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Inhibition of Alkyne Cyclotrimerization to Arenes on a Metal Site by Four-Electron Donation through Simultaneous Sigma and Pi Bonding: The Tris(alkyne)Tungsten Carbonyls

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Reactions of *fac*-$(CH_3CN)_3W(CO)_3$ with the alkynes RC≡CR are known experimentally to give the very stable $(RC{\equiv}CR)_3WL$ (L = CO or CH_3CN) complexes without the complexed alkyne ligands on the tungsten site undergoing cyclotrimerization to the corresponding benzene derivatives C_6R_6. In order to evaluate the thermodynamics of these systems, the structures and energetics of the tris(alkyne)tungsten carbonyls $(RC{\equiv}CR)_3W(CO)_n$ and the corresponding arene-tungsten carbonyls $(\eta^6\text{-}C_6R_6)W(CO)_n$ (R = CH_3, CF_3; n = 3, 2, 1, 0) have been optimized using density functional theory. The cyclotrimerizations of the alkyne ligands in $(RC{\equiv}CR)_3W(CO)_n$ (n = 3, 2) to a benzene ligand in $(\eta^6\text{-}C_6R_6)W(CO)_n$ are predicted to be very exothermic. However, the corresponding cyclotrimerizations of the alkyne ligands in $(RC{\equiv}CR)_3W(CO)$ and $(RC{\equiv}CR)_3W$ to a benzene ligand in $(\eta^6\text{-}C_6R_6)W(CO)$ and $(\eta^6\text{-}C_6R_6)W$, respectively, are predicted to range from nearly thermoneutral (R = CH_3) to highly endothermic (R = CF_3). This can be related to the bonding mode of the alkyne ligands to the tungsten atom. Alkyne ligands bonded to tungsten as four-electron donors (with one σ bond and one π bond) are resistant to cyclotrimerization reactions. However, alkyne ligands bonded to tungsten as two-electron donors through only σ bonding of the C≡C triple bond are reactive towards cyclotrimerization reactions. The CF_3 derivatives are found to be less reactive towards cyclotrimerization than the CH_3 derivatives. The inhibition of alkyne cyclotrimerization on a metal site by bonding as a four-electron donor through both σ and π bonding can be related to the fact that known alkyne cyclotrimerization catalysts are generally based on late transition metals of groups 8, 9, and 10, rather than early transition metals such as tungsten.

Introduction

The cyclotrimerization of alkynes (RC≡CR) to the corresponding benzene derivatives, R_6C_6, in the presence of transition-metal catalysts, was discovered by Reppe and Schweckendiek in 1948.[1] In recent years, such alkyne cyclotrimerizations have been used for the regioselective syntheses of polysubstituted benzene derivatives.[2] Such reactions require alkyne activation by coordination to the transition metal. However, tris(alkyne)tungsten compounds of the type $(RC{\equiv}CR)_3WL$ (L = two-electron donor ligand such as CO[3] and CH_3CN[4]) are known to be very stable. The three alkyne units in these $(RC{\equiv}CR)_3WL$ derivatives exhibit very little tendency to trimerize to the corresponding benzene derivatives, despite the fact that they are all coordinated to the same tungsten atom.

The first tris(alkyne)tungsten derivative to be prepared was $(C_2H_5C{\equiv}CC_2H_5)_3W(CO)$, which was synthesized in 1964 by the reaction of *fac*-$(CH_3CN)_3W(CO)_3$ with diethylacetylene.[3] A similar reaction of *fac*-$(CH_3CN)_3W(CO)_3$ with bis(trifluoromethyl)acetylene was subsequently reported to give the related compound[4] $(CF_3C{\equiv}CCF_3)_3W(CH_3CN)$, in which an acetonitrile ligand rather than a carbonyl ligand remains on the tungsten after reaction with $CF_3C{\equiv}CCF_3$. Both $(C_2H_5C{\equiv}CC_2H_5)_3W(CO)$ and $(CF_3C{\equiv}CCF_3)_3W(CH_3CN)$ are very stable, decomposing only under vigorous reactions conditions. In fact, $(CF_3C{\equiv}CCF_3)_3W(CH_3CN)$ appears to be almost unique among transition-metal organometallic compounds by being unreactive towards $SbCl_5$, a very aggressive chlorinating/oxidizing agent.[5] Even notoriously robust organometallic compounds such as ferrocene, $Cr(CO)_6$, and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ are rapidly decomposed by $SbCl_5$ under ambient conditions.

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At first glance the formulas $(RC{\equiv}CR)_3WL$ appear very peculiar for these tungsten compounds. If all three alkynes are two-electron donors (Figure 1) then the formula giving the favored 18-electron configuration for the tungsten atom should be $(RC{\equiv}CR)_3WL_3$. Similarly, if all three alkynes are four-electron donors (Figure 1), then the formula giving the favored 18-electron configuration for the tungsten atom should be the homoleptic $(RC{\equiv}CR)_3W$ without any additional ligands. The 18-electron rule suggests one two-electron donor and two four-electron donor alkyne ligands for the $(RC{\equiv}CR)_3WL$ derivatives. The retention of the threefold symmetry in such structures can then be attributed to resonance between the three possible $(RC{\equiv}CR)_3WL$ structures having one two-electron donor and two four-electron donor alkyne ligands. The resulting structure is thus a resonance hybrid, analogous to the formulation of benzene as a resonance hybrid of the two possible 1,3,5-hexatriene structures. Furthermore, King[6] noted in 1968 that the coordination of all three alkynes to a metal as four-electron donors in a structure with threefold symmetry (e.g., C_{3v}) is symmetry forbidden. From the mathematical point of view the question of π-bonding in the $(RC{\equiv}CR)_3WL$ derivatives is similar to that in the carbonate ion, CO_3^{2-}.

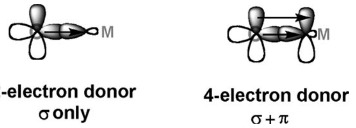


Figure 1. Two-electron and four-electron donor alkyne ligands to a transition metal (M). In order to show its orthogonal π orbitals the C≡C triple bond more clearly, the C≡C triple bond is oriented perpendicular to the plane of the paper so that only one carbon atom shows. The other carbon atom is behind this carbon atom and thus is not seen.

This paper uses density functional theory (DFT) to find the optimum structures for $(RC{\equiv}CR)_3W(CO)_n$ ($R = CH_3$, CF_3; $n = 3, 2, 1, 0$) containing three discrete alkyne ligands. The energies of the resulting structures are then compared with those of the corresponding isomeric (arene)tungsten carbonyls, namely $(\eta^6\text{-}R_6C_6)W(CO)_n$ ($R = CH_3$ and CF_3). These particular R groups were chosen to model the acetylenes in the known compounds[3,4] $(C_2H_5C{\equiv}CC_2H_5)_3W(CO)$ and $(CF_3C{\equiv}CCF_3)W(CH_3CN)$. The results from these studies are significant, since they suggest that four-electron donation of an alkyne to a metal atom through simultaneous σ and π bonding (Figure 1) inhibits its participation in cyclotrimerization on a metal site to give the corresponding benzene derivatives. This also accounts for the experimental observation[2] that late transition metals of groups 8, 9, and 10 are used as alkyne cyclotrimerization catalysts, rather than early transition metals such as tungsten studied in this work.

Theoretical Methods

Density functional theory methods (DFT) have been acknowledged to be a practical and effective computational tool, especially for organometallic compounds.[7–21] Two DFT methods were used in this study. The first functional is the BP86 method, which uses Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[22,23] The other DFT method used in this paper is MPW1PW91, which is a combination of the modified Perdew–Wang exchange functional with the Perdew–Wang 91 gradient-correlation functional.[24] The MPW1PW91 functional has been shown to be typically more reliable than the first generation functionals for carbonyl derivatives of the second and third row transition metals.[25,26]

For the third-row transition-metal derivatives effective core potential (ECP) and related basis sets provide a simple but efficient approach for reducing the computational effort while considering relativistic effects. In this study the ECP basis set SDD (Stuttgart-Dresden ECP plus DZ),[27,28] is used for the tungsten atom. For the carbon, oxygen, and fluorine atoms the double-ζ plus polarization (DZP) basis sets, which add one set of pure spherical harmonic d functions with orbital exponents $a_d(C) = 0.75$, $a_d(O) = 0.85$, and $a_d(F) = 1.00$ to the Huzinaga–Dunning standard contracted DZ sets,[29,30] are used and designated (9s5p1d/4s2p1d). For hydrogen a set of p polarization functions, $a_p(H) = 0.75$ was added to the Huzinaga–Dunning DZ set.

The geometries of all structures were fully optimized with the two levels of theory MPW1PW91/SDD and BP86/SDD. The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates at the same levels. The corresponding infrared intensities were also evaluated analytically. Except as otherwise noted, no imaginary vibrational frequencies were found in the final optimized structures. All of the computations were carried out with the Gaussian 03 program,[31] in which the fine grid (75,302) is the default for evaluating integrals numerically,[32] and the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence. The finer grid (120, 974) was used only for investigating small imaginary vibrational frequencies.[32]

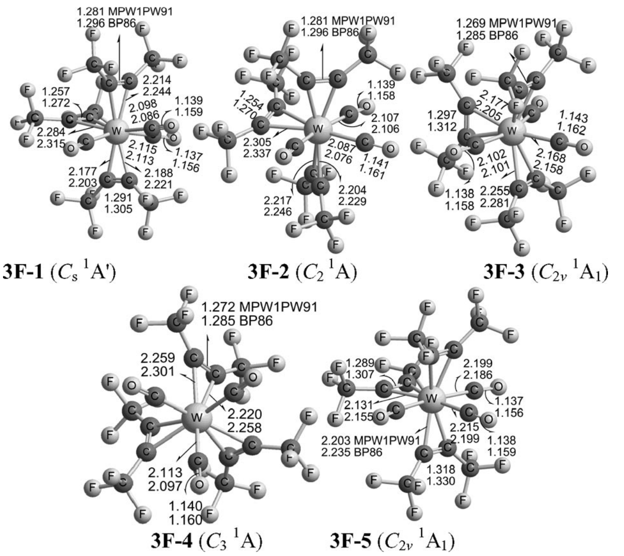
In the present study, the MPW1PW91 and BP86 methods are found to agree fairly well with each other in predicting the structures of the $(R_2C_2)_3W(CO)_n$ ($R = CH_3$, CF_3) derivatives. Since previous work[25] indicates that the MPW1PW91 method generally gives closer agreement with experimental bond lengths, the bond lengths obtained by the MPW1PW91 method are given in the discussion unless otherwise indicated. A total of 24 structures for the neutral $(R_2C_2)_3W(CO)_n$ ($R = CH_3,CF_3$) ($n = 3, 2, 1, 0$) compounds are reported in this paper. Except as otherwise noted for the arenetungsten complexes, all structures reported in this paper have singlet spin multiplicity.

Results

$(R_2C_2)_3W(CO)_3$ ($R = CH_3$, CF_3)

The 18-electron rule suggests that in tris(alkyne)tungsten tricarbonyl complexes each alkyne ligand functions as a two-electron donor using only one of the two carbon–carbon π bonds. Such alkyne ligands are completely analogous to simple olefin ligands. The corresponding $(\eta^2\text{-olefin})_3W(CO)_3$ complexes of simple monoolefins have been detected[33] in photoprocesses of $W(CO)_4(\eta^2\text{-alkene})_2$ in alkane solution at low temperatures but are reported to be unstable under ambient conditions.[34] However, the analogous *mer*-$(\eta^2\text{-ethene})(\eta^4\text{-norbornadiene})W(CO)_3$ is much more stable,[35] since two of the three double bonds complexed to the tungsten atom arise from the chelating diolefin norbornadiene.

The optimized equilibrium geometries for $(R_2C_2)_3W(CO)_3$ (R = CH_3 and CF_3) are shown in Figure 2 (labeled **3H-1** to **3H-5**) and Figure 3 (**3F-1** to **3F-5**) and their relative energies are listed in Table 1. Both *fac* and *mer* structures were investigated. Single *fac* structures (see **3H-4** in Figure 2 and **3F-4** in Figure 3) of C_3 symmetry were found in which the three carbonyl ligands occupy one face of the tungsten coordination octahedron and the three alkyne ligands occupy the opposite face of the octahedron. These *fac* structures are predicted to lie ca. 11 kcal/mol (**3H-4**) or ca. 17 kcal/mol (**3F-4**) in energy above the corresponding global minima **3H-1** and **3F-1**, respectively. The predicted carbon–carbon bond lengths of the alkyne ligands by MPW1PW91 are 1.252 Å in **3H-4** (Figure 2) and 1.272 Å in **3F-4** (Figure 3). The W–C(alkyne) bond lengths are 2.35 to 2.42 Å for **3H-4** (MPW1PW91), and 2.22 to 2.26 Å for **3F-4**. These C–C and W–C distances are consistent with stronger back bonding in the $CF_3C{\equiv}CCF_3$ complex relative to the $CH_3C{\equiv}CCH_3$ complex, in accord with the expected electron-withdrawing effect of the CF_3 substituents, relative to the CH_3 substituents.

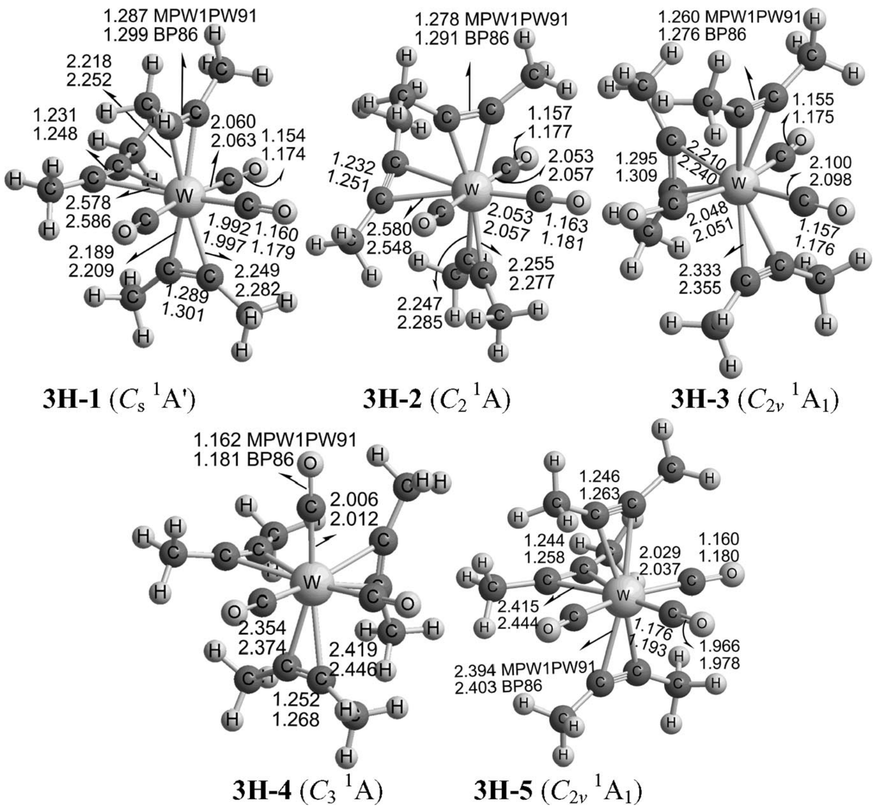


3F-1 (C_s $^1A'$) **3F-2** (C_2 ^1A) **3F-3** (C_{2v} $^1A_1$)

3F-4 (C_3 ^1A) **3F-5** (C_{2v} $^1A_1$)

Figure 3. The five optimized structures of $[(CF_3)_2C_2]_3W(CO)_3$.

Four *mer*-$(R_2C_2)_3W(CO)_3$ structures were found in which the three carbonyl ligands are coplanar. In the C_{2v} structures *mer*-$(R_2C_2)_3W(CO)_3$ **3H-3** and **3F-3**, as well as **3H-5** and **3F-5**, the two alkyne groups in relative *trans* positions are parallel to the plane containing the three carbonyl



3H-1 (C_s $^1A'$) **3H-2** (C_2 ^1A) **3H-3** (C_{2v} $^1A_1$)

3H-4 (C_3 ^1A) **3H-5** (C_{2v} $^1A_1$)

Figure 2. The five optimized structures of $[(CH_3)_2C_2]_3W(CO)_3$.

Table 1. The relative energies (Δ*E*, in kcal/mol), numbers of imaginary vibrational frequencies (Nimag), and infrared active *ν*(CO) frequencies [BP86 (cm^{-1})] for $(R_2C_2)_3W(CO)_3$ (R = CH_3, CF_3). The infrared intensities (km/mol) are listed in parentheses.

		$[(CH_3)_2C_2]_3W(CO)_3$ **3H-1**(*C_s*)	**3H-2** (*C_2*)	**3H-3** (*C_{2v}*)	**3H-4** (*C_3*)	**3H-5** (*C_{2v}*)
MPW1PW91	Δ*E*	0.0	5.3	16.2	12.5	24.6
	Nimag	0	1 (54*i*)	0	0	1 (71*i*)
BP86	Δ*E*	0.0	3.4	15.2	9.4	22.5
	Nimag	1 (15*i*)[a]	1 (40*i*)	1 (16*i*)[a]	0	1 (78*i*)
	ν(CO)	1936 (1388), 1940 (623), 2001 (179)	1914 (1442), 1923 (623), 1989 (160)	1935 (813), 1936 (1242), 1993 (24)	1914 (845), 1914 (845), 1960 (1052)	1871 (566), 1911 (1304), 1963 (417)
		$[(CF_3)_2C_2]_3W(CO)_3$ **3F-1** (*C_s*)	**3F-2** (*C_2*)	**3F-3** (*C_{2v}*)	**3F-4** (*C_3*)	**3F-5** (*C_{2v}*)
MPW1PW91	Δ*E*	0.0	10.8	16.6	19.2	57.5
	Nimag	0	1(40*i*)	1(4*i*)	0	3 (278*i*,276*i*,59*i*)
BP86	Δ*E*	0.0	8.3	15.2	16.1	52.3
	Nimag	0	1 (33*i*)	2 (9*i*, 8*i*)	0	4 (282*i*,226*i*,51*i*,10*i*)
	ν(CO)	2057 (420), 2062 (856), 2102 (153)	2039 (435), 2043 (955), 2089 (139)	2030 (518), 2055 (827), 2088 (4)	2038 (495), 2038 (495), 2074 (684)	2043 (313), 2043 (583), 2083 (91)

[a] Imaginary vibrational frequency can be eliminated[32] by using the finer integration grid (120, 974).

groups. For **3H-3** and **3F-3**, the plane containing the two alkyne carbon atoms of the unique alkyne ligand and the central tungsten atom is orthogonal to the plane containing the three carbonyl groups. However, for **3H-5** and **3F-5**, the two alkyne carbon atoms of the unique alkyne ligand are in the same plane as the three carbonyl groups. Structures **3H-3** and **3F-3** lie ca. 16 kcal/mol above the respective global minima **3H-1** and **3F-1**. Both **3H-5** and **3F-5** are predicted to be the highest energy structures considered, lying more than 20 kcal/mol above the respective global minima **3H-1** and **3F-1** (Table 1). Meanwhile, both **3H-5** and **3F-5** are predicted to have imaginary vibrational frequencies (Table 1), suggesting that they are not local minima. Following the normal mode of the imaginary vibrational frequencies leads these C_{2v} structures to the lower symmetry structures **3H-2** and **3F-2**. Thus, the C_2 *mer*-$(R_2C_2)_3W(CO)_3$ (R = CH_3 and CF_3) structures are predicted to lie ca. 5 kcal/mol (**3H-2**, MPW1PW91) or ca. 10 kcal/mol (**3F-2**, MPW1PW91) in energy above the corresponding global minima **3H-1** and **3F-1** (Table 1 and Figures 2 and 3). They also have small imaginary vibrational frequencies at 40*i* cm^{-1} (**3H-2**) or 33*i* cm^{-1} (**3F-2**). Following the corresponding normal modes lead to the corresponding global minima **3H-1** and **3F-1**, suggesting that the structures **3H-2** and **3F-2** are transition states rather than genuine minima.

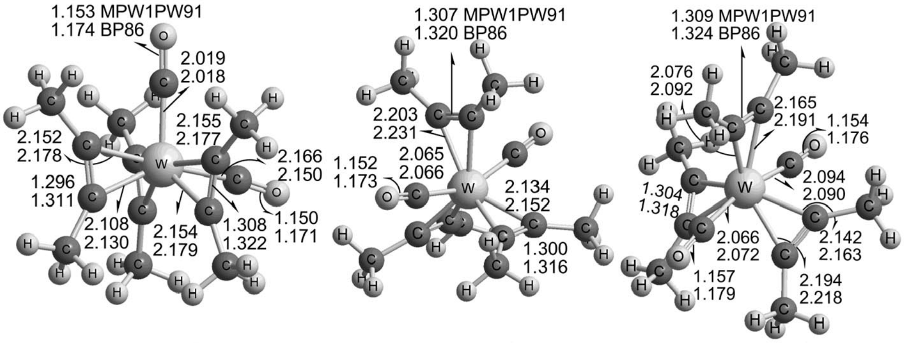
The global minima (Table 1) of $(R_2C_2)_3W(CO)_3$ (R = CH_3 and CF_3) are the C_s *mer* structures **3H-1** (Figure 2) and **3F-1** (Figure 3) having arrangements of the three alkyne ligands similar to those in the structure of *mer*-(η^2-ethene)(η^4-norbornadiene)W(CO)$_3$ determined by X-ray diffraction.[35] The predicted carbon–carbon bond lengths in the alkyne ligands are 1.23 to 1.29 Å (**3H-1**) or 1.25 to 1.29 Å (**3F-1**). The W–C(alkyne) bond lengths in **3H-1** range from 2.19 to 2.58 Å whereas in **3F-1**, these bond lengths fall in the narrower range of 2.17 to 2.28 Å. The W–C(alkyne) bond lengths for the alkyne *trans* to a carbonyl ligand are predicted to be ca. 0.3 Å (**3H-1**) or 0.1 Å (**3F-1**) longer than those of the alkynes *trans* to another alkyne. This is consistent with the expected *trans* effect[36] series of CO > $CF_3C{\equiv}CCF_3$ > $CH_3C{\equiv}CCH_3$.

$(R_2C_2)_3W(CO)_2$ (R = CH_3, CF_3)

Three structures (Figures 4 and 5 and Table 2) were optimized for the dicarbonyls $(R_2C_2)_3W(CO)_2$ (R = CH_3 and CF_3). The global minima **2H-1** and **2F-1** are singlet C_s structures in which the tungsten coordination can be approximated by a distorted square pyramid with a carbonyl group in the apical position. Structure **2H-1** has no imaginary vibrational frequencies. However, two small imaginary vibrational frequencies (20*i* and 16*i* cm^{-1}, BP86) are predicted for **2F-1**. Using a finer integration grid (120, 974) eliminates one of these imaginary vibrational frequencies and reduces the other one to 14*i* cm^{-1}. Following the normal mode corresponding to this small imaginary vibrational frequency leads to very little structural change and reduces the energy by only ca. 0.2 kcal/mol.

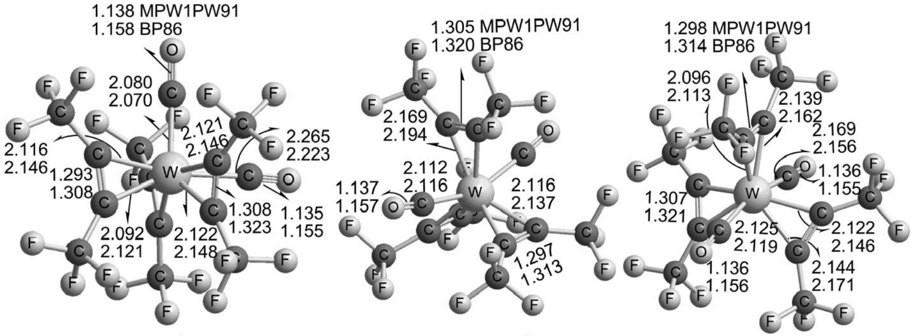
The second lowest energy structures for $(R_2C_2)_3W(CO)_2$ (R = CH_3 and CF_3) are the C_{2v} geometries **2H-2** and **2F-2** (Figures 4 and 5 and Table 2) lying <2 kcal/mol in energy above the corresponding global minima **2H-1** and **2F-1** (Table 2). The tungsten coordination in **2H-2** and **2F-2** can be approximated by a trigonal bipyramid with the two carbonyl ligands in the axial positions. The small energy differences between structures **2H-1** and **2H-2** and between **2F-1** and **2F-2** suggest highly fluxional systems, as is typical for five-coordinate complexes.[37,38]

The final $(R_2C_2)_3W(CO)_2$ (R = CH_3 and CF_3) structures (Figures 4 and 5 and Table 2) are the C_s structures **2H-3** and **2F-3**, lying ca. 8 kcal/mol (**2H-3**) and ca. 10 kcal/mol (**2F-3**) in energy above the respective global minima **2H-1** and **2F-1**. The tungsten coordination in **2H-3** and **2F-3**, like that in **2H-2** and **2F-2**, can be approximated by a trigonal



2H-1(C_s, ^{1}A') **2H-2**(C_{2v}, ^{1}A$_1$) **2H-3**(C_s, ^{1}A')

Figure 4. Optimized structures of $[(CH_3)_2C_2]_3W(CO)_2$.



2F-1(C_s, ^{1}A') **2F-2**(C_{2v}, ^{1}A$_1$) **2F-3**(C_s, ^{1}A')

Figure 5. Optimized structures of $[(CF_3)_2C_2]_3W(CO)_2$.

Table 2. The relative energies (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (Nimag), and infrared active ν(CO) frequencies [BP86 (cm^{-1})] for $(R_2C_2)_3W(CO)_2$ (R = CH_3, CF_3). The infrared intensities (km/mol) are listed in parentheses.

		$[(CH_3)_2C_2]_3W(CO)_2$		
		2H-1 (C_s)	**2H-2** (C_{2v})	**2H-3** (C_s)
MPW1PW91	ΔE	0	1.7	8.5
	Nimag	0	0	1 (49*i*)
BP86	ΔE	0	1.8	6.8
	Nimag	0	0	1 (42*i*)
	ν(CO)	1965 (659) 1985 (593)	1961 (1112) 1991 (42)	1927 (1061) 1961 (30)
		$[(CF_3)_2C_2]_3W(CO)_2$		
		2F-1 (C_s)	**2F-2** (C_{2v})	**2F-3** (C_s)
MPW1PW91	ΔE	0	2.0	10.7
	Nimag	2 (17*i*,10*i*)	0	3 (22*i*,17*i*,13*i*)
BP86	ΔE	0	1.6	9.5
	Nimag	2 (20*i*,16*i*)	1 (13*i*)	3 (21*i*,19*i*,15*i*)
	ν(CO)	2075 (396) 2088 (444)	2069 (732) 2092 (39)	2067 (739) 2093 (28)

bipyramid with the two carbonyl groups in the axial positions. Both **2H-3** and **2F-3** are predicted to have at least one small imaginary vibrational frequency (Table 2). Following the normal mode of the largest imaginary vibrational frequency leads the C_s structures to the closely related C_{2v} structures **2H-2** or **2F-2**.

Table 3. The relative energies (ΔE, in kcal/mol), and numbers of imaginary vibrational frequencies (Nimag), and infrared active ν(CO) frequencies [BP86 (cm^{-1})] for $(R_2C_2)_3W(CO)$ (R = CH_3, CF_3). The infrared intensities (km/mol) are listed in parentheses.

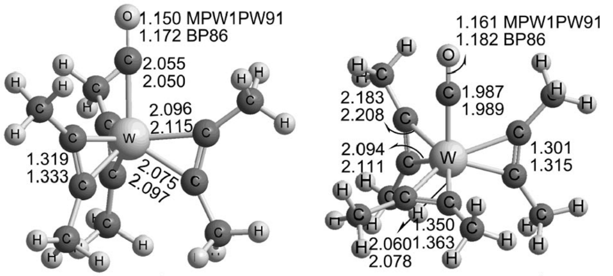
		$[(CH_3)_2C_2]_3W(CO)$		$[(CF_3)_2C_2]_3W(CO)$	
		1H-1 (C_{3v})	**1H-2** (C_s)	**1F-1** (C_3)	**1F-2** (C_s)
MPW1PW91	ΔE relative	0	15.4	0	18.2
	Nimag	0	1 (46*i*)	0	2 (25*i*,11*i*)
BP86	ΔE relative	0	14.2	0	15.7
	Nimag	0	1 (48*i*)	0	1 (22*i*)
	ν(CO)	1982 (761)	1945 (702)	2091 (485)	2061 (525)

$(R_2C_2)_3W(CO)$ (R = CH_3 and CF_3)

The global minima of $(R_2C_2)_3W(CO)$ (R = CH_3 and CF_3) are the beautiful C_{3v} structure **1H-1** and the C_3 structure **1F-1** (Table 3, Figures 6 and 7), analogous to the experimentally known[3,4,39] tris(alkyne)tungsten monocarbonyl derivatives. For the equivalent alkyne groups, the predicted carbon–carbon bond lengths by MPW1PW91 are 1.319 Å for **1H-1** and 1.314 Å for **1F-1**, which are reasonably close to the experimental[39] value of 1.30 Å for $(C_6H_5C{\equiv}CC_6H_5)_3W(CO)$. The W–C(alkyne) bond lengths predicted by MPW1PW91 are 2.08 Å to 2.10 Å for **1H-1** and 2.06 Å to 2.07 Å for **1F-1**, which are also close to the experimental[39] value of 2.06 Å for $(C_6H_5C{\equiv}CC_6H_5)_3W(CO)$.

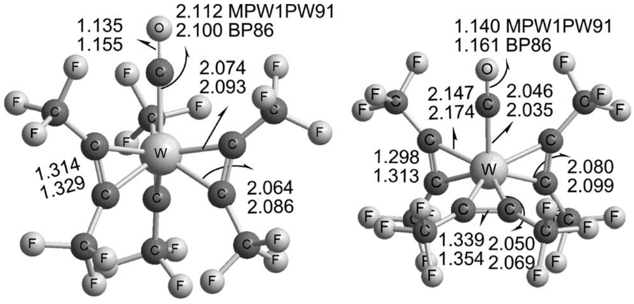
Table 4. The relative energies (ΔE, in kcal/mol), and the numbers of imaginary vibrational frequencies (Nimag) for $(R_2C_2)_3W$ (R = CH_3 and CF_3).

		$[(CH_3)_2C_2]_3W$		$[(CF_3)_2C_2]_3W$	
		0H-1 (C_3)	**0H-2** (C_s)	**0F-1** (C_3)	**0F-2** (C_s)
MPW1PW91	ΔE	0	28.5	0	28.8
	Nimag	0	1(57*i*)	0	2(31*i*,13*i*)
BP86	ΔE	0	28.0	0	28.4
	NImag	0	1(58*i*)	0	2(35*i*,10*i*)



1H-1 (C_{3v}, $^1A_1$) **1H-2** (C_s, $^1A'$)

Figure 6. The two optimized structures of $[(CH_3)_2C_2]_3W(CO)$.



1F-1 (C_3, ^1A) **1F-2** (C_s, $^1A'$)

Figure 7. Optimized structures of $[(CF_3)_2C_2]_3W(CO)$.

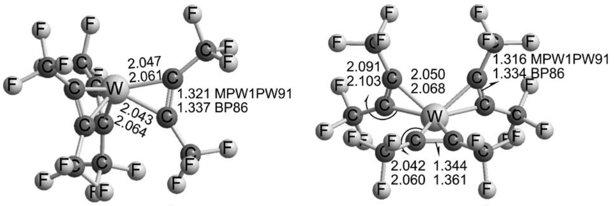
The additional structures **1H-2** and **1F-2** (Figures 6 and 7 and Table 3) are analogous C_s structures for $[(CH_3)_2C_2]_3W(CO)$ and $[(CF_3)_2C_2]_3W(CO)$, respectively. These structures have the same tungsten coordination geometry as the corresponding global minima **1H-1** and **1F-1** and differ only in the rotations of the three alkyne ligands. Structures **1H-2** and **1F-2** are predicted to lie in energy above the corresponding global minima **1H-1** and **1F-1** by ca. 15 kcal/mol (**1H-2**) and ca. 17 kcal/mol (**1F-2**). Both **1H-2** and **1F-2** are found to have small imaginary vibrational frequencies (Table 3). Following the corresponding normal modes leads to **1H-1** and **1F-1**, respectively. The difference in energy between **1H-1**/**1F-1** and **1H-2**/**1F-2** could be considered as an energy barrier for alkyne rotation. Thus, the predicted results of ca. 15 kcal/mol (**1H-2**) or ca. 17 kcal/mol (**1F-2**) are close to the experimental results, namely 15–17 kcal/mol for $Mo(PhC{\equiv}CCO_2Et)_3(PMe_3)$[40] and $W(PhC{\equiv}CPh)_3CO$.[41,42]

$(R_2C_2)_3W$ (R = CH_3, CF_3)

The global minima of the carbonyl-free homoleptic acetylene complexes $(R_2C_2)_3W$ (R = CH_3 and CF_3) are the C_3 structures **0H-1** and **0F-1** (Table 4, Figures 8 and 9). These structures are derived from the global minima of $(R_2C_2)_3W(CO)$ (R = CH_3, CF_3) by removal of the CO group. The predicted C≡C bond lengths in the equivalent alkyne ligands are 1.32 Å to 1.33 Å (MPW1PW91), which are ca. 0.01 Å longer than those in $(R_2C_2)_3W(CO)$ (R = CH_3, CF_3). The predicted W–C(alkyne) bond lengths are 2.04 Å to 2.06 Å (**0H-1**,MPW1PW91) or ca. 2.04 Å (**0F-1**, MPW1PW91).

0H-1(C_3, ^1A) **0H-2** (C_s, $^1A'$)

Figure 8. Optimized structures of $[(CH_3)_2C_2]_3W$.



0F-1 (C_3, ^1A) **0F-2** (C_s, $^1A'$)

Figure 9. Optimized structures of $[(CF_3)_2C_2]_3W$.

The C_s structures of $(R_2C_2)_3W$ (R = CH_3 and CF_3), namely **0H-2** and **0F-2** (Table 4, Figures 8 and 9), are predicted to lie ca. 29 kcal/mol in energy above the global minima **0H-1** and **0F-1**, respectively. Structures **0H-2** and **0F-2** are generated by removal of the carbonyl group from the C_s structures **1H-2** and **1F-2** (Figures 6 and 7), respectively. Both **0H-2** and **0F-2** are predicted to have small imaginary vibrational frequencies (Table 4), which could not be removed by a finer integration grid.

The Arenetungsten Carbonyls $(\eta^6\text{-}C_6R_6)W(CO)_n$ (R = CH_3, CF_3; n = 3, 2, 1, 0)

The chromium and molybdenum complexes $(\eta^6\text{-}C_6R_6)M(CO)_n$ (M = Cr, Mo) complexes have been studied extensively.[43,44] The eight arenetungsten complexes $(\eta^6\text{-}C_6R_6)W(CO)_n$ (R = CH_3, CF_3; n = 3, 2, 1, 0) have now been optimized for comparison of their energies of their global minima with those of the isomeric tris(alkyne)tungsten complexes $(R_2C_2)_3W(CO)_n$ (R = CH_3, CF_3; n = 3, 2, 1, 0). The resulting eight global minimum geometries are shown in the Supporting Information and their total energies with zero-point energy corrections are reported in Table 5. Higher energy structures for $(\eta^6\text{-}C_6R_6)W(CO)_n$ are not considered in this paper.

Table 5. The total energies (–E, in hartrees with zero-point corrections) and electronic states for the lowest energy structures of (η^6-C_6R_6)W(CO)$_n$ (R = CH_3, CF_3; n = 3, 2, 1, 0).

	[η^6-$(CH_3)_6C_6$]W(CO)$_n$ (n = 3, 2, 1, 0)			
	3AHS-1	**2AHS-1**	**1AHT-1**	**0AHT-1**
	C_3	C_s	C_1	C_6
Electronic state	^1A	$^1A'$	^3A	^3A
MPW1PW91/–E	874.99867	761.60569	648.21682	534.82857
BP86/–E	875.28543	761.85762	648.43139	535.00018
	[η^6-$(CF_3)_6C_6$]W(CO)$_n$ (n = 3, 2, 1, 0)			
	3AFS-1	**2AFS-1**	**1AFQ-1**	**0AFS-1**
	C_{3v}	C_s	C_1	C_{3v}
Electronic state	$^1A_1$	$^1A'$	^5A	$^1A_1$
MPW1PW91/–E	2661.50337	2548.12758	2434.72615	2321.38708
BP86/–E	2662.20762	2548.79545	2435.34832	2321.97453

The global minimum of [η^6-$C_6(CH_3)_6$]W(CO)$_3$ is predicted to be the singlet C_3 structure **3AHS-1**. The W–CO bond lengths are 1.973 Å (MPW1PW91), which are reasonably close to the experimental results[45] (1.951 Å) for (η^6-C_6H_6)W(CO)$_3$. The average W–C(benzene) bond lengths, namely 2.38 Å, are also close to the experimental value[45] of 2.365 Å. For the trifluoromethyl analogue [η^6-$C_6(CF_3)_6$]W(CO)$_3$, the global minimum is a C_{3v} structure **3AFS-1**. Similar to **3AHS-1**, the predicted W–CO bond lengths are 2.01 Å and the average W–C(benzene) bond lengths are 2.33 Å.

For the unsaturated [η^6-C_6R_6]W(CO)$_2$ (R = CH_3, CF_3), the singlet C_s structures **2AHS-1** and **2AFS-1** can be obtained from **3AHS-1** and **3AFS-1** by removing one carbonyl group. These structures are similar to the reported structure of (η^6-C_6H_6)Cr(CO)$_2$.[46,47] The benzene ring in **2AFS-1** deviates significantly from planarity with a maximum C–C–C–C torsion angle of 14°.

The lowest energy structure for the monocarbonyl [η^6-$C_6(CH_3)_6$]W(CO) is an unsymmetrical triplet structure **1AHT-1**. The tungsten atom is predicted to remain close to the center of the C_6 ring with W–C(benzene) bond lengths of 2.27 ± 0.1 Å. The quintet structure [η^4-$C_6(CF_3)_6$]W(CO), **1AFQ-1**, is predicted to be the global minimum of the trifluoromethyl analogue. This structure has only a tetrahapto benzene ring with the tungsten atom bonded to only four of the six carbon atoms. This tetrahapto benzene ring is very strongly bent as indicated by a maximum ring C–C–C–C torsion angle of 53°.

The global minima for the carbonyl-free **0AHT-1** and **0AFS-1** are triplet and singlet structures, respectively, with the relatively high symmetries C_6 and C_{3v}, respectively. The W–C(benzene) bond lengths in **0AHT-1** are 2.212 Å with six equal C–C bond lengths (1.444 Å) in the benzene ring. For **0AFS-1**, the W–C(benzene) bond lengths alternate between 2.143 Å or 2.203 Å to give the structure threefold but not sixfold symmetry.

Thermodynamics

Table 6 lists the carbonyl dissociation energies for the tris(alkyne)tungsten carbonyls (R_2C_2)$_3$W(CO)$_n$ (R = CH_3, CF_3) (n = 3, 2, 1) using the lowest energy structures found in this work. These data indicate that the carbonyl dissociation energy for the processes (R_2C_2)$_3$W(CO) → (R_2C_2)$_3$W + CO (R = CH_3, CF_3) is more than ca. 30 kcal/mol higher than the dissociation energies of carbonyl groups from (R_2C_2)$_3$W(CO)$_3$ and (R_2C_2)$_3$W(CO)$_2$. In fact, the carbonyl dissociation from (R_2C_2)$_3$W(CO)$_2$ to give (R_2C_2)$_3$W(CO) is essentially thermoneutral. These carbonyl dissociation energies are consistent with the isolation of (R_2C_2)$_3$W(CO) rather than (R_2C_2)$_3$W(CO)$_3$ or (R_2C_2)$_3$W(CO)$_2$ as the product from the reactions of *fac*-(CH_3CN)$_3$W(CO)$_3$ with alkynes.

Table 7 lists the energies for the conversion of the tris(alkyne)tungsten derivatives (R_2C_2)$_3$W(CO)$_n$ (R = CH_3, CF_3) (n = 3, 2, 1, 0) into the isomeric arenetungsten derivatives (η^6-C_6R_6)W(CO)$_n$ (R = CH_3, CF_3) (n = 3, 2, 1, 0), based on the lowest energy structures. Such isomerization processes involve the cyclotrimerization of the three alkyne ligands bonded to the tungsten atom. In all cases the isomerization of the dimethylacetylene derivatives [$(CH_3)_2C_2$]$_3$W(CO)$_n$ (n = 3, 2, 1, 0) to the corresponding hexamethylbenzene derivatives [η^6-$(CH_3)_6C_6$]W(CO)$_n$ is more thermodynamically favorable than the corresponding isomerization reactions of the trifluoromethyl analogues. Furthermore, as the number of carbonyl groups on tungsten is decreased from three to one, the isomerization reactions be-

Table 6. Dissociation energies (kcal/mol) for (R_2C_2)$_3$W(CO)$_n$ (R = CH_3, CF_3) (n = 3,2,1) involving the lowest energy structures. The zero-point vibrational-energy (ZPE) corrections have been included.

Process					MPW1PW91	BP86
(CH_3CCCH_3)$_3$W(CO)$_3$ **(3H-1)**	→	(CH_3CCCH_3)$_3$W(CO)$_2$ **(2H-1)**	+	CO	12.6	14.4
(CH_3CCCH_3)$_3$W(CO)$_2$ **(2H-1)**	→	(CH_3CCCH_3)$_3$W(CO) **(1H-1)**	+	CO	–2.0	1.4
(CH_3CCCH_3)$_3$W(CO) **(1H-1)**	→	(CH_3CCCH_3)$_3$W **(0H-1)**	+	CO	38.8	41.2
(CF_3CCCF_3)$_3$W(CO)$_3$ **(3F-1)**	→	(CF_3CCCF_3)$_3$W(CO)$_2$ **(2F-1)**	+	CO	7.0	9.6
(CF_3CCCF_3)$_3$W(CO)$_2$ **(2F-1)**	→	(CF_3CCCF_3)$_3$W(CO) **(1F-1)**	+	CO	–0.6	1.7
(CF_3CCCF_3)$_3$W(CO) **(1F-1)**	→	(CF_3CCCF_3)$_3$W **(0F-1)**	+	CO	38.9	39.8

Table 7. Energies (kcal/mol) of the conversion of the tris(alkyne)tungsten derivatives $(R_2C_2)_3W(CO)_n$ (R = CH_3, CF_3) (n = 3, 2, 1, 0) into the isomeric arenetungsten derivatives $(\eta^6\text{-}C_6R_6)W(CO)_n$ (R = CH_3, CF_3) (n = 3, 2, 1, 0) based on the lowest energy structures. The zero point vibrational energy (ZPE) corrections have been included.

Process			MPW1PW91	BP86
$(CH_3CCCH_3)_3W(CO)_3$ **3H-1**	→	$W[\eta^6\text{-}C_6(CH_3)_6](CO)_3$ **3AHS-1**	–120.5	–112.2
$(CH_3CCCH_3)_3W(CO)_2$ **2H-1**	→	$W[\eta^6\text{-}C_6(CH_3)_6](CO)_2$ **2AHS-1**	–65.9	–58.2
$(CH_3CCCH_3)_3W(CO)$ **1H-1**	→	$W[\eta^6\text{-}C_6(CH_3)_6](CO)$ **1AHT-1**	7.2	16.6
$(CH_3CCCH_3)_3W$ **0H-1**	→	$W[\eta^6\text{-}C_6(CH_3)_6]$ **0AHT-1**	24.9	36.0
$(CH_3CCCF_3)_3W(CO)_3$ **3F-1**	→	$W[\eta^6\text{-}C_6(CF_3)_6](CO)_3$ **3AFS-1**	–79.8	–72.6
$(CH_3CCCF_3)_3W(CO)_2$ **2F-1**	→	$W[\eta^6\text{-}C_6(CF_3)_6](CO)_2$ **2AFS-1**	–30.6	–23.8
$(CH_3CCCF_3)_3W(CO)$ **1F-1**	→	$W[\eta^6\text{-}C_6(CF_3)_6](CO)$ **1AFQ-1**	41.5	54.2
$(CF_3CCCF_3)_3W$ **0F-1**	→	$W[\eta^6\text{-}C_6(CF_3)_6]$ **0AFS-1**	35.4	48.3

come successively less favorable. However, this trend does not continue from the monocarbonyls $(R_2C_2)_3W(CO)$ to the carbonyl-free complexes, where the isomerization energies are very similar. Thus for the tricarbonyls, where (arene)tungsten tricarbonyls are stable isolable compounds, these isomerizations are highly exothermic. For the dicarbonyls the isomerization is still highly exothermic for $[(CH_3)_2C_2]_3W(CO)_2$ at –65.9 kcal/mol (MPW1PW91) or –58.2 kcal/mol (BP86) but only moderately exothermic for the trifluoromethyl analogue $[(CF_3)_2C_2]_3W(CO)_2$ at –30.6 kcal/mol (MPW1PW91) or –23.8 kcal/mol (BP86). For the monocarbonyls the isomerization is essentially thermoneutral for the very stable $[(CH_3)_2C_2]_3W(CO)$ but very strongly exothermic for the trifluoromethyl analogue $[(CF_3)_2C_2]_3W(CO)$ at 41.5 kcal/mol (MPW1PW91) or 54.2 kcal/mol (BP86).

Discussion

The theoretical studies on $(alkyne)_3W(CO)_n$ and (arene)-$W(CO)_3$ (n = 3, 2, 1, 0) presented in this paper provide considerable insight as to why some transition metal systems are often good catalysts for the cyclotrimerization of acetylenes to the corresponding benzene, but yet there exist some very stable tris(alkyne)metal complexes. More specifically, these studies suggest that trimerization of alkyne on a transition metal site can be inhibited if both π orbitals of the alkyne ligand are tied up by bonding to the metal atom as a four-electron donor (Figure 1). The examples in this paper, chosen because of their relationship to known tris(alkyne) tungsten compounds, demonstrate this point very well. For the tris(alkyne)tungsten tricarbonyls $(R_2C_2)_3$-$W(CO)_3$ where all three alkyne ligands are necessarily two-electron donors to give the tungsten atom the favored 18-electron configuration, the isomerization to the corresponding arenetungsten tricarbonyls $(\eta^6\text{-}C_6R_6)W(CO)_3$ is predicted to be highly exothermic (Table 7). This is consistent with the fact that no tris(alkyne)tungsten tricarbonyls are known experimentally. In the tris(alkyne)tungsten dicarbonyls $(R_2C_2)_3W(CO)_2$, the favored 18-electron configuration for the tungsten atom requires two two-electron donor alkyne ligands and one four-electron donor alkyne ligand. The isomerization of the tris(alkyne)tungsten dicarbonyls to the corresponding arenetungsten dicarbonyls $(\eta^6\text{-}C_6R_6)$-$W(CO)_2$ is still exothermic but less so than the corresponding tricarbonyls (Table 7). For the dicarbonyls $(R_2C_2)_3$-$W(CO)_2$ a 16-electron reaction intermediate with only two-electron donor alkyne ligands is conceivable.

The tris(alkyne) complexes $(R_2C_2)_3WL$ (R = C_2H_5, L = CO; R = CF_3, L = CH_3CN) are known experimentally[3,4] to be very stable towards cyclotrimerization of the alkynes to give the corresponding benzene. In these tris(alkyne) complexes the favored 18-electron configuration requires two four-electron donor alkyne ligands and only one two-electron donor alkyne. The presence of two four-electron donor alkyne ligands is seen to inhibit the alkyne cyclotrimerization, by donation of electron pairs from both of the alkyne π bonding orbitals to the metal atom.

Coordination of three alkyne ligands as four-electron donors to a single metal atom in a structure with threefold symmetry has been shown to be symmetry forbidden.[6] Therefore, the carbonyl-free tris(alkyne)tungsten complexes $(R_2C_2)_3W$ (R = CH_3, CF_3) must be regarded as 16-electron complexes, with two four-electron donor alkynes and one two-electron donor alkyne. This is consistent with the relationship of the lowest energy $(R_2C_2)_3W$ (R = CH_3, CF_3) structures to those of the corresponding monocarbonyls $(R_2C_2)_3W(CO)$ by simple removal of the carbonyl group. In addition, the dissociation energies of the carbonyl group from monocarbonyls $(R_2C_2)_3W(CO)$ to give the corresponding carbonyl-free complexes is rather high at 40 ± 2 kcal/mol (Table 6). These dissociation energies are similar to those of the simple stable 18-electron metal carbonyls to give 16-electron complexes. Thus the dissociation energies of $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ are about 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively.[48]

This formulation of $(R_2C_2)_3W$ (R = CF_3) with two four-electron donor alkynes and one two-electron donor alkyne similar to the monocarbonyls $(R_2C_2)_3W(CO)$ is consistent with the similarity of the isomerization energies of tris(alkyne)tungsten complexes to the corresponding (arene)tungsten complexes, within 6 kcal/mol (Table 7). For $(R_2C_2)_3W$ and $(R_2C_2)_3W(CO)$ (R = CH_3), the energy difference are ca. 30 kcal/mol (Table 7).

A comparison of the analogous methyl and trifluoromethyl derivatives is of interest. For the tricarbonyls and dicarbonyls $(R_2C_2)_3W(CO)_n$ (n = 3, 2) the cyclotrimerization to the corresponding arene derivatives $(\eta^6\text{-}C_6R_6)W(CO)_n$ is less exothermic with the CF_3 derivatives than with the corresponding CH_3 derivatives (Table 7). Correspondingly, for $(R_2C_2)_3W(CO)$ and $(R_2C_2)_3W$ the cyclotrimerization to $(\eta^6\text{-}C_6R_6)W(CO)$ and $(\eta^6\text{-}C_6R_6)W$, respectively, for CF_3 is more endothermic than for CH_3. This probably relates to the increased electronegativity of the CF_3 group relative to the CH_3 group which reduces the electron density on the alkyne carbons of the CF_3 derivatives relative to the CH_3 derivatives. This might be expected to make the formation of new carbon–carbon bonds in the cyclotrimerization reaction less favorable for the CF_3 derivatives than for the CH_3 derivatives.

Conclusions

The cyclotrimerizations of the alkyne ligands in the tris(alkyne)tungsten complexes $(RC{\equiv}CR)_3W(CO)_n$ (n = 3, 2) to a benzene ligand in the corresponding isomeric arene-tungsten complexes $(\eta^6\text{-}C_6R_6)W(CO)_n$ are predicted to be very exothermic. However, the cyclotrimerizations of the alkyne ligands in $(RC{\equiv}CR)_3W(CO)$ and $(RC{\equiv}CR)_3W$ to a benzene ligand in $(\eta^6\text{-}C_6R_6)W(CO)$ and $(\eta^6\text{-}C_6R_6)W$, respectively, are predicted to range from nearly thermoneutral (R = CH_3) to highly endothermic (R = CF_3). This can be related to the bonding mode of the alkyne ligands to the tungsten atom. Thus alkyne ligands bonded to tungsten as four-electron donors through both σ and π bonding of the C≡C triple-bond electrons are resistant towards cyclotrimerization reactions. However, alkyne ligands bonded to tungsten as two-electron donors through only σ bonding of the C≡C triple bond are reactive towards cyclotrimerization reactions. The CF_3 derivatives are found to be less reactive towards cyclotrimerization than the CH_3 derivatives.

The formation of alkyne metal complexes containing four-electron donor alkyne ligands using both alkyne π orbitals to form one σ and one π metal–ligand bond (Figure 1) is likely to be favored for the early transition metals such as tungsten, because such metals require more ligand electrons to attain the favored 18-electron configuration. Conversely, alkynes are more likely to bond to the late transition metals as two-electron donors using only one of their π-orbitals to bond to the metal atom (Figure 1). This can account for the experimental observations[2] that the known alkyne trimerization catalysts are based on late transition metals of groups 8, 9, and 10 such as cobalt, nickel, and palladium, rather than early transition metals, such as tungsten.

Supporting Information (see also the footnote on the first page of this article): Figures S1 to S4: Optimized lowest energy structures of $(\eta^6\text{-}C_6R_6)W(CO)_n$ (R = CH_3, CF_3, n = 3, 2, 1, 0); Tables S1 to S12: Coordinates of $[(CH_3)_2C_2]_3W(CO)_n$ (n = 3, 2, 1, 0); Tables S13 to S25: Coordinates of $[(CF_3)_2C_2]_3W(CO)_n$ (n = 3, 2, 1, 0); Tables S26 to S37: Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (km/mol) of $[(CH_3)_2C_2]_3W(CO)_n$ (n = 3, 2, 1, 0); Tables S38 to S50: Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (km/mol) of $[(CF_3)_2C_2]_3W(CO)_n$ (n = 3, 2, 1, 0); complete Gaussian 03 reference (ref.[31]).

Acknowledgments

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