Intermediates for Methyl Carbon-Hydrogen Activation in Binuclear Dimethylfulvene Ruthenium Carbonyl Complexes

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Abstract

The methyl C–H bonds in the dimethylfulvene complex $[\eta^5, \eta^1\text{-C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{-}[\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_4]$ are known experimentally to be activated by the central Ru_2 unit to give the dehydrogenation product $[\eta^5, \eta^3\text{-C}_5\text{H}_4\text{C}(\text{CH}_2)_2][\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_3]$. The mechanistic aspects of this process are explored by a theoretical investigation of the two series of complexes $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_n$ and $[\text{C}_5\text{H}_4\text{C}(\text{CH}_2)_2]\text{Ru}_2(\text{CO})_n$ ($n = 6, 5, 4$). Potential reaction intermediates with agostic hydrogen atoms as well as ruthenium carbonyl hydrides and dihydrogen complexes are found.

1. Introduction

The catalytic functionalization of unreactive C–H bonds has recently revolutionized synthetic methodologies for the production of pharmaceuticals and natural products and for providing new routes to molecular materials and polymers.^{1,2,3} In this connection palladium,^{4,5,6,7,8} rhodium,^{9,10,11,12,13} cobalt,¹⁴ manganese,¹⁵ and iridium¹⁶ complexes have been found useful for activating C–H bonds under mild conditions.¹ More recently, catalysts containing the less expensive metal ruthenium have been found to be more efficient in some systems for the catalytic activation of C–H bonds.^{17,18,19,20,21,22,23,24,25,26,27}

In an effort to understand the mechanisms of catalytic C–H activation by various transition metal complexes, stoichiometric reactions of metal complexes with organic compounds leading to C–H activation to give stable well-defined products are of interest. Early examples in ruthenium chemistry involve the dehydrogenative transannular cyclisation of cyclooctatetraenes and cyclooctatrienes by ruthenium carbonyls to form stable complexes of the unstable hydrocarbon pentalene and its substitution products.^{28,29} More recently, dimethylfulvene was shown to react with $\text{Ru}_3(\text{CO})_{12}$ to give a stable binuclear complex $[\eta^5, \eta^3\text{-C}_5\text{H}_4\text{C}(\text{CH}_2)_2]\text{Ru}_2(\text{CO})_5$ in which a H_2 molecule has been eliminated from the methyl substituents (Figure 1).³⁰ This process is significant since it appears to involve activation of C–H bonds in the CH_3 groups by the ruthenium carbonyl complex to give a stable product that can be structurally characterized by X-ray crystallography. A similar stable diiron complex $[\eta^5, \eta^3\text{-C}_5\text{H}_4\text{C}(\text{CH}_2)_2]\text{Fe}_2(\text{CO})_5$ was synthesized by the reaction of dimethylfulvene with $\text{Fe}(\text{CO})_5$.³¹

Figure 1. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with dimethylfulvene to give first the fulvene complex $[\eta^5, \eta^1\text{-C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_6$ and then the dehydrogenation product $[\eta^5, \eta^3\text{-C}_5\text{H}_4\text{C}(\text{CH}_2)_2]\text{Ru}_2(\text{CO})_5$

In order to understand more fully the nature of the activation of the methyl groups in dimethylfulvene by ruthenium carbonyl derivatives, we have used density functional theory to examine the structures and thermochemistry of the complexes $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_n$ ($n = 6, 5, 4$) containing intact dimethylfulvene ligands, as well as their dehydrogenation products $[\text{C}_5\text{H}_4\text{C}(\text{CH}_2)_2]\text{Ru}_2(\text{CO})_n$. Binuclear fulvene metal carbonyls of the type $[\text{C}_5\text{H}_4\text{CRR}']\text{M}_2(\text{CO})_6$ ($\text{M} = \text{Fe}, \text{Ru}$) have been known for some time.³²

2. Theoretical Methods

Electron correlation effects have been included to some degree using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.^{33,34,35,36,37,38,39} The reliability of such density functional theory (DFT) methods is governed by the quality of the approximate exchange-correlation (XC) energy functional. Two differently constructed DFT methods, B3LYP, and BP86, were used in the present study. The B3LYP method is a hybrid HF/DFT method, combining the three-parameter Becke functional (B3) with the Lee-Yang-Parr (LYP) generalized gradient correlation functional.^{40,41} This method includes exact exchange and is calibrated by fitting three parameters to a set of experimental results. The BP86 method combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient-corrected correlation functional method (P86).^{42,43} This method does not include exact exchange and is mainly deduced by forcing the functional to satisfy certain exact constraints based on first principles. The Grimme's D3 dispersion correction and the solvent effect of the experimentally used xylene were considered when fully optimizing each structure. When these two conceptually different DFT methods agree, confident predictions can be made.

Scalar relativistic effects were incorporated using an (8s7p6d2f1g/6s5p3d2f1g) effective core potential (ECP) basis set with 28 core electrons for the ruthenium atoms.⁴⁴ The Ahlrichs TZVP valence triple- ζ basis sets with polarization functions were used for all of the other atoms.^{45,46}

Extensive searches for the global and local minimum $[(\text{C}_5\text{H}_4)\text{C}(\text{CH}_m)_2]\text{Ru}_2(\text{CO})_n$ structures ($m = 2, 3$; $n = 4, 5, 6$) were made using the B3LYP and BP86 methods. The lowest energy triplet structures were found to lie 19 kcal/mol or more in energy above the corresponding lowest energy singlet structures. Therefore only singlet spin state structures are considered in this paper.

The geometries of all structures were fully optimized in the Gaussian09 program without imposing any symmetry constraints on the starting geometries.⁴⁷ Harmonic vibrational frequencies and infrared intensities **for all the optimized structures and the transition states were determined at the same levels.** The tight designation was the default for the SCF energy convergence. In the search for minima, low-magnitude imaginary vibrational frequencies may be suspect, because the numerical integration procedures used in existing DFT methods have significant limitations.⁴⁸ All of the final optimized structures reported in this paper have only real vibrational frequencies unless otherwise indicated.

The structures are designated as **aHb-c** where **a** is the number of hydrogen atoms, **b** is the number of CO groups, and **c** orders the structures according to their relative energies obtained by the BP86 method. Thus the lowest energy $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_6$ structure is designated as **10H6-1**.

3. Results and Discussion

3.1 Dimethylfulvene Complexes

The lowest energy $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_6$ structure **10H6-1** lies 26.0 kcal/mol below the next lowest energy $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_6$ isomer and thus appears to be a very favorable structure (Figure 2). Structure **10H6-1** corresponds to a variety of known³² $[\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CRR}']\text{Ru}_2(\text{CO})_6$ complexes where R and R' are alkyl or aryl groups. The $\text{Ru}(\text{CO})_2$ moiety in **10H6-1** is bonded to the C_5H_4 ring, and the $\text{Ru}(\text{CO})_4$ moiety is bonded to the exocyclic fulvene carbon atom. The predicted Ru–Ru distance of 2.850 Å (B3LYP-D3) or 2.835 Å (BP86-D3) can be interpreted as a formal single bond, thereby giving each ruthenium atom the favored 18-electron configuration. This Ru–Ru single bond distance is very close to the experimental Ru–Ru distance of 2.854 Å in $\text{Ru}_3(\text{CO})_{12}$ as determined by X-ray crystallography.^{49,50}

Three structures are predicted for the pentacarbonyl $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_5$ system (Figure 2). The lowest energy structure **10H5-1** is noteworthy since a hydrogen atom of one methyl group has migrated from carbon to ruthenium. Thus **10H5-1** is more accurately described as $[\eta^5, \eta^2\text{-C}_5\text{H}_4\text{C}(\text{CH}_3)=\text{CH}_2][\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_3\text{H}]$, with an Ru–H bond. In this structure the $\text{Ru}(\text{CO})_2$ moiety is bonded to all five carbon atoms of the fulvene ring, and the $\text{Ru}(\text{CO})_3\text{H}$ moiety is bonded to an exocyclic C=C double bond. Thus the dimethylfulvene unit loses a hydrogen to become a pentahaptodihapto ligand. The predicted Ru–Ru distance of 2.910 Å (B3LYP-D3) or 2.896 Å (BP86-D3) is consistent with a formal single bond, allowing each ruthenium atom to have the favored 18-electron configuration.

The second predicted $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_5$ structure is the singlet **10H5-2**, lying only 1.7 kcal/mol (B3LYP-D3) or 0.1 kcal/mol (BP86-D3) in energy above **10H5-1**. The geometry of **10H5-2** is similar to **10H5-1**, except that the hydrogen atom from a CH_3 group is not fully transferred to the ruthenium atom, but instead forms a Ru-H-C agostic bridge. This agostic Ru-H-C bridge effectively arises from the electron pair of the C-H bond being donated to the ruthenium atom and thus corresponds to a two-electron donor ligand. This ruthenium atom also receives an additional electron from the exocyclic fulvene carbon atom, so the neutral dimethylfulvene ligand in **10H5-2** effectively functions as an eight-electron donor to the Ru_2 unit. The predicted Ru-Ru distance of 2.840 Å (B3LYP-D3) or 2.827 Å (BP86-D3) can be considered to be a single bond, thereby giving each ruthenium atom the favored 18-electron configuration. A transition state structure is found connecting structure **10H5-1** and **10H5-2** with a low barrier of 9.0 kcal/mol (B3LYP-D3) or 8.1 kcal/mol (BP86-D3).

Figure 2. The optimized $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_n$ ($n = 6, 5, 4$) structures. Relative energies in kcal/mol by the B3LYP-D3 and BP86-D3 methods are indicated in parentheses.

The third predicted $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_5$ structure is the singlet **10H5-3**, lying in energy 1.8 kcal/mol above (B3LYP-D3) or 0.8 kcal/mol below (BP86-D3) **10H5-1** (Figure 2). In **10H5-3** both methyl groups remain intact with their hydrogens bonded to carbon through the usual two-center two-electron bonds. The intact dimethylfulvene ligand is bonded to the Ru_2 unit as a pentahapto-monohapto ligand, very similar to that in the $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_6$ structure **10H6-1**. The predicted Ru–Ru distance of 2.866 Å (B3LYP-D3) or 2.824 Å (BP86-D3) is consistent with a formal single bond. This Ru–Ru single bond is bridged by one of the CO groups. In **10H5-3** the ruthenium bonded to the five-membered fulvene ring has the favored 18-electron configuration, but the other ruthenium has only a 16-electron configuration.

Three low-energy structures are predicted for the tetracarbonyl $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_4$ (Figure 2). The lowest energy structure **10H4-1** is actually $[\eta^5, \eta^2\text{-C}_5\text{H}_4\text{C}(\text{CH}_3)=\text{CH}_2][\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_2\text{H}]$, which can be derived from **10H5-1** by loss of a CO group from the $\text{Ru}(\text{CO})_3\text{H}$ moiety. The Ru–Ru distance of 2.806 Å (B3LYP-D3) or 2.778 Å (BP86-D3) in **10H4-1** is ~ 0.11 Å shorter than that in **10H5-1** but still can be interpreted as a formal single bond. This gives the ruthenium atom in the $\text{Ru}(\text{CO})_2$ moiety bonded to the fulvene ring the favored 18-electron configuration but the ruthenium atom in the $\text{Ru}(\text{CO})_2\text{H}$ moiety with the hydride ligand only a 16-electron configuration.

The second predicted $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_4$ structure is the *cis* structure **10H4-2**, lying 5.6 kcal/mol (B3LYP-D3) or 4.2 kcal/mol (BP86-D3) above **10H4-1** (Figure 2). In **10H4-2** the dimethylfulvene ligand remains intact using the five ring carbons to bond to one $\text{Ru}(\text{CO})_2$ moiety as a pentahapto ligand and the exocyclic carbon atom to bond to the other $\text{Ru}(\text{CO})_2$ moiety by a simple Ru–C single bond. The Ru= Ru distance of 2.579 Å (B3LYP-D3) or 2.557 Å (BP86-D3) in **10H4-2** is ~ 0.3 Å shorter than the Ru–Ru single bonds in the $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_n$ ($n = 6, 5$) structures discussed above and thus can be interpreted as a formal double bond. Placing a formal positive charge on the ruthenium bonded to the five-membered ring and a balancing formal negative charge on the ruthenium bonded to a single carbon atom gives the former ruthenium atom the favored 18-electron configuration but the other ruthenium atom only a 16-electron configuration.

The third predicted $[\text{C}_5\text{H}_4\text{C}(\text{CH}_3)_2]\text{Ru}_2(\text{CO})_4$ structure **10H4-3**, lying 11.0 kcal/mol (B3LYP-D3) or 10.0 kcal/mol (BP86-D3) in energy above **10H4-1**, has an intact dimethylfulvene ligand bonded to one $\text{Ru}(\text{CO})_2$ moiety as a pentahapto ligand and the other $\text{Ru}(\text{CO})_2$ moiety only as a monohapto ligand (Figure 2). The Ru–Ru

distance of 2.770 Å (B3LYP-D3) or 2.772 Å (BP86-D3) can be interpreted as a formal single bond, giving the former ruthenium atom the favored 18-electron configuration but the other ruthenium atom only a 14-electron configuration. However, the Wiberg bond index of 0.42 for **10H4-3** is closer to the expected value for a formal double bond involving two d-block transition metals. Such a formal Ru=Ru double bond coupled with a formal positive charge on the ruthenium atom bonded to the five-membered ring and a formal negative charge on the other ruthenium atom gives the former ruthenium atom the favored 18-electron configuration and the latter ruthenium atom a 16-electron configuration. Structure **10H4-3** can be derived from **10H6-1** by loss of a *cis* pair of CO groups from the Ru(CO)₄ moiety.

3.2 Dehydrogenated Dimethylfulvene Complexes.

Four low-energy structures are predicted to lie within 20 kcal/mol for the dehydrogenated [(C₅H₄)C(CH₂)₂]Ru₂(CO)₆ system (Figure 3). The lowest energy such structure predicted is the *cis* structure **8H6-1**. Structure **8H6-1** has an unsymmetrical distribution of the CO groups on the ruthenium atoms with an Ru(CO)₂ moiety bonded to the C₅H₄ ring functioning as a pentahapto ligand, but the Ru(CO)₄ moiety bonded only to the carbon atom in one of the two CH₂ groups, leaving of C=C double bond of 1.339 Å (B3LYP-D3) or 1.350 Å (BP86-D3). A formal Ru–Ru single bond of length 2.893 Å (B3LYP-D3) or 2.874 Å (BP86-D3) in **8H6-1** gives each ruthenium atom the 18-electron configuration.

Structure **8H6-2** also has an unsymmetrical distribution of the CO groups on the ruthenium atoms with an Ru(CO)₂ moiety bonded to the C₅H₄ ring functioning as a pentahapto ligand and an Ru(CO)₄ moiety bonded only to the exocyclic fulvene carbon atom. Structure **8H6-2** lies 8.6 kcal/mol (B3LYP-D3) or 7.1 kcal/mol (BP86-D3) above **8H6-1**. The two CH₂ carbons of the exocyclic C(CH₂)₂ group couple to form a C–C bond of length 1.513 Å (B3LYP-D3) or 1.521 Å (BP86-D3) leading to an external cyclopropane ring. A formal Ru–Ru single bond of length 2.853 Å (B3LYP-D3) or 2.839 Å (BP86-D3) in **8H6-2** gives each ruthenium atom the 18-electron configuration.

The *trans* [(C₅H₄)C(CH₂)₂]Ru₂(CO)₆ structure **8H6-3** lies 14.1 kcal/mol (B3LYP-D3) or 9.9 kcal/mol (BP86-D3) above **8H6-1** (Figure 3). In this structure four of the carbon atoms in the (C₅H₄)C(CH₂)₂ ligand form a tetrahapto 1,3-butadiene ligand to one Ru(CO)₃ moiety and the other four carbon atoms form a tetrahapto Y-shaped trimethylenemethane ligand to the other Ru(CO)₃ moiety. Although there clearly is no Ru–Ru bond in the *trans* structure **8H6-3**, each ruthenium atom nevertheless attains the favored 18-electron configuration.

Figure 3. The optimized $[(C_5H_4)C(CH_2)_2]Ru_2(CO)_n$ ($n = 6, 5, 4$) structures. Relative energies in kcal/mol by the B3LYP-D3 and BP86-D3 methods are indicated in parentheses.

The fourth $[(C_5H_4)C(CH_2)_2]Ru_2(CO)_6$ structure **8H6-4**, lying at the appreciably higher energy of 20.3 kcal/mol (B3LYP-D3) or 16.9 kcal/mol (BP86-D3) above **8H6-1**, is a *cis* structure with the hydrocarbon ligand bonded to the $Ru_2(CO)_6$ unit as a bis(trihapto) ligand (Figure 3). The local environment of the ruthenium atoms in **8H6-4** is similar to that of the iron atoms in the experimentally known tetramethyleneethane complex $\eta^3, \eta^3-(CH_2)_4C_2Fe_2(CO)_6$, obtained from reactions of iron carbonyls with allene.^{51,52} This mode of bonding of the $(C_5H_4)C(CH_2)_2$ ligand leaves an uncomplexed C=C double bond of length 1.367 Å (B3LYP-D3) or 1.376 Å (BP86-D3) within the C_5H_4 ring. The Ru–Ru distance of 3.011 Å (B3LYP-D3) or 2.997 Å (BP86-D3) is interpreted as a very long formal single bond thereby giving each ruthenium atom the favored 18-electron configuration.

The lowest energy structure for the pentacarbonyl $[(C_5H_4)C(CH_2)_2]Ru_2(CO)_5$ system is the experimentally known³⁰ *cis* structure **8H5-1** (Figure 3). In this structure the five-membered ring is bonded to an $Ru(CO)_2$ moiety as a pentahapto ligand and the three carbon atoms of the external $C(CH_2)_2$ group are bonded to an $Ru(CO)_3$ moiety as a trihaptoallylic ligand. The predicted Ru–Ru distance of 2.971 Å (B3LYP-D3) or 2.958 Å (BP86-D3) in **8H5-1**, which is somewhat longer than the experimental distance of

2.902 Å,³⁰ can be interpreted as a formal single bond, giving each ruthenium atom the favored 18-electron configuration. The harmonic $\nu(\text{CO})$ frequencies and their infrared intensities (in parentheses) of 2041(1200), 1976(1754), 1971(1509), 1958(107), and 1922(511) cm^{-1} predicted by the BP86-D3 method, are very close to the experimentally observed $\nu(\text{CO})$ frequencies of 2066, 1996, 1979, 1963, and 1923 cm^{-1} . In addition, the predicted bond distances in **8H5-1** are close to the experimental bond distances (Table 1). Structure **8H5-1** lies at least 26 kcal/mol lower in energy below any isomeric $[(\text{C}_5\text{H}_4)\text{C}(\text{CH}_2)_2]\text{Ru}_2(\text{CO})_5$ structures (Supporting Information). This indicates that **8H5-1** is a very favorable structure consistent with its synthesis as a very stable molecule.

The lowest energy structure for the tetracarbonyl $[(\text{C}_5\text{H}_4)\text{C}(\text{CH}_2)_2]\text{Ru}_2(\text{CO})_4$ system is the *cis* structure **8H4-1** with the fulvene five-membered ring bonded to a $\text{Ru}(\text{CO})_2$ group as a pentahapto ligand and the three carbon atoms of the external $\text{C}(\text{CH}_2)_2$ group bonded to a $\text{Ru}(\text{CO})_2$ group as a trihapto ligand, similar to the metal-ligand bonds in **8H5-1** (Figure 3). In fact, **8H4-1** can be derived from **8H5-1** by loss of the CO group from the $\text{Ru}(\text{CO})_3$ moiety *trans* to the Ru–Ru bond. This CO loss shortens the Ru=Ru distance by ~ 0.13 Å to 2.841 Å (B3LYP-D3) or 2.834 Å (BP86-D3). Structure **8H4-1** is obviously a favorable structure, since it lies more than 20 kcal/mol energy below any other isomeric $(\text{C}_5\text{H}_4)\text{C}(\text{CH}_2)_2\text{Ru}_2(\text{CO})_4$ structures.

Table 1: Comparison between the theoretical bond distances and the experimental bond distances for $[(\text{C}_5\text{H}_4)\text{C}(\text{CH}_2)_2]\text{Ru}_2(\text{CO})_5$ determined by X-ray crystallography.³⁰

	B3LYP-D3	BP86-D3	Exp.
Ru1-Ru2	2.971	2.957	2.9017
Ru1-C1	2.270	2.263	2.216
Ru1-C2	2.302	2.277	2.249
Ru1-C3	2.302	2.277	2.272
Ru1-C4	2.270	2.263	2.215
Ru1-C5	2.258	2.254	2.212
Ru2-C6	2.225	2.215	2.178
Ru2-C7	2.273	2.271	2.225
Ru2-C8	2.273	2.271	2.249
Ru2-C9	1.892	1.880	1.883
Ru2-C10	1.922	1.911	1.916
Ru2-C11	1.922	1.911	1.914
C6-C7	1.423	1.432	1.415
C6-C8	1.423	1.432	1.413

3.3 NBO analysis of the ruthenium-ruthenium bonding

The Wiberg bond indices (WBI) predicted by the NBO5 program⁵³ and the predicted Ru-Ru distances suggest formal Ru–Ru single bonds in most of the low energy *cis*-[(C₅H₄)C(CH₃)₂]Ru₂(CO)_n and *cis*-[(C₅H₄)C(CH₂)₂]Ru₂(CO)_n structures (Table 2). Such structures have Ru–Ru distances ranging from 2.58 to 3.01 Å and WBIs ranging from 0.15 to 0.50. In **10H4-2** the unusually short Ru=Ru distance of 2.579 Å (B3LYP-D3) combined with the WBI of 0.34 suggests a formal double bond. The *cis*-[(C₅H₄)C(CH₃)₂]Ru₂(CO)₄ structure **10H4-3** is anomalous since its Ru–Ru distance of 2.771 Å (B3LYP-D3) lies in the single bond range but its WBI of 0.42 lies in the double bond range.

Table 2. Wiberg bond indices, compared with the Ru-Ru bond distances (in Å) for the singlet [(C₅H₄)C(CH_m)₂]Ru₂(CO)_n structures (*m* = 2 or 3, *n* = 6 to 4) by the B3LYP-D3 method.

	Wiberg bond index	Ru-Ru distance (Å)
(C ₅ H ₄)C(CH ₃) ₂ Ru ₂ (CO) ₆ (10H6-1)	0.20	2.850
(C ₅ H ₄)C(CH ₃) ₂ Ru ₂ (CO) ₅ (10H5-1)	0.21	2.910
(C ₅ H ₄)C(CH ₃) ₂ Ru ₂ (CO) ₅ (10H5-2)	0.24	2.840
(C ₅ H ₄)C(CH ₃) ₂ Ru ₂ (CO) ₅ (10H5-3)	0.15	2.866
(C ₅ H ₄)C(CH ₃) ₂ Ru ₂ (CO) ₄ (10H4-1)	0.24	2.805
(C ₅ H ₄)C(CH ₃) ₂ Ru ₂ (CO) ₄ (10H4-2)	0.34	2.579
(C ₅ H ₄)C(CH ₃) ₂ Ru ₂ (CO) ₄ (10H4-3)	0.42	2.771
(C ₅ H ₄)C(CH ₂) ₂ Ru ₂ (CO) ₆ (8H6-1)	0.23	2.893
(C ₅ H ₄)C(CH ₂) ₂ Ru ₂ (CO) ₆ (8H6-2)	0.18	2.853
(C ₅ H ₄)C(CH ₂) ₂ Ru ₂ (CO) ₆ (8H6-4)	0.21	3.012
(C ₅ H ₄)C(CH ₂) ₂ Ru ₂ (CO) ₅ (8H5-1)	0.22	2.971
(C ₅ H ₄)C(CH ₂) ₂ Ru ₂ (CO) ₄ (8H4-1)	0.50	2.841

3.4 Thermochemistry of Dissociation and Disproportionation Reactions

Table 3 reports the energies of the following single carbonyl dissociation reactions, disproportionation reactions, and single hydrogen molecule dissociation reactions for the [(C₅H₄)C(CH_m)₂]Ru₂(CO)_n structures (*m* = 2 or 3, *n* = 6 to 4), based on the lowest energy structures.

For the $[(C_5H_4)C(CH_3)_2]Ru_2(CO)_n$ system, the predicted energies for CO dissociation and disproportionation suggest that the most viable structure is the hexacarbonyl **10H6-1** consistent with the experimental isolation of stable $[C_5H_4CRR']M_2(CO)_6$ derivatives.³² Thus the predicted CO dissociation energy of 30.3 kcal/mol (B3LYP-D3) or 34.9 kcal/mol (BP86-D3) for **10H6-1** is comparable to the experimental CO dissociation energies of 27, 41, and 37 kcal/mol for the stable binary metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively.⁵⁴ Furthermore, the disproportionation of the pentacarbonyl $[C_5H_4C(CH_3)_2]Ru_2(CO)_5$ (**10H5-1**) into the tetracarbonyl **10H4-1** and the hexacarbonyl **10H6-1** is predicted to be slightly exothermic by ~4 kcal/mol.

The relative stability of derivatives with different numbers of CO groups is very different for the dehydrogenated species $[(C_5H_4)C(CH_2)_2]Ru_2(CO)_n$ ($n = 6, 5, 4$). Thus the CO dissociation from the lowest energy dehydrogenated hexacarbonyl structure **8H6-1** to give **8H5-1** is the lowest at 10.8 kcal/mol (B3LYP-D3) or 14.0 kcal/mol (BP86-D3). However, the disproportionation of the lowest energy and experimentally known $[(C_5H_4)C(CH_2)_2]Ru_2(CO)_5$ structure **8H5-1** into **8H6-1** and **8H4-1** is strongly endothermic, requiring ~30 kcal/mol and implying considerable stability of **8H5-1**. This is consistent with the experimental synthesis of the stable **8H5-1** and its structural characterization by X-ray crystallography.³⁰

Table 3. CO dissociation energies, H_2 dissociation energies, and disproportionation energies (kcal/mol) based on the lowest energy $[(C_5H_4)C(CH_3)_2]Ru_2(CO)_n$ structures predicted by the B3LYP-D3 and BP86-D3 methods ($m = 2, 3$; $n = 4$ to 6).

	B3LYP	BP86
$(C_5H_4)C(CH_3)_2Ru_2(CO)_6$ (10H6-1) $\rightarrow$ $(C_5H_4)C(CH_3)Ru_2(CO)_5$ (10H5-1) + CO	30.3	34.9
$(C_5H_4)C(CH_3)_2Ru_2(CO)_5$ (10H5-1) $\rightarrow$ $(C_5H_4)C(CH_3)Ru_2(CO)_4$ (10H4-1) + CO	25.3	32.1
$2 (C_5H_4)C(CH_3)_2Ru_2(CO)_5$ (10H5-1) $\rightarrow$ $(C_5H_4)C(CH_3)_2Ru_2(CO)_6$ (10H6-1) + $(C_5H_4)C(CH_3)_2Ru_2(CO)_4$ (10H4-1)	-5.0	-2.7
$(C_5H_4)C(CH_2)_2Ru_2(CO)_6$ (8H6-1) $\rightarrow$ $(C_5H_4)C(CH_2)_2Ru_2(CO)_5$ (8H5-1) + CO	10.8	14.0
$(C_5H_4)C(CH_2)_2Ru_2(CO)_5$ (8H5-1) $\rightarrow$ $(C_5H_4)C(CH_2)_2Ru_2(CO)_4$ (8H4-1) + CO	40.5	47.5
$2 (C_5H_4)C(CH_2)_2Ru_2(CO)_5$ (8H5-1) $\rightarrow$ $(C_5H_4)C(CH_2)_2Ru_2(CO)_6$ (8H6-1) + $(C_5H_4)C(CH_2)_2Ru_2(CO)_4$ (8H4-1)	29.7	33.6
$(C_5H_4)C(CH_3)_2Ru_2(CO)_6$ (10H6-1) $\rightarrow$ $(C_5H_4)C(CH_2)Ru_2(CO)_6$ (8H6-1) + H_2	33.4	34.2
$(C_5H_4)C(CH_3)_2Ru_2(CO)_5$ (10H5-1) $\rightarrow$ $(C_5H_4)C(CH_2)Ru_2(CO)_5$ (8H5-1) + H_2	13.9	13.3
$(C_5H_4)C(CH_3)_2Ru_2(CO)_4$ (10H4-1) $\rightarrow$ $(C_5H_4)C(CH_2)Ru_2(CO)_4$ (8H4-1) + H_2	29.2	28.7

The predicted dihydrogen dissociation energies for the processes $[(C_5H_4)C(CH_3)_2]Ru_2(CO)_n \rightarrow [(C_5H_4)C(CH_2)_2]Ru_2(CO)_n + H_2$ ($n = 6, 5, 4$) are also listed in Table 3. All such H_2 dissociation processes are seen to be endothermic requiring energies from 13 to 34 kcal/mol. The energy for H_2 removal from the pentacarbonyl $[C_5H_4C(CH_3)_2]Ru_2(CO)_5$ **10H5-1** to give the corresponding dehydrogenation product $[C_5H_4C(CH_2)_2]Ru_2(CO)_5$ **8H5-1** is by far the lowest at only ~13 kcal/mol as compared with ~34 kcal/mol for the hexacarbonyl **10H6-1** and ~29 kcal/mol for the tetracarbonyl **10H4-1**. This again is consistent with the isolation of **8H5-1** from the thermal reaction of $Ru_3(CO)_{12}$ with dimethylfulvene.³⁰ The endothermic dehydrogenation of **10H5-1** to **8H5-1** can be driven by escape of the liberated H_2 and/or hydrogenation of excess dimethylfulvene.

3.5 Mechanistic implications

Figure 4 depicts a possible mechanism for the dehydrogenation of $[(C_5H_4)C(CH_3)_2]Ru_2(CO)_5$ to $[(C_5H_4)C(CH_2)_2]Ru_2(CO)_5$ based on the thermochemistry of the $[C_5H_4C(CH_3)_2]Ru_2(CO)_n$ and $[C_5H_4C(CH_2)_2]Ru_2(CO)_n$ systems ($n = 6, 5, 4$). This suggested mechanism contains intermediates with agostic Ru-H-C interactions, Ru-H bonds, Ru-H--H-C dihydrogen bonds in **10H5-4**, and finally an $Ru(\eta^2-H_2)$ dihydrogen complex **10H-5**. In the final step of the suggested mechanism the dihydrogen ligand in **10H-5** is lost to give the dehydrogenated $[(C_5H_4)C(CH_2)_2]Ru_2(CO)_5$ structure **8H5-1**. This reaction path involves successive activation of one C–H bond in each methyl group. The relatively high-energy structures **10H5-4** and **10H5-5** and the two transition states **10H5-TS1** and **10H5-TS2** (Figure 5) are thus seen to be key intermediates in this dehydrogenation process. The conversion of **10H5-1** to **10H5-4** may involve other transition states not found in this work.

The energy of the final products **8H5-1** + H_2 molecule is ~13 kcal/mol above the lowest energy $[(C_5H_4)C(CH_3)_2]Ru_2(CO)_5$ structure **10H5-1**. In addition, the CO dissociation energy from **10H6-1** to **10H5-1** is relatively high at ~32 kcal/mol. The above facts indicate that the reaction is thermochemically disfavored. However, the Gibbs free energy ΔG at $T = 298.15$ K and $P = 1$ atm of the final products **8H5-1** + H_2 is –1.0 kcal/mol (B3LYP-D3) or –0.2 kcal/mol (BP86-D3) lower than that of the lowest energy $[(C_5H_4)C(CH_3)_2]Ru_2(CO)_5$ structure **10H5-1**. This suggests that the reaction is dominated by the entropy effect such that the reduction of the free energy makes the reaction possible. The thermochemistry of the suggested reaction mechanism is consistent with the relatively high temperature of 145° and the long reaction time of 10 hours for the reaction as well as the low yield of 36% for the final product **8H5-1**.³⁰

Figure 4. The reaction path from the [(C₅H₄)C(CH₃)₂]Ru₂(CO)₅ structure **10H5-2** to the (C₅H₄)C(CH₂)₂Ru₂(CO)₅ structure **8H5-1** by extrusion of H₂ (ΔE is the electronic energy, ΔG is the Gibbs free energy).

Figure 5. The two optimized [(C₅H₄)C(CH₂)₂]Ru₂(CO)₅ transition state structures. The numbers in the parenthesis are the values of the corresponding imaginary frequencies predicted by the B3LYP-D3 and BP86-D3 methods.

4. Summary

The dimethylfulvene complex [η^5, η^1 -C₅H₄C(CH₃)₂][Ru(CO)₂][Ru(CO)₄] (**10H6-1**) and its experimentally known dehydrogenation product [η^5, η^3 -C₅H₄C(CH₂)₂]-[Ru(CO)₂][Ru(CO)₃] (**8H5-1**) formed by C–H activation of both fulvene methyl groups are both shown by density functional theory to be energetically favorable species. Possible reaction intermediates with agostic hydrogen atoms as well as ruthenium carbonyl hydrides and dihydrogen complexes are found.

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Supporting Information. Tables S1 to **S15**: Optimized coordinates for the $[(C_5H_4)C(CH_3)_2]Ru_2(CO)_n$ structures ($m = 3$ to 2 , $n = 6$ to 4) and the $(C_5H_4)C(CH_3)_2Ru_2(CO)_5$ **transition states**; complete Gaussian09 reference (Reference 47).

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Graphical Abstract

Intermediates for Methyl Carbon-Hydrogen Activation in Binuclear Dimethylfulvene Ruthenium Carbonyl Complexes

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Activation of the methyl C–H bonds in the dimethylfulvene ruthenium carbonyl complex $[\eta^5, \eta^1\text{-C}_5\text{H}_4\text{C}(\text{CH}_3)_2][\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_4]$ to give $[\eta^5, \eta^3\text{-C}_5\text{H}_4\text{C}(\text{CH}_2)_2][\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_3]$ is shown to involve intermediates with agostic C–H–Ru hydrogens as well as ruthenium carbonyl hydride and ruthenium dihydrogen complexes.