−C11	114.8(3)
Fe2−C1−C2	130.0(2)	C3−C12−C121	122.1(3)
Ru1−C1−C2	73.9(2)	C11−C12−C121	120.5(3)
Fe1−C1−Fe2	83.2(1)	Ru1−C3−C12	113.1(2)
Ru1−C1−Fe1	90.5(1)	Ru1−C3−O3	125.8(3)
Ru1−C1−Fe2	81.4(1)	O3−C3−C12	121.1(3)
Ru1−C2−C1	69.3(2)	Ru2−Ru1−Fe1	102.49(1)
Ru1−C2−Ru2	78.7(1)	Ru2−Ru1−Fe2	126.51(2)
Ru1−C2−C11	115.2(2)	Fe1−Ru1−Fe2	55.34(2)
C2−C11−C12	112.6(3)	Ru1−Ru2−P1	118.39(2)
C2−C11−C111	120.8(3)	Ru1−Fe1−Fe2	57.95(2)
C12−C11−C111	126.5(3)	Ru1−Fe2−Fe1	66.71(2)

complex **7** (1:1 adduct) and the μ-alkynyl−μ-alkenyl complex **8** (2:1 adduct) (Scheme 2), which were separated by column chromatography and characterized by X-ray crystallography (Figure 1b,c and Tables 2 and 3).[10] The unit cell of **7** contains two independent molecules with essentially the same geometry, and one of them is shown in Figure 1b. An increase of the ratio of $Ph_3SiC{\equiv}CH$ to **2** caused preferential formation of the 2:1 adduct **8** (**8**:**7** = 0.5 ($Ph_3SiC{\equiv}CH$:**2** = 3) → 1.6 ($Ph_3SiC{\equiv}CH$:**2** = 5)).

Table 2. Selected Structural Parameters for 7[a]

Bond Lengths (Å)			
C11−C12	1.40(1)	C13−Ru12	2.25(1)
C12−C13	1.47(1)	C14−Ru11	2.15(1)
C13−C14	1.39(1)	C14−Ru12	2.320(9)
C11−Ru11	2.03(1)	C14−Si1	1.87(1)
C11−Ru12	2.35(1)	Fe11−Ru11	2.666(2)
C11−Fe11	1.89(1)	Ru11−Ru12	2.794(1)
C12−Ru12	2.12(1)	Ru12−Fe12	2.668(2)
C12−Fe12	2.013(8)		
Bond Angles (deg)			
Ru11−C11−Fe11	85.4(4)	Fe12−C12−C11	122.4(7)
Ru11−C11−C12	121.4(8)	Fe12−C12−C13	116.1(7)
Fe11−C11−C12	152.8(9)	C12−C13−C14	115.5(9)
C11−Ru11−C14	76.1(4)	Ru11−C14−Si1	123.5(5)
C11−C12−C13	110.2(8)	Si1−C14−C13	120.0(8)
Dihedral Angles (deg)			
Fe11−Ru11−Ru12−Fe12	36.76(7)		
Ru11−C11−C12−C13	14(1)		
C11−C12−C13−C14	15(1)		
Ru11−C14−C13−C12	11(1)		

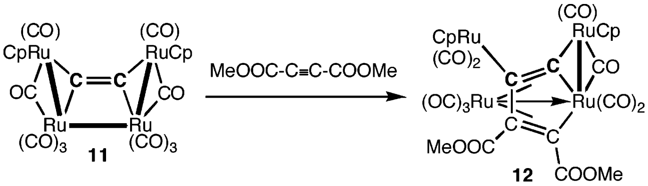
[a] A unit cell contains two independent molecules with essentially the same geometry, and the data for one of them are listed.

The metallole complex **7** results from 1:1 oxidative metallacyclization of the C_2 part in **2** and an external alkyne molecule at the Ru12 center. Dinuclear μ-metallole complexes, μ-η^1(M1):η^1(M1):η^4(M2)-diene-1,4-diyl complexes, have many precedents.[12] The two Fe parts are regarded as the substituents of the metallole ring and are also incorporated into the acyclic tetrametallic linkage. The fused structure causes distortion of the carbocyclic part, as can be seen, in particular, for C12 (the sum of the bond angles around C12 is 348.8°; cf. the corres-

Table 3. Selected Structural Parameters for 8

Bond Lengths (Å)			
C1−C2	1.269(8)	C21−C22	1.408(7)
C1−Fe1	1.909(6)	C21−Fe2	1.931(6)
C1−Ru1	2.207(4)	C21−Ru2	2.187(5)
C2−Fe2	1.905(5)	Si2−C22	1.868(6)
C2−Ru2	2.263(5)	C22−Ru2	2.317(5)
C11−C12	1.226(8)	Fe1−Ru1	2.7236(7)
C11−Ru1	2.317(4)	Ru1−Ru2	2.9285(5)
C11−Ru2	2.019(5)	Ru2−Fe2	2.7568(8)
C12−Si1	1.848(5)		
Bond Angles (deg)			
Ru1−C1−C2	111.5(4)	C11−Ru1−C12	29.4(2)
Fe1−C1−C2	164.7(4)	Fe2−C21−C22	125.9(4)
Ru1−C1−Fe1	82.5(2)	Si2−C22−C21	117.4(4)
Ru2−C2−Fe2	82.3(2)	C21−Ru2−C22	36.3(2)
Ru2−C2−C1	112.1(3)	Ru2−Ru1−Fe1	113.10(2)
Fe2−C2−C1	165.1(4)	Ru1−Ru2−Fe2	110.21(2)
Ru2−C11−C12	167.4(4)	Ru1−C1−Fe1	82.5(2)
Si1−C12−C11	148.8(4)		
Dihedral Angles (deg)			
Ru1−C1−C2−Ru2	0.1(4)		
Fe1−Ru1−Ru2−Fe2	1.98(3)		
Fe1−C1−C2−Fe2	9(2)		

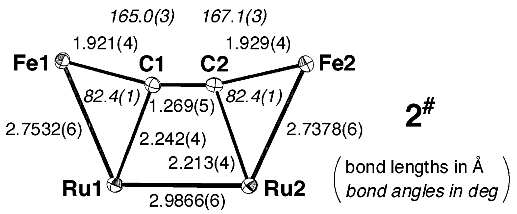
Scheme 3



ponding data for C11, 359.4°). The bulky $SiPh_3$ group occupies the α-position to reduce steric repulsion with the FeCp* part. Electron counting indicates that the Ru11−Ru12 interaction is a dative bond from Ru12 to Ru11 (2.795(1) Å). Koutsantonis et al. reported formation of a related compound, **12**, from (μ_4-C═C)$Ru_4Cp_2(CO)_{10}$ (**11**) (the RuCp analogue of **2**) and dimethyl acetylenedicarboxylate (Scheme 3).[13] In comparison to the case for **11**, complex **12** contains one more CO ligand, which causes cleavage of one of the two CpRu−Ru bonds. It is known that CO bridging between the second-row metal elements (Ru) with a larger atomic radius, as in **12**, is less common than that involving a first-row metal element (Fe), as in **7**.[14] Complex **7** shows a characteristic, highly deshielded ^{13}C NMR signal at δ_C 315.6, which is tentatively assigned to C11.[11]

In contrast, the other product **8** does not arise from coupling but from disproportionation of two 1-alkyne molecules, leading to the alkynyl and alkenyl ligands via formal hydrogen transfer. Initial C−H oxidative addition followed by insertion of a second molecule of 1-alkyne into the resultant Ru−H bond should furnish the two types of functional groups.[15] In this case, the tetranuclear (μ_4-C═C)Fe_2Ru_2 skeleton simply serves as a template for the reaction, and no interaction with the C_2 ligand occurs. Parameters for the (μ_4-C═C)Fe_2Ru_2 core, including the C═C separation (1.269(8) Å), are comparable to those for the parent compound (**2#** (η^5-C_5Me_4Et derivative); Chart 1),[16] and the μ-η^1:η^2-acetylide ligand flattens the (μ_4-C═C)Fe_2Ru_2 moiety, as is evident from comparison of the Fe−Ru−Ru−Fe dihedral angles (1.98(3)° (**8**); cf. 24.40(9)° (**2**), 28.65(2)° (**2#**), 84.38(1)° (**4**), 36.76(7)° (**7**), 19.91(7)° (**9**)). Other structural parameters are in the normal range.

Chart 1



2#

While we also examined reactions of **2** with a variety of alkenes, **2** was sluggish and no characterizable product was isolated from reaction mixtures.

Labile (MeCN)$_2$ Adduct (μ_4-C═C)$Ru_2(FeCp^*)_2(CO)_8$(NCMe)$_2$ (9). An early stage of the coupling reactions of **2** with alkynes should involve a CO dissociation process to form a coordinatively unsaturated intermediate, which captures the alkyne substrate. Judging from the reaction conditions for **2**, heating is essential for CO dissociation to form the intermediate. In order to generate the intermediate under milder reaction conditions complex **2** was converted to the labile species **9**, which was lightly stabilized by weakly coordinating MeCN ligands.[18]

(i) Synthesis. Heating **2** in refluxing MeCN gave the (MeCN)$_2$ adduct **9** as deep purple microcrystals. No mono- and triadducts were detected. The composition (1:2 adduct) and the symmetrical structure of the adduct were readily confirmed by a ^1H NMR spectrum, containing a single set of Cp* and MeCN singlet signals appearing in a 30:6 intensity ratio. The MeCN adduct **9**, characterized by X-ray crystallography (Figure 1d),[10] is isostructural with the parent complex **2**, and their structural parameters, including the C═C length (1.24(1) Å), are comparable (Table 4 and Chart 1). The two CO ligands in **2** projected perpendicular to the (μ_4-C═C)Fe_2Ru_2 plane and not sterically shielded by the Cp* ligands are replaced by MeCN to form an apparent C_2-symmetrical structure. No mono- or triadducts were detected.[17]

(ii) Reactivity. It is found that the reactions of **9** readily proceed at room temperature, in sharp contrast to the reaction

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(12) Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 4, Chapter 31.4. Fagan, P. J.; Hains, R. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 7, Chapters 3 and 11. For a recent example, see: Bruce, M. I.; Zaitseva, N. N.; Skeleton, B. W.; White, A. H. *Inorg. Chim. Acta* **1996**, *250*, 129. Bruce, M. I. *Coord. Chem. Rev.* **1997**, *166*, 91.

(13) Byrne, L. T.; Hos, J. P.; Koutsantonis, G. A.; Sanford, V.; Skelton, B. W.; White, A. H. *Organometallics* **2002**, *21*, 3147.

(14) Dyson, P. J.; McIndo, J. S. *Transition Metal Carbonyl Cluster Chemistry*; Gordon and Breach: Amsterdam, 2000.

(15) Kovalev, I. P.; Yevdakov, K. V.; Strelenko, Yu. A.; Vinogradov, M. G.; Nikishin, G. I. *J. Organomet. Chem.* **1990**, *386*, 139. Kuncheria, J.; Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *J. Organomet. Chem.* **2000**, *593−594*, 77. Crementieri, S.; Leoni, P.; Marchetti, F.; Marchetti, L.; Pasquali, M. *Organometallics* **2002**, *21*, 2575.

(16) We prepared the η^5-C_5Me_4Et derivative of **2**, (μ_4-C═C)Ru_2Fe_2(η^5-C_5Me_4Et)$(CO)_{10}$ (**2#**), to obtain derivatives of different crystallinity. Complex **2#** was prepared by the method described for **2** by simply replacing the starting compound $(Cp^*Fe(CO)_2{-}I \rightarrow (\eta^5\text{-}C_5Me_4Et)Fe(CO)_2{-}I)$.[5] **2#**: δ_H ($CDCl_3$) 2.46, 2.45 (2H × 2, q, CH_2), 1.98, 1.83, 1.73, 1.72 (6H × 4, Me), 1.06 (6H, t, CH_2CH_3); IR (KBr) 2083, 2048, 2002, 1981, 1965, 1955, 1780 cm^{-1}. Furthermore, because **2#** formed single crystals of quality better than that of **2**, **2#** was subjected to X-ray crystallography (R1 = 0.0408; Chart 1).[10] While **2** sits on a crystallographic C_2 axis passing through the midpoints of the C−C and Ru−Ru bonds, **2#** has no element of crystallographic symmetry in the molecule.

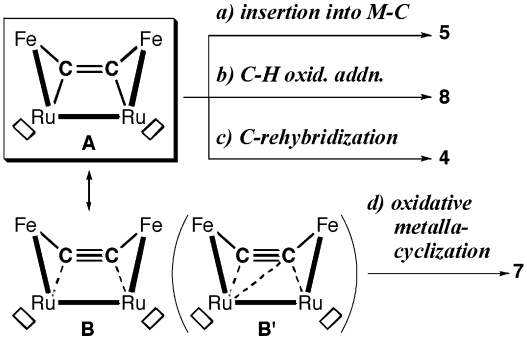
(17) While some byproduct was detected by ^1H NMR monitoring of the reaction mixture, it could not be identified by the ^1H NMR features alone, owing to overlap with the signals of **9**.

(18) See, for example: Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *124*, C19. Doherty. N. M.; Howard, J. K.; Knox, S. A. R.; Terril, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 638. Akita, M.; Hua, R.; Nakanishi, S.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1997**, *16*. 5572.

Table 4. Selected Structural Parameters for 9

Bond Lengths (Å)			
C1−C2	1.24(1)	Ru1−C12	1.88(1)
Fe1−C1	1.98(1)	Ru1−C13	2.01(1)
Ru1−C1	2.23(1)	Ru2−N2	2.16(1)
Fe2−C2	1.931(9)	Ru2−C21	1.89(1)
Ru2−C2	2.22(1)	Ru2−C22	1.84(1)
Ru1−Ru2	3.017(1)	Ru2−C23	2.07(1)
Ru1−Fe1	2.755(3)	Fe1−C13	1.97(1)
Ru2−Fe2	2.750(2)	Fe1−C14	1.77(1)
Ru1−N1	2.117(9)	Fe2−C23	1.98(1)
Ru1−C11	1.91(1)	Fe2−C24	1.75(1)
Bond Angles (deg)			
Ru1−C1−Fe1	81.5(4)	Ru2−C2−C1	110.6(8)
Ru1−C1−C2	114.8(8)	Fe2−C2−C1	166.0(9)
Fe1−C1−C2	163.2(9)	Ru2−Ru1−Fe1	109.65(4)
Ru2−C2−Fe2	82.7(4)	Ru1−Ru2−Fe2	110.95(5)
Dihedral Angle (deg)			
Ru1−C1−C2−Ru2	17.5(9)		
Fe1−C1−C2−Fe2	16(6)		
Fe1−Ru1−Ru2−Fe2	19.91(7)		

Scheme 4



conditions applied to the CO complex **2** (in refluxing THF). Treatment with CO and dppm gave the CO complex **2** and the substituted product **10**, respectively.[19] The dppm complex **10** can be alternatively prepared by thermolysis of **2** in the presence of dppm, as we reported previously.[6] Furthermore, reaction with alkynes afforded the corresponding adducts (**4** (from PhC≡CPh) and **7′** (from $Me_3SiC{\equiv}CH$)), which are also obtained from the CO complex **2**, as described above.

Because the CO complex **2** and the MeCN adduct **9** provide the same types of products, such as **4**, **7**, and **10**, they should be derived from the common divacant intermediate **9′** (Scheme 2).

Conclusion. The transformations of **2** and **4** described above can be interpreted in terms of the canonical structures **A** and **B**, shown in Scheme 4, where other ligands are omitted for clarity. C−C coupling can occur through two pathways: (a) insertion of a C−C unsaturated bond into the M−C σ bond in the σ-bonded permetalated ethene structure **A** leading to **5** and (d) oxidative metallacyclization on the π-bonded structure **B** (**B′**), while the previous structural and theoretical studies reveal that the **A**-type σ-bonded structure is the dominant contributor for the starting, non-decarbonylated species **2**.[5,20] Furthermore, C−H oxidative addition of 1-alkyne to **A** (b) triggers formation of **8**, and rehybridization of the carbon atoms of the C_2 ligand in **A** (c) leads to the unique μ_4-ethandiylidyne structure **4**.

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. THF (Na−K alloy) and MeCN (P_2O_5) were treated with appropriate drying agents, distilled, and stored under argon. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (^1H, 200 MHz) and JEOL EX-400 spectrometers (^1H, 400 MHz; ^{13}C, 100 MHz). Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR spectra (KBr pellets) were obtained on a JASCO FT/IR 5300 spectrometer. FD-MS and ESI-MS spectra were recorded on JEOL JMS-700 and ThermoQuest Finnigan LCQ Duo mass spectrometers, respectively. Complex **2** was prepared as reported by us,[5] and other chemicals were purchased and used as received. Chromatography was performed on alumina. Details of X-ray crystallography are included in the Supporting Information.

Reaction of 2 with PhC≡CPh: Preparation of 4 and 5. A mixture of **2** (243 mg, 0.27 mmol) and PhC≡CPh (243 mg, 1.36 mmol) in THF (25 mL) was refluxed, and the reaction was followed by IR after appropriate time intervals. After 2 h consumption of **2** was confirmed by disappearance of the $\nu(\mu\text{-CO})$ vibration at 1791 cm^{-1}. Then the volatiles were removed under reduced pressure and the residue was washed with hexane (12 mL × 2) to remove the excess PhC≡CPh. The residue was dissolved in a CH_2Cl_2−hexane mixture (1:3) and this solution placed on the top of an alumina column prepared under Ar (3 cm × 12 cm). Elution with a CH_2Cl_2−hexane mixture (1:2) gave three bands. The first red-purple band contained $Fe_2Cp^*_2(CO)_4$. Complexes **4** and **5** were obtained from the second reddish gray band and the third brownish gray band, respectively. **4** (black-purple crystals; 96 mg, 0.10 mmol, 37% yield): δ_H (THF-d_8) 2.00 (15H, s, Cp*); δ_C (THF-d_8) 249.2 (s, μ-CO), 244.9 (s, μ_4-C_2),[21] 216.6, 211.4 (s × 2, CO), 141.3 (s, *ipso*-Ph), 127.6 (s, Cctrb≡C); IR (KBr) 1960, 1922, 1799 cm^{-1}. Anal. Calcd for $C_{43}H_{42}O_6Cl_2Fe_2Ru_2$ (**4**·CH_2Cl_2): C, 49.68; H, 4.04; Cl, 6.82. Found: C, 49.55; H, 4.28; Cl, 6.84. **5** (black-purple crystals; 204 mg, 0.17 mmol, 62% yield): δ_H ($CDCl_3$) 7.50−7.48 (10H, m, Ph), 7.35−7.31 (10H, m, Ph), 1.75, 1.66 (15H × 2, s × 2, Cp*); δ_C ($CDCl_3$) 262.3 (μ-CO), 215.0, 214.7, 206.8, 201.6 (CO), 204.1 (=C−Ru), 151.6, 141.8, 138.1, 133.0 (t, J = 7.3 Hz, *ipso*-Ph), 142.7 (C=O), 140.6, 138.9, 137.6 (=C−Ph), 132.6, 130.0, 129.7, 129.5, 129.1, 128.5, 127.9, 127.7, 127.5, 127.1, 123.9 (Ph), 131.3 (≡C−Fe), 98.5 (=C*C*≡), 100.3, 97.4 (*C*$_5$Me$_5$), 9.7, 9.2 (q, J = 127 Hz, C$_5$*Me*$_5$); IR (KBr) 2032, 2012, 1972, 1937, 1786, 1749 cm^{-1}. Anal. Calcd for $C_{60}H_{52}O_9Cl_2Fe_2Ru_2$ (**5**·CH_2Cl_2): C, 55.37; H, 4.00. Found: C, 55.55; H, 4.27.

Reaction of 4 with PPh$_3$: Preparation of 6. A THF solution (10 mL) containing **4** (100 mg, 0.10 mmol) and PPh_3 (80 mg, 0.3 mmol) was refluxed for 12 h. After removal of the volatiles the residue was subjected to column chromatography under Ar. Elution with CH_2Cl_2−hexane (1:2 → 1:1) gave pale brown and pale gray bands, from which characterizable products could not be obtained. Further elution with CH_2Cl_2 and acetone gave a charcoal gray band, from which **6** was isolated as black crystals (98 mg, 0.08 mmol, 79%). **6**: δ_H (C_6D_6) 8.41−8.37 (2H, m, Ph), 7.74−7.70 (2H, m, Ph), 7.57−7.51 (6H, m, Ph), 7.00−6.93 (12H, m, Ph), 6.79−6.72 (3H, m, Ph), 1.67, 1.37 (15H × 2, s × 2, Cp*); δ_P (C_6D_6) 41.7; IR (KBr) 2014, 1914, 1890, 1799, 1765, 1584 cm^{-1}. Anal. Calcd for $C_{61}H_{55}O_7PFe_2Ru_2$: C, 58.85; H, 4.45. Found: C, 60.59; H, 4.65.

Reaction of 2 with Ph$_3$SiC≡CH: Preparation of 7 and 8. A THF solution (40 mL) containing **2** (382 mg, 0.43 mmol) and $Ph_3SiC{\equiv}CH$ (61 mg, 2.2 mmol) was refluxed. After 2 h consumption of **2** was confirmed by IR. After removal of the volatiles the residue was separated by column chromatography under Ar. Elution with CH_2Cl_2−hexane (1:4) gave a red-purple band, which contained Fe$_2$-

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[19] Reaction with PEt_3 afforded the corresponding adduct (μ_4-C_2)Ru_2-($FeCp^*$)$_2$(CO)$_8$(PEt_3)$_2$, which could not be isolated in a pure form but was characterized spectroscopically. (μ-C=C)Ru_2($FeCp^*$)$_2$(CO)$_8$(PEt_3)$_2$: δ_H (C_6D_6) 1.88 (30H, s, Cp*), 1.2−0.8 (30H, PEt_3); δ_P (C_6D_6) 24.5 (s).

[20] Frapper, G.; Halet, J.-F. Bruce, M. I. *Organometallics* **1995**, *14*, 5044. Frapper, G.; Halet, J.-F.; Bruce, M. I. *Organometallics* **1997**, *16*, 2590.

[21] The μ_4-C_2 signal was discriminated from the μ-CO signal by comparison with a ^{13}CO-enriched sample.

$Cp^*{}_2(CO)_4$. Elution with CH_2Cl_2−hexane (1:3) and with CH_2Cl_2−hexane (2:1) gave a charcoal gray band containing **8** and a dark brown band containing **7**, respectively. The products were recrystallized from CH_2Cl_2−hexane. **7** (black crystals, 158 mg, 0.12 mmol, 27%): δ_H ($CDCl_3$) 7.78−7.76, 7.36−7.26 (15H, m, Ph), 6.78 (1H, s, ═CH), 1.70, 1.68 (15H × 2, s × 2, Cp*); δ_C ($CDCl_3$) 315.6 (d, ^3J = 12 Hz, FeRuC═), 251.7 (μ-CO), 216.8, 212.9 (Fe−CO), 214.6 (C−Si), 199.2, 197.0 (Ru−CO), 138.5, 137.0, 129.1, 127.5 (Ph), 136.2 (Fe−C═), 133.2 (d, J = 160 Hz, ═CH), 99.3, 99.1 (C_5Me_5), 10.0, 9.1 (C_5Me_5); IR (KBr) 2017, 1984, 1971, 1956, 1943, 1928, 1814, 1786, 1780 cm^{-1}; FD-MS m/z 1117 (M^+). Anal. Calcd for $C_{51}H_{48}O_8SiCl_2Fe_2Ru_2$ (**7**·CH_2Cl_2): C, 40.97; H, 3.99; Cl, 5.90. Found: C, 50.52; H, 4.13; Cl, 6.08. **8** (black crystals, 83 mg, 0.07 mmol, 17%): δ_H ($CDCl_3$) 9.75 (1H, d, J = 14.7 Hz, Fe−CH═), 7.62−7.30, 7.40−7.35, 7.24−7.21 (30H, m, Ph), 2.71 (d, J = 14.7 Hz, Si−CH═), 1.84, 1.76 (15H × 2, s × 2, Cp*); δ_C ($CDCl_3$) 260.2 (μ-CO), 185.6 (d, J = 148.9 Hz, Fe−CH═), 145.5, 136.1, 136.0, 134.3, 129.3, 129.1, 127.7, 127.2 (Ph), 135.1 (C≡), 98.3, 98.1 (*C*$_5$Me$_5$), 69.3 (d, J = 146.5 Hz, Si−CH═), 10.7, 9.7 (C_5*Me*$_5$); IR (KBr) 2019, 1991, 1979, 1951, 1938, 1899, 1800, 1786 cm^{-1}. Anal. Calcd for $C_{69}H_{62}O_7Si_2Fe_2Ru_2$: C, 60.35; H, 4.55. Found: C, 60.43; H, 4.32.

Preparation of MeCN Adduct 9. A MeCN solution (100 mL) of **2** (100 mg, 0.11 mmol) was refluxed for 5 h. Filtration through an alumina plug followed by crystallization from MeCN−toluene−hexane gave **9** as purple crystals (40 mg, 0.043 mmol, 46%). **9**: δ_H (C_6D_6) 1.81 (30H, s, Cp*), 0.33 (6H, MeCN); IR (MeCN) 1995, 1966, 1933, 1910, 1758 cm^{-1}. Despite several attempts, an analytically pure sample could not be obtained, owing to the instability.

Reactions of 9. (i) With CO. An NMR tube containing a C_6D_6 solution of **9** was filled with CO. After 15 min **9** was quantitatively converted into **2**, as confirmed by ^{1}H NMR analysis.

(ii) With dppm. A THF solution (40 mL) containing **9** (223 mg, 0.24 mmol) and dppm (282 mg, 0.73 mmol) was stirred for 1 h at room temperature. After removal of the volatiles the residue was subjected to column chromatography with benzene and then CH_2Cl_2 as eluents under Ar. The benzene eluent was evaporated under reduced pressure and further subjected to column chromatography with CH_2Cl_2−hexane (1:2) as eluent to give the purple solid **10** (242 mg, 0.20 mmol, 83%), which was identified by comparison of spectroscopic data with those of an authentic sample. From the CH_2Cl_2 eluent a yellow byproduct was isolated and characterized as a cationic species, [{μ-η^1:η^2-C≡C−FeCp*(CO)$_2$}-Ru$_2$(CO)$_4$(μ-dppm)$_2$]$^+$, by NMR and preliminary X-ray crystallography (after conversion to a BPh$_4$ salt):[22] δ_H (CD_2Cl_2) 1.55 (s, Cp*) (other signals were too broad, owing to windshield wiper like motion, to be characterized); δ_P (CD_2Cl_2) 20.0 (s); IR (CH_2Cl_2) 2050, 2024, 1995, 1966, 1910 cm^{-1}; ESI-MS m/z M^+.

(iii) With PhC≡CPh. A THF solution (30 mL) of **9** (219 mg, 0.24 mmol) and PhC≡CPh (107 mg, 0.60 mmol) was refluxed for 2 h. After removal of the volatiles the amount of **4** (37%) was quantified by ^{1}H NMR by comparison with an authentic sample of **4**.

(iv) With Me$_3$SiC≡CH. To a THF solution (25 mL) of **9** (168 mg, 0.18 mmol) was added Me$_3$SiC≡CH (50 mL, 0.36 mmol), and the resultant mixture was stirred for 10 min at room temperature. After removal of the volatiles the product was isolated by chromatography (eluted with CH_2Cl_2−hexane, 1:5 → 1:2). The metallacycle **7′** was obtained as dark brown crystals. **7′** (60 mg, 0.06 mmol, 36%): δ_H (CD_2Cl_2) 6.91 (1H, s, HC═), 1.91, 1.58 (15H × 2, s × 2, Cp*), 0.08 (9H, s, SiMe$_3$); δ_C (CD_2Cl_2) 315.5 (d, J = 11 Hz, FeRuC═), 217.6, 214.4, 203.6, 198.9 (CO), 214.5 (d, J = 15 Hz, C−Si), 147.1 (Fe−C═), 132.4 (d, J = 166 Hz, ═CH), 100.4, 99.1 (s × 2, *C*$_5$Me$_5$), 11.3, 9.8 (q × 2, J = 127 Hz, C$_5$Me$_5$), 2.6 (q, J = 119 Hz, SiMe$_3$); IR (CH_2Cl_2) 2014, 1981, 1973, 1941, 1800 cm^{-1}. An analytically pure sample of **7′** could not be obtained. The molecular structure of **7′**, similar to that of **7**, was confirmed by preliminary X-ray crystallography: monoclinic, space group $P2_1/a$, a = 16.971(8) Å, b = 11.461(7) Å, c = 20.14(1) Å, β = 109.25(2)°, V = 3698(4) Å^3, current R1 value 0.22.

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Supporting Information Available: CIF files, figures, and tables giving crystallographic results. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] The formation mechanism of the yellow product is unknown. Its structure could not be refined satisfactorily because of the small number of diffraction data. Crystallographic data for the BPh$_4$ salt: formula $C_{92}H_{69}BO_6FeRu_2$, fw = 1663.3, triclinic, space group $P\bar{1}$, a = 12.426(10) Å, b = 18.677(17) Å, c = 21.731(15) Å, α = 103.85(3)°, β = 105.80(3)°, γ = 101.55(4)°, V = 4518(7) Å^3, Z = 2, current R1 value 0.15.