

The Energy Difference between the Triply-Bridged and All-Terminal Structures of $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{Ir}_4(\text{CO})_{12}$: A Difficult Test for Conventional Density Functional Methods

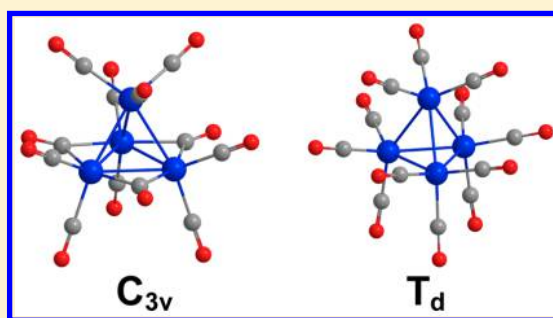
Hairong Ding,[†] Yunxiang Lu,^{*,†,‡} Yaoming Xie,[‡] Honglai Liu,[†] and Henry F. Schaefer, III^{*,‡}

[†]Key Laboratory for Advanced Materials and Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China

[‡]Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, United States

S Supporting Information

ABSTRACT: The $\text{M}_4(\text{CO})_{12}$ molecules $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{Ir}_4(\text{CO})_{12}$ have two low-lying structures, the all-terminal structure with T_d symmetry and the triply bridged structure with C_{3v} symmetry. A total of 45 density functional theory (DFT) methods have been used to predict structures and vibrational frequencies for $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{Ir}_4(\text{CO})_{12}$. The different DFT methods show a broad range of energy differences $\Delta E = E_{T_d} - E_{C_{3v}}$. For $\text{Rh}_4(\text{CO})_{12}$, none of the 45 DFT predictions is within 11 kcal/mol of the 2005 experimental value of 5.1 ± 0.6 kcal/mol reported by Allian and Garland (*Dalton Trans.* **2005**, 1957–1965). For the challenging $\text{Ir}_4(\text{CO})_{12}$ molecule, 21 DFT methods predict the correct T_d structure, while 24 DFT methods predict the C_{3v} structure to lie lower in energy. This research reveals many peculiar problems in the computation of the vibrational frequencies for the all-terminal structure.

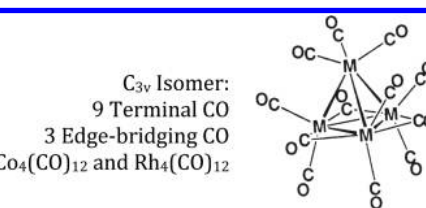
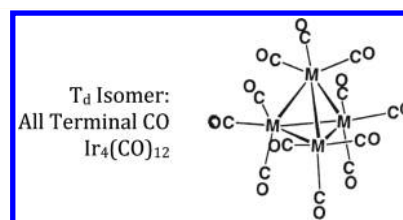


INTRODUCTION

Methods using classical force fields¹ have greatly expanded the size of molecular systems addressable by computational chemistry.² Force fields are now very reliable for the description of potential energy surfaces of molecules composed of H, C, N, and O atoms.¹ However, modern force fields are far more ambitious, promising to span the entire range of the periodic table.^{3–7} Among the more challenging systems for force field studies are molecules containing one or more cobalt, rhodium, or iridium atoms.^{8–10} In recent years, force fields have often been derived, at least in part, from density functional theory (DFT) computations, which may provide helpful guideposts. Is this a reasonable expectation for transition-metal-containing systems?

The present research was initiated in light of challenges to DFT methods from a rather simple organometallic system, tetrairidium dodecarbonyl, $\text{Ir}_4(\text{CO})_{12}$. This molecule falls among a handful of the most stable and least reactive of the homoleptic metal carbonyls synthesized to date.¹¹ X-ray crystallographic studies demonstrate that the structure of $\text{Ir}_4(\text{CO})_{12}$ is all-terminal. That is, there are no bridging carbonyl groups.¹² Tetrahedral structures were also deduced from solid-state¹³ and solution-phase¹⁴ vibrational spectroscopy. This tetrahedral T_d geometry for the iridium system is in contrast with the triply bridged C_{3v} structures observed for the valence-isoelectronic $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ molecules.

Given the known T_d all-terminal structure of $\text{Ir}_4(\text{CO})_{12}$, it is interesting that the popular DFT methods BP86 and



MPW1PW91 both predict a triply bridged C_{3v} structure.¹⁵ In light of the good track record of these two methods for organotransition-metal complexes, this result is perhaps surprising. Since any reliable force field for iridium-containing systems should get this T_d – C_{3v} energy ordering correct, it raises concerns about using DFT to constrain future force fields. In order to understand the issues arising, this study examines the $\text{Ir}_4(\text{CO})_{12}$ problem with many different density functionals and applies the same tests to the valence-isoelectronic $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ molecules.

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Among previous theoretical studies of $\text{Ir}_4(\text{CO})_{12}$, the most important is the 2012 research of Chen, Dyer, Gates, Katz, and Dixon.¹⁶ Those authors optimized the T_d and C_{3v} structures of $\text{Ir}_4(\text{CO})_{12}$ with the SVWN5 DFT method. Subsequently they carried out computations at these SVWN5 geometries with a range of methods, including CCSD(T). Their prediction that the T_d structure for $\text{Ir}_4(\text{CO})_{12}$ lies lower than the C_{3v} structure by ~ 4 kcal/mol is consistent with the fact that the T_d structure is observed experimentally. Dixon and co-workers have studied a number of $\text{Ir}_m(\text{CO})_n$ complexes ($m = 1, 2, 3, 4$, and 6) with nine functionals. Among iridium systems, in the present paper we focus on only the $\text{Ir}_4(\text{CO})_{12}$ species with many current available DFT functionals. The present research may thus be viewed as an extension of Dixon's iridium research, but with analogous attention to the valence-isoelectronic $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ molecules.

■ COMPUTATIONAL METHODS

In this research, the double- ζ and triple- ζ correlation-consistent basis sets of Kendall, Dunning, and Harrison,¹⁷ designated cc-pVDZ and cc-pVTZ, respectively, were used for the carbon and oxygen atoms. For the transition metals Co, Rh, and Ir, the analogous cc-pVDZ(-PP) and cc-pVTZ(-PP) basis sets of Peterson and co-workers^{18–20} were used. The (-PP) notation indicates that relativistic effective core potentials are used for the core electrons (e.g., $1s^2 2s^2 2p^6 3s^2 3p^6$ for cobalt). A total of 45 DFT methods were applied in this research: M05,²¹ SVWN5,^{22–24} OLYP,^{25,26} mPWB95,^{27,28} HCTH93,²⁹ PBE,³⁰ O3LYP,^{26,31} TPSS,³² HCTH,²⁹ PW91,²⁷ BP86,^{33,34} τ HCTH,³⁵ M06-L,³⁶ B1B95,³⁷ HCTH147,³⁸ TPSSH,³² B3P86,^{33,39} B3PW91,^{39,40} mPW3PBE,^{30,41} mPW1PBE,^{30,41} PBE1PBE,^{30,42} B97-2,⁴³ mPW1PW91,^{40,41} HSE2PBE,^{44–50} HSEh1PBE,^{44–50} PBEh1PBE,^{30,51} τ HCTHhyb,³⁵ M06,⁵² BLYP,^{26,34} B97-1,⁵³ M06-2X,⁵² B98,⁵⁴ B3LYP,^{26,39} LC- ω PBE,⁵⁵ X3LYP,⁵⁶ ω B97X-D,⁵⁷ B1LYP,^{26,28} BHandH,⁵⁸ mPW1LYP,^{26,41} CAM-B3LYP,⁵⁹ M05-2X,⁶⁰ ω B97X,⁶¹ ω B97,⁶¹ B97-D,⁶² and BHandHLYP.^{26,58} The reader should consult the cited papers for details of the different DFT methods. The computations were carried out with the program package Gaussian 09.⁶³

The ultrafine Gaussian integration grid (99, 590) was used, and the self-consistent-field convergence was set at 10^{-8} . Harmonic vibrational frequencies were computed for each structure and each DFT method from analytical second derivatives, and the zero-point vibrational energies were taken as one-half the sum of the harmonic frequencies. In a few cases (see below) we used larger integration grids⁶⁴ and tighter SCF convergence. Concerning the reliability of DFT methods, Curtiss and co-workers reported poor performance for B3LYP on the enthalpies of formation of alkanes, and their results are relevant to the current study.⁶⁵

■ RESULTS AND DISCUSSION

Tables 1–3 report the energy differences $\Delta E(T_d - C_{3v}) = E_{T_d} - E_{C_{3v}}$ for $\text{Ir}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{Co}_4(\text{CO})_{12}$, respectively, and Tables 4–6 report the corresponding zero-point vibrational energies (ZPVEs) and ZPVE differences between the T_d and C_{3v} structures.

a. $\text{Ir}_4(\text{CO})_{12}$. The iridium system is considered first, as both the T_d and C_{3v} structures are predicted to be genuine minima by all 45 DFT methods. The DFT predictions for $\text{Ir}_4(\text{CO})_{12}$ are seen in Table 1. Twenty-four of the 45 DFT methods make predictions contrary to the experimentally observed all-terminal

Table 1. Computations for $\text{Ir}_4(\text{CO})_{12}$ ^a

	cc-pVDZ(-PP)		cc-pVTZ(-PP)	
	ΔE	ΔE_{ZPVE}	ΔE	ΔE_{ZPVE}
M05	8.12	7.86	6.30	6.40
SVWN5	7.71	7.73	5.74	5.94
OLYP	5.08	4.94	4.74	4.71
mPWB95	5.19	4.95	4.09	4.23
HCTH93	3.80	3.69	3.13	3.12
PBE	4.10	4.11	2.92	3.04
O3LYP	3.31	3.28	2.86	2.91
TPSS	2.93	3.03	2.60	2.79
HCTH	3.27	3.23	2.66	2.70
PW91	3.77	3.77	2.46	2.60
BP86	3.79	3.73	2.50	2.56
τ HCTH	3.48	3.45	2.25	2.32
M06-L	1.07	1.86	1.48	2.14
B1B95	2.28	2.11	1.59	1.66
HCTH147	2.57	2.54	1.56	1.65
TPSSH	1.66	1.79	1.34	1.56
B3P86	1.86	1.90	0.65	0.84
B3PW91	1.57	1.65	0.60	0.80
mPW3PBE	1.54	1.64	0.51	0.74
mPW1PBE	1.33	1.46	0.45	0.70
PBE1PBE	0.98	1.12	0.08	0.36
B97-2	0.87	0.96	0.06	0.26
mPW1PW91	0.93	1.07	−0.01	0.25
HSE2PBE	0.89	1.00	−0.12	0.11
HSEh1PBE	0.55	0.66	−0.47	−0.22
PBEh1PBE	0.41	0.54	−0.58	−0.32
τ HCTHhyb	0.16	0.10	−1.11	−1.01
M06	0.41	1.52	−2.49	−1.22
BLYP	−0.43	−0.47	−2.15	−2.05
B97-1	−1.45	−1.36	−2.67	−2.40
M06-2X	−2.05	−1.79	−2.96	−2.51
B98	−1.80	−1.73	−3.12	−2.88
B3LYP	−2.37	−2.30	−3.85	−3.62
LC- ω PBE	−3.30	−2.96	−4.59	−4.07
X3LYP	−2.83	−2.74	−4.34	−4.09
ω B97X-D	−4.13	−3.82	−5.33	−4.77
B1LYP	−3.78	−3.67	−5.23	−4.96
BHandH	−4.34	−3.93	−5.56	−5.01
mPW1LYP	−4.18	−4.03	−5.70	−5.40
CAM-B3LYP	−4.83	−4.58	−6.50	−6.08
M05-2X	−5.02	−4.50	−7.27	−6.51
ω B97X	−5.92	−5.55	−7.24	−6.69
ω B97	−7.00	−6.52	−8.06	−7.50
B97-D	−6.98	−6.55	−8.20	−7.63
BHandHLYP	−7.48	−7.15	−8.70	−8.23

^aThe reported results are the energy differences (in kcal/mol) between the tetrahedral (T_d) and triply-bridged (C_{3v}) structures of $\text{Ir}_4(\text{CO})_{12}$. Both structures are found to be equilibrium geometries by all 45 DFT methods. The energy differences are ordered sequentially on the basis of the zero-point-corrected cc-pVTZ(-PP) results. Negative ΔE values agree with the experimental finding that the T_d structure lies energetically below the C_{3v} structure. The wrong $T_d - C_{3v}$ energy ordering is predicted by 24 methods.

structure with T_d symmetry.⁹ Twenty-one of the 45 methods yield the known T_d structure as the lower-energy isomer. The method that most favors the T_d structure is BHandHLYP, for which $\Delta E(T_d - C_{3v}) = -8.23$ kcal/mol. The median prediction is $\Delta E(T_d - C_{3v}) = 0.25$ kcal/mol (mPW1PW91).

Table 2. Computations for $\text{Rh}_4(\text{CO})_{12}$ ^a

	cc-pVDZ(-PP)			cc-pVTZ(-PP)		
	ΔE	ΔE_{ZPVE}	IMAG	ΔE	ΔE_{ZPVE}	IMAG
M05	33.02	32.50	T_d (81i, t_1)	30.74	30.43	T_d (75i, t_1)
M06-2X	31.98	31.99	T_d (117i, t_1)	29.92	30.12	T_d (122i, t_1)
LC- ω PBE	28.06	27.96	T_d (6i, t_1)	25.72	25.95	
M05-2X	28.18	28.39	T_d (57i, t_1)	25.30	25.81	T_d (58i, t_1)
B1B95	27.13	27.09		25.45	25.28	
O3LYP	26.34	25.97		25.28	25.04	
<i>m</i> PW1PBE	26.51	26.32		24.90	24.90	
<i>m</i> PW1PW91	26.22	26.03		24.58	24.58	
B97-2	26.03	25.77		24.56	24.47	
B3P86	26.24	25.98		24.46	24.40	
PBE1PBE	26.05	25.86		24.35	24.36	
OLYP	25.57	25.12		24.67	24.33	
B3PW91	25.93	25.68		24.36	24.29	
M06	26.24	27.08	T_d (61i, t_1)	23.29	24.20	T_d (52i, t_1)
<i>m</i> PW3PBE	25.80	25.58		24.14	24.10	
SVWN5	26.59	26.39		24.02	24.07	
HSE2PBE	25.83	25.64		24.07	24.07	
PBEh1PBE	25.57	25.40		23.79	23.83	
HSEh1PBE	25.39	25.21		23.61	23.62	
BHandH	25.11	25.32		22.93	23.35	
HCTH93	24.78	24.32		23.65	23.34	
ω B97X-D	25.09	24.88	T_d (1i, t_1)	23.12	23.15	
ω B97	25.28	25.22	T_d (33i, t_1)	22.94	23.13	T_d (19i, t_1)
τ HCTH	24.86	24.54		23.31	23.12	
BHandHLYP	24.74	24.73		22.89	23.10	
ω B97X	25.30	25.25	T_d (28i, t_1)	23.00	23.09	T_d (24i, t_1)
TPSSh	24.01	23.83		22.90	22.87	
HCTH	24.22	23.83		22.90	22.66	
CAM-B3LYP	24.64	24.56		22.44	22.58	
TPSS	23.32	23.15		22.30	22.25	
PBE	24.06	23.77		22.33	22.23	
BP86	24.02	23.68		22.35	22.17	
HCTH147	23.84	23.47		22.37	22.15	
<i>m</i> PWB95	24.42	24.01		22.70	22.09	
τ HCTHhyb	23.84	23.52		22.18	22.08	
PW91	23.88	23.59		22.07	21.98	
B98	23.43	23.20		21.71	21.72	
B97-1	23.28	23.06		21.58	21.58	
M06-L	22.26	22.39	T_d (36i, t_1)	21.15	21.30	T_d (38i, t_1)
B3LYP	22.88	22.63		21.06	20.99	
B1LYP	22.72	22.50		20.91	20.88	
X3LYP	22.77	22.55		20.88	20.86	
<i>m</i> PW1LYP	22.28	22.11		20.38	20.40	
BLYP	20.57	20.25		18.70	18.53	
B97-D	18.27	18.35		16.63	16.86	

^aThe reported results are the energy differences (in kcal/mol) between the tetrahedral (T_d) and triply-bridged (C_{3v}) structures of $\text{Rh}_4(\text{CO})_{12}$. For each structure found not to be an equilibrium geometry, the imaginary vibrational frequency (IMAG) and its symmetry are reported. All of the methods predict the C_{3v} structure to lie below the T_d structure, in agreement with experiments.

Some comments on the $\text{Ir}_4(\text{CO})_{12}$ results with the most popular DFT methods are appropriate. Truhlar's family of Minnesota functionals provide a range of results: 6.4 (M05), 2.1 (M06-L), -1.2 (M06), -2.5 (M06-2X), and -6.5 kcal/mol (M05-2X). The M06-L result is surprising given that M06-L often does well for molecules containing transition-metal atoms. Along the same lines, the BP86 method, which is often very good for transition-metal systems, predicts $\Delta E(T_d - C_{3v}) = 2.6$ kcal/mol, quite wide of Dixon's high-level theoretical finding.¹⁶

Now we turn to the DFT methods that get the correct ordering of the T_d and C_{3v} structures. BLYP does well, yielding $\Delta E(T_d - C_{3v}) = -2.1$ kcal/mol. The ever-popular B3LYP method does even better, with the T_d structure lying 3.6 kcal below the C_{3v} structure. A functional receiving high marks is the ω B97X-D method of Chai and Head-Gordon,⁵⁷ which predicts $\Delta E(T_d - C_{3v}) = -4.8$ kcal/mol, very close to the energy difference predicted by the high-level CCSD(T) theoretical method.¹⁶

Table 3. Computations for $\text{Co}_4(\text{CO})_{12}$ ^a

	cc-pVDZ(-PP)			cc-pVTZ(-PP)		
	ΔE	ΔE_{ZPVE}	IMAG	ΔE	ΔE_{ZPVE}	IMAG
LC- ω PBE	35.14	35.23	T_d (82i, t_1 ; 21i, a_2)	33.16	33.39	T_d (78i, t_1 ; 16i, a_2)
M05	34.82	34.52	T_d (92i, t_1 ; 11i, a_2)	32.96	32.85	T_d (89i, t_1 ; 5i, a_2)
M06-2X	32.96	32.91	T_d (407i, t_1 ; 13i, t_1) C_{3v} (257i, e)	32.52	32.58	T_d (511i, t_1 ; 35i, t_1) C_{3v} (285i, e)
M05-2X	33.24	33.39	T_d (276i, t_1) C_{3v} (215i, e)	31.50	31.60	T_d (308i, t_1) C_{3v} (239i, e)
SVWN5	31.26	31.18	T_d (60i, t_1 ; 17i, a_2)	29.61	29.65	T_d (56i, t_1 ; 10i, a_2)
B1B95	29.74	30.24	T_d (58i, t_1)	28.35	28.97	T_d (57i, t_1)
ω B97	30.10	30.45	T_d (86i, t_1 ; 16i, a_2)	28.25	28.75	T_d (83i, t_1 ; 12i, a_2)
O3LYP	29.15	28.86	T_d (50i, t_1 ; 22i, a_2)	28.38	28.12	T_d (50i, t_1 ; 21i, a_2)
ω B97X-D	29.42	29.56	T_d (57i, t_1 ; 22i, a_2)	27.58	27.92	T_d (53i, t_1 ; 19i, a_2)
ω B97X	29.08	29.44	T_d (70i, t_1 ; 16i, a_2)	27.18	27.68	T_d (67i, t_1 ; 11i, a_2)
mpW1PBE	29.02	28.94	T_d (43i, t_1 ; 16i, a_2)	27.58	27.61	T_d (41i, t_1 ; 12i, a_2)
B97-2	28.81	28.60	T_d (50i, t_1 ; 18i, a_2)	27.55	27.44	T_d (49i, t_1 ; 15i, a_2)
PBE1PBE	28.61	28.56	T_d (44i, t_1 ; 15i, a_2)	27.13	27.20	T_d (43i, t_1 ; 10i, a_2)
OLYP	28.06	27.68	T_d (48i, t_1 ; 23i, a_2)	27.55	27.18	T_d (50i, t_1 ; 23i, a_2)
mpW1PW91	28.49	28.42	T_d (42i, t_1 ; 16i, a_2)	27.03	27.07	T_d (39i, t_1 ; 11i, a_2)
mpW3PBE	28.20	28.07	T_d (43i, t_1 ; 17i, a_2)	26.80	26.78	T_d (40i, t_1 ; 13i, a_2)
BHandH	27.61	28.18	T_d (41i, t_1)	26.09	26.78	T_d (38i, t_1)
rHCTH	28.17	27.76	T_d (59i, t_1 ; 22i, a_2)	27.11	26.74	T_d (57i, t_1 ; 21i, a_2)
B3P86	28.26	28.12	T_d (43i, t_1 ; 16i, a_2)	26.70	26.69	T_d (39i, t_1 ; 10i, a_2)
B3PW91	28.13	27.97	T_d (42i, t_1 ; 18i, a_2)	26.69	26.64	T_d (39i, t_1 ; 14i, a_2)
HCTH	27.61	27.18	T_d (60i, t_1 ; 22i, a_2)	26.99	26.56	T_d (62i, t_1 ; 21i, a_2)
HSE2PBE	27.88	27.81	T_d (41i, t_1 ; 13i, a_2)	26.36	26.43	T_d (39i, t_1 ; 6i, a_2)
HCTH93	27.55	27.13	T_d (57i, t_1 ; 23i, a_2)	26.79	26.39	T_d (54i, t_1 ; 22i, a_2)
PBEh1PBE	27.83	27.78	T_d (42i, t_1 ; 14i, a_2)	26.29	26.38	T_d (40i, t_1 ; 8i, a_2)
M06	28.23	28.53	T_d (70i, t_1)	25.81	26.36	T_d (61i, t_1)
HSEh1PBE	27.54	27.48	T_d (41i, t_1 ; 13i, a_2)	26.02	26.10	T_d (38i, t_1 ; 7i, a_2)
mpWB95	26.86	27.16	T_d (55i, t_1)	25.76	26.00	T_d (55i, t_1)
HCTH147	26.56	26.19	T_d (55i, t_1 ; 21i, a_2)	25.64	25.29	T_d (54i, t_1 ; 19i, a_2)
TPSSH	26.26	26.08	T_d (38i, t_1 ; 16i, a_2)	25.34	25.26	T_d (38i, t_1 ; 12i, a_2)
CAM-B3LYP	26.69	26.76	T_d (46i, t_1 ; 15i, a_2)	24.97	25.17	T_d (40i, t_1 ; 6i, a_2)
PBE	26.30	26.05	T_d (45i, t_1 ; 20i, a_2)	25.05	24.89	T_d (42i, t_1 ; 16i, a_2)
PW91	26.00	25.77	T_d (42i, t_1 ; 19i, a_2)	24.75	24.62	T_d (39i, t_1 ; 16i, a_2)
TPSS	25.41	25.13	T_d (38i, t_1 ; 19i, a_2)	24.65	24.48	T_d (38i, t_1 ; 15i, a_2)
BP86	25.80	25.53	T_d (41i, t_1 ; 20i, a_2)	24.47	24.27	T_d (36i, t_1 ; 17i, a_2)
rHCTHhyb	24.15	24.08	T_d (31i, t_1 ; 15i, a_2)	22.83	22.86	T_d (26i, t_1 ; 10i, a_2)
BHandHLYP	23.54	23.91	T_d (83i, t_1) C_{3v} (104i, e)	22.02	22.51	T_d (89i, t_1) C_{3v} (127i, e)
B3LYP	23.18	23.09	T_d (24i, t_1 ; 15i, a_2)	21.72	21.73	T_d (15i, t_1 ; 9i, a_2)
B98	22.99	22.99	T_d (21i, t_1 ; 13i, a_2)	21.57	21.69	T_d (12i, t_1 ; 6i, a_2)
X3LYP	23.05	23.00	T_d (23i, t_1 ; 14i, a_2)	21.59	21.64	T_d (14i, t_1 ; 7i, a_2)
B97-1	22.65	22.65	T_d (22i, t_1 ; 12i, a_2)	21.21	21.36	T_d (15i, t_1 ; 4i, a_2)
B1LYP	22.50	22.48	T_d (16i, t_1 ; 13i, a_2)	21.04	21.16	T_d (6i, a_2)
mpW1LYP	22.10	22.11	T_d (14i, t_1 ; 12i, a_2)	20.68	20.85	T_d (2i, a_2)
B97-D	20.90	21.04	T_d (21i, a_2 ; 16i, t_1)	19.80	19.97	T_d (19i, a_2 ; 8i, t_1)
M06-L	20.99	21.19	T_d (54i, t_1)	19.65	19.90	T_d (59i, t_1)
BLYP	20.51	20.28	T_d (25i, t_1 ; 18i, a_2)	19.18	19.00	T_d (16i, t_1 ; 16i, a_2)

^aThe reported results are the energy differences (in kcal/mol) between the tetrahedral (T_d) and triply-bridged (C_{3v}) structures of $\text{Co}_4(\text{CO})_{12}$. For each structure found not to be an equilibrium geometry, the imaginary vibrational frequencies (IMAG) and their symmetries are reported. Lines separate methods for which both the T_d and C_{3v} structures are predicted to have imaginary frequencies.

For $\text{Ir}_4(\text{CO})_{12}$, the ZPVE corrections to $\Delta E(T_d - C_{3v})$ (Table 4) are, for the most part, fairly small. Nine ΔZPVE values are less than or equal to 0.1 kcal/mol. Generally speaking, ΔZPVE increases as the relative energy of the T_d structure is lowered with respect to C_{3v} . Similarly, with very few exceptions ΔZPVE increases as one moves from the cc-pVDZ(-PP) basis set to the larger cc-pVTZ(-PP) basis set.

One puzzling result is that the M06 method gives a much larger ΔZPVE , 1.12 kcal/mol with the DZ basis and 1.27 kcal/mol with the TZ basis. It was suspected that this inconsistency might arise from the known requirement of the Minnesota methods for larger integration grids, as discussed in the research of Wheeler and Houk.⁶⁶ Therefore, the M06 results were studied in greater depth. Tables S1 and S2 in the Supporting

Table 4. Zero-Point Vibrational Energies (kcal/mol) for Ir₄(CO)₁₂

	cc-pVDZ(-PP)			cc-pVTZ(-PP)		
	ZPVE(<i>T_d</i>)	ZPVE(<i>C_{3v}</i>)	ΔZPVE	ZPVE(<i>T_d</i>)	ZPVE(<i>C_{3v}</i>)	ΔZPVE
M05	61.83	62.10	−0.26	62.65	62.55	0.10
SVWN5	63.61	63.59	0.02	64.06	63.86	0.20
OLYP	61.89	62.03	−0.14	62.19	62.21	−0.03
<i>m</i> PWB95	60.89	61.13	−0.24	61.54	61.40	0.13
HCTH93	61.94	62.05	−0.11	62.27	62.28	−0.01
PBE	61.68	61.67	0.01	62.02	61.90	0.12
O3LYP	63.43	63.46	−0.03	63.68	63.63	0.05
TPSS	61.72	61.63	0.09	62.12	61.94	0.18
HCTH	62.17	62.21	−0.04	62.43	62.38	0.05
PW91	61.64	61.64	0.00	62.04	61.91	0.13
BP86	61.25	61.32	−0.07	61.66	61.60	0.06
<i>τ</i> HCTH	61.92	61.94	−0.03	62.35	62.27	0.08
M06-L	63.11	62.32	0.79	63.41	62.75	0.66
B1B95	64.61	64.77	−0.17	64.95	64.88	0.07
HCTH147	61.75	61.79	−0.04	62.11	62.02	0.09
TPSSh	63.09	62.96	0.13	63.46	63.24	0.22
B3P86	64.28	64.24	0.04	64.66	64.48	0.19
B3PW91	64.23	64.16	0.08	64.59	64.39	0.20
<i>m</i> PW3PBE	64.36	64.26	0.10	64.71	64.48	0.23
<i>m</i> PW1PBE	65.07	64.93	0.13	65.40	65.14	0.26
PBE1PBE	65.06	64.92	0.13	65.37	65.09	0.28
B97-2	64.27	64.19	0.09	64.60	64.40	0.21
<i>m</i> PW1PW91	64.95	64.82	0.14	65.29	65.03	0.26
HSE2PBE	64.74	64.64	0.10	65.06	64.83	0.23
HSEh1PBE	64.69	64.58	0.12	65.01	64.77	0.25
PBEh1PBE	64.83	64.69	0.14	65.14	64.88	0.27
<i>τ</i> HCTHhyb	63.09	63.15	−0.06	63.51	63.40	0.11
M06	63.61	62.49	1.12	64.17	62.91	1.27
BLYP	59.93	59.96	−0.03	60.39	60.28	0.11
B97-1	63.70	63.61	0.09	64.07	63.80	0.27
M06-2X	65.43	65.17	0.27	65.62	65.17	0.45
B98	63.83	63.76	0.07	64.22	63.97	0.25
B3LYP	63.03	62.96	0.07	63.44	63.22	0.23
LC- <i>ω</i> PBE	66.87	66.53	0.34	67.12	66.61	0.51
X3LYP	63.28	63.19	0.10	63.69	63.43	0.25
<i>ω</i> B97X-D	65.36	65.05	0.31	65.82	65.26	0.55
B1LYP	63.40	63.28	0.11	63.79	63.53	0.27
BHandH	68.43	68.02	0.41	68.71	68.16	0.55
<i>m</i> PW1LYP	63.44	63.30	0.14	63.84	63.54	0.30
CAM-B3LYP	65.01	64.75	0.25	65.36	64.94	0.41
M05-2X	65.83	65.30	0.52	66.06	65.30	0.76
<i>ω</i> B97X	65.47	65.09	0.38	65.77	65.22	0.55
<i>ω</i> B97	65.49	65.01	0.48	65.64	65.08	0.56
B97-D	61.86	61.43	0.43	62.32	61.75	0.57
BHandHLYP	66.41	66.08	0.33	66.74	66.25	0.49

Information report the cc-pVDZ(-PP) M06 vibrational frequencies for the *T_d* and *C_{3v}* equilibrium geometries using five different Gaussian integration grids. The standard grid in all of the results in Tables 1–6 is the “ultrafine” pruned (99, 590) grid. Results from the smaller “fine” pruned (75, 302) grid and the larger (120, 974), (150, 974), and (225, 974) grids are also included in Tables S1 and S2. To focus challenges on the integration grid, a tighter SCF convergence of 10^{−10} was adopted. For the purpose of precise future comparisons, we note that Gaussian 09, revision A.02, was used for all of the computations reported in Tables S1 and S2.

Table S1 shows the difficulty of computing consistent vibrational frequencies for tetrahedral all-terminal Ir₄(CO)₁₂.

For example, for the lowest *a₁* vibrational frequency, the harmonic results are 115, 167, 142, 100, and 97 cm^{−1} with the (75,302), (99,590), (120,974), (150,974), and (225, 974) integration grids, respectively. Thus, the precise value of this *a₁* frequency with the M06/cc-pVDZ(-PP) method is somewhat uncertain. For the higher-energy triply bridged structure, the situation is about what is normally expected, with the largest deviation from the standard (99, 590) frequencies being 16 cm^{−1}.

The challenges with the *T_d* vibrational frequencies are reflected in the predicted zero-point vibrational frequencies. Table 7 shows that the contributions of the ZPVE to Δ*E*(*T_d* − *C_{3v}*) are 0.49, 1.13, 0.67, 0.23, and 0.20 kcal/mol with the five

Table 5. Zero-Point Vibrational Energies (kcal/mol) for $\text{Rh}_4(\text{CO})_{12}$

	cc-pVDZ(-PP)			cc-pVTZ(-PP)		
	ZPVE(T_d)	ZPVE(C_{3v})	ΔZPVE	ZPVE(T_d)	ZPVE(C_{3v})	ΔZPVE
M05	59.49	60.02	-0.53	60.06	60.38	-0.32
M06-2X	61.50	61.49	0.01	61.63	61.43	0.20
LC- ω PBE	64.88	64.98	-0.10	65.20	64.97	0.23
M05-2X	62.54	62.33	0.21	62.69	62.18	0.51
B1B95	63.03	63.07	-0.04	62.98	63.15	-0.16
O3LYP	61.41	61.79	-0.38	61.63	61.87	-0.24
mPW1PBE	63.25	63.45	-0.19	63.55	63.55	-0.01
mPW1PW91	63.12	63.31	-0.19	63.42	63.42	0.00
B97-2	62.25	62.51	-0.25	62.53	62.62	-0.09
B3P86	62.56	62.81	-0.26	62.88	62.94	-0.06
PBE1PBE	63.22	63.41	-0.19	63.50	63.49	0.01
OLYP	59.97	60.42	-0.45	60.18	60.52	-0.34
B3PW91	62.44	62.68	-0.24	62.75	62.81	-0.07
M06	61.51	60.67	0.84	61.94	61.04	0.91
mPW3PBE	62.60	62.82	-0.22	62.91	62.94	-0.03
SVWN5	62.54	62.74	-0.20	62.96	62.91	0.05
HSE2PBE	62.90	63.09	-0.19	63.19	63.20	0.00
PBEh1PBE	62.98	63.16	-0.17	63.29	63.25	0.03
HSEh1PBE	62.86	63.04	-0.18	63.15	63.14	0.01
BHandH	66.76	66.55	0.21	67.01	66.59	0.42
HCTH93	59.90	60.36	-0.46	60.19	60.50	-0.31
ω B97X-D	63.30	63.50	-0.21	63.63	63.60	0.02
ω B97	63.04	63.10	-0.06	63.25	63.07	0.18
τ HCTH	60.16	60.48	-0.32	60.51	60.70	-0.19
BHandHLYP	64.04	64.05	0.00	64.31	64.10	0.21
ω B97X	63.22	63.27	-0.05	63.39	63.29	0.09
TPSSh	61.45	61.62	-0.17	61.77	61.80	-0.03
HCTH	60.11	60.51	-0.40	60.36	60.61	-0.24
CAM-B3LYP	63.09	63.17	-0.09	63.38	63.24	0.14
TPSS	60.21	60.39	-0.18	60.55	60.60	-0.05
PBE	60.11	60.40	-0.29	60.43	60.54	-0.11
BP86	59.76	60.10	-0.34	60.10	60.27	-0.18
HCTH147	59.83	60.20	-0.37	60.12	60.34	-0.22
mPWB95	59.37	59.77	-0.40	59.32	59.93	-0.61
τ HCTHhyb	61.41	61.73	-0.32	61.79	61.89	-0.09
PW91	60.13	60.42	-0.29	60.49	60.59	-0.09
B98	61.96	62.18	-0.23	62.30	62.30	0.00
B97-1	61.80	62.02	-0.22	62.12	62.12	0.00
M06-L	60.72	60.60	0.13	61.08	60.93	0.15
B3LYP	61.13	61.38	-0.25	61.45	61.51	-0.06
B1LYP	61.38	61.61	-0.22	61.69	61.72	-0.03
X3LYP	61.38	61.60	-0.22	61.69	61.72	-0.03
mPW1LYP	61.46	61.64	-0.18	61.77	61.75	0.02
BLYP	58.29	58.61	-0.32	58.62	58.80	-0.17
B97-D	59.99	59.91	0.08	60.35	60.12	0.24

integration grids. Thus, it appears that we are finally approaching convergence with respect to integration grid size.

We understand that most DFT integration grids do not have the correct symmetry for molecules with very high symmetry, such as IF_7 with D_{5h} symmetry. Fortunately, the Lebedev angular integration grids used in this paper are of the cubic type, which are able to fit the T_d structure if the molecule is placed in the proper orientation. Thus, there is no adverse effect on the predicted T_d structures. For the C_{3v} structures, since the C_3 axis is collinear with the z axis, the Lebedev grids are less effective and there is some symmetry breaking. The consequence is that the e-symmetric vibrational modes lose their strict degeneracy. However, these effects are very small.

With the fine pruned (75, 302) grid, the differences among the degenerate frequencies are less than 0.1 cm^{-1} . Thus, there are no substantial effects on our predicted vibrational frequencies and zero-point energies.

b. $\text{Rh}_4(\text{CO})_{12}$. Our rhodium results are reported in Table 2. All 45 DFT methods agree with the triply bridged structure determined by X-ray crystallography.^{67,68} The range of $\Delta E(T_d - C_{3v})$ values is from 30.4 to 16.9 kcal/mol, a span of 13.5 kcal/mol. The median prediction is 23.1 kcal/mol (ω B97). The 2005 experimental paper by Allian and Garland⁶⁹ is pertinent in this context. Those authors reported the FTIR spectra of n -hexane solutions of triply bridged $\text{Rh}_4(\text{CO})_{12}$ in the interval 268–288 K. They concluded that the all-terminal T_d (or nearly

Table 6. Zero-Point Vibrational Energies (kcal/mol) for $\text{Co}_4(\text{CO})_{12}$

	cc-pVDZ(-PP)			cc-pVTZ(-PP)		
	ZPVE(T_d)	ZPVE(C_{3v})	Δ ZPVE	ZPVE(T_d)	ZPVE(C_{3v})	Δ ZPVE
LC- ω PBE	68.19	68.10	0.08	68.26	68.04	0.23
M05	64.18	64.48	-0.30	64.36	64.47	-0.11
M06-2X	62.25	62.30	-0.05	62.02	61.95	0.07
M05-2X	63.57	63.42	0.15	63.29	63.19	0.10
SVWN5	66.02	66.10	-0.08	66.26	66.21	0.05
B1B95	66.49	66.00	0.50	66.64	66.02	0.62
ω B97	66.67	66.32	0.35	66.60	66.10	0.50
O3LYP	64.71	65.01	-0.30	64.67	64.93	-0.26
ω B97X-D	66.66	66.51	0.14	66.72	66.39	0.34
ω B97X	66.76	66.40	0.36	66.72	66.22	0.50
<i>m</i> PW1PBE	66.46	66.55	-0.09	66.59	66.55	0.03
B97-2	65.49	65.69	-0.21	65.57	65.68	-0.11
PBE1PBE	66.47	66.52	-0.05	66.57	66.50	0.07
OLYP	63.25	63.63	-0.38	63.16	63.53	-0.37
<i>m</i> PW1PW91	66.34	66.42	-0.08	66.47	66.43	0.04
<i>m</i> PW3PBE	65.86	65.99	-0.13	65.99	66.01	-0.02
BHandH	69.93	69.37	0.56	70.01	69.32	0.69
τ HCTH	63.38	63.80	-0.41	63.51	63.88	-0.37
B3P86	65.88	66.01	-0.14	66.04	66.05	-0.02
B3PW91	65.68	65.85	-0.17	65.83	65.88	-0.05
HCTH	63.38	63.82	-0.43	63.27	63.70	-0.42
HSE2PBE	66.28	66.35	-0.07	66.40	66.33	0.07
HCTH93	63.11	63.53	-0.43	63.11	63.51	-0.40
PBEh1PBE	66.32	66.37	-0.05	66.44	66.35	0.09
M06	65.12	64.81	0.30	65.71	65.15	0.56
HSEh1PBE	66.21	66.28	-0.06	66.34	66.26	0.08
<i>m</i> PWB95	63.09	62.80	0.29	63.10	62.85	0.25
HCTH147	63.05	63.41	-0.37	63.06	63.40	-0.35
TPSSH	64.65	64.83	-0.18	64.84	64.92	-0.08
CAM-B3LYP	66.33	66.26	0.07	66.44	66.24	0.20
PBE	63.36	63.60	-0.24	63.45	63.61	-0.16
PW91	63.41	63.63	-0.23	63.55	63.68	-0.13
TPSS	63.33	63.60	-0.28	63.72	63.55	0.17
BP86	63.01	63.28	-0.27	63.15	63.35	-0.20
τ HCTHhyb	64.70	64.76	-0.07	64.88	64.85	0.03
BHandHLYP	66.47	66.10	0.37	66.51	66.02	0.49
B3LYP	64.47	64.56	-0.09	64.59	64.58	0.01
B98	65.03	65.03	-0.01	65.18	65.06	0.12
X3LYP	64.71	64.77	-0.05	64.83	64.77	0.05
B97-1	64.89	64.89	0.00	65.02	64.87	0.15
B1LYP	64.66	64.69	-0.03	64.81	64.68	0.12
<i>m</i> PW1LYP	64.76	64.75	0.01	64.90	64.73	0.16
B97-D	63.01	62.87	0.14	63.12	62.95	0.17
M06-L	64.58	64.38	0.20	64.78	64.53	0.25
BLYP	61.64	61.87	-0.23	61.73	61.91	-0.18

Table 7. Predicted Zero-Point Vibrational Energies (in kcal/mol) for $\text{Ir}_4(\text{CO})_{12}$ with the M06/cc-pVDZ(-PP) Method Using Different Integration Grids

grid	T_d	C_{3v}	$\Delta(T_d - C_{3v})$
"fine" pruned (75, 302)	62.90	62.41	0.49
"ultrafine" pruned (99, 590)	63.62	62.49	1.13
(120, 974)	63.15	62.48	0.67
(150, 974)	62.64	62.41	0.23
(225, 974)	62.57	62.37	0.20

T_d structure lies 5.1 ± 0.6 kcal/mol above the global-minimum C_{3v} structure. It is surprising that none of our 45 DFT methods

predicts a value of $\Delta E(T_d - C_{3v})$ within 11 kcal/mol of this experimental result. In order to test the effect of the solvent (*n*-hexane, with its dielectric constant of 1.8819), we have studied the $\text{Rh}_4(\text{CO})_{12}$ system with the B97-D functional and two continuum models. The $\Delta E(T_d - C_{3v})$ values reflect little change, from 18.27 kcal/mol (gas phase) to 18.37 kcal/mol (PCM) and 18.49 kcal/mol (CPCM).^{70,71} Thus, there appears to be a genuine disagreement between theory and experiment. The small solvent effect is understandable since the *n*-hexane solvent is not very polar ($\epsilon = 1.8819$) and the dipole moments of the $\text{Rh}_4(\text{CO})_{12}$ structures are not substantial. Table 8 shows that the dipole moment is only 0.33 D (B3LYP) or 0.46 D

(ω B97X-D) for C_{3v} $Rh_4(CO)_{12}$ and necessarily zero for the T_d structure.

Table 8. Dipole Moments (in D) of the Structures Using the B3LYP/cc-pVDZ(-PP) and ω B97X-D/cc-pVDZ(-PP) Methods

	$Co_4(CO)_{12}$		$Rh_4(CO)_{12}$		$Ir_4(CO)_{12}$	
	T_d	C_{3v}	T_d	C_{3v}	T_d	C_{3v}
B3LYP	0.0	0.59	0.0	0.33	0.0	0.52
ω B97X-D	0.0	0.63	0.0	0.46	0.0	0.63

A new feature appears with the $Rh_4(CO)_{12}$ system, namely, imaginary vibrational frequencies for the T_d structure. With the cc-pVTZ(-PP) basis set, seven of the 45 functionals show an imaginary vibrational frequency. When it exists, the corresponding vibrational mode is always of t_1 symmetry (i.e., triply degenerate). When the magnitude of the imaginary frequency is small [e.g., $19i\text{ cm}^{-1}$ for the ω B97/cc-pVTZ(-PP) method], it seems clear that the true equilibrium geometry is only slightly distorted from T_d symmetry. However, for the M06-2X/cc-pVTZ(-PP) method, the imaginary t_1 frequency is larger ($122i\text{ cm}^{-1}$). We return to this point in the discussion of $Co_4(CO)_{12}$, where imaginary frequencies of much larger magnitude (e.g., $511i\text{ cm}^{-1}$) are predicted.

c. $Co_4(CO)_{12}$. The present results for $Co_4(CO)_{12}$ are reported in Table 3. The results are ordered on the basis of the zero-point vibrationally corrected cc-pVTZ values, shown in the last column. It is encouraging that all 45 DFT methods predict the global minimum to be the observed^{72,73} triply bridged structure of C_{3v} symmetry. There is yet no experimental value for $\Delta E(T_d - C_{3v})$ for $Co_4(CO)_{12}$. The theoretical predictions range from 33.4 (LC- ω BE) to 19.0 (BLYP), a span of 14.4 kcal/mol. The median prediction for $\Delta E(T_d - C_{3v})$ is 26.6 kcal/mol (HCTH), but there is no guarantee that this is the most reliable prediction. The $\Delta E(T_d - C_{3v})$ values are thus rather similar for $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$.

Our lightest molecule, $Co_4(CO)_{12}$, is the most challenging electronically. With the larger cc-pVTZ(-PP) basis set, none of the 45 DFT methods predict the T_d stationary point to be a genuine minimum. Nine of the functionals predict T_d stationary points with one imaginary vibrational frequency. For two of the nine (B1LYP and mPW1LYP), the corresponding vibrational modes are of a_2 symmetry, and the frequencies are so small ($6i$ and $2i\text{ cm}^{-1}$) that there may be an equilibrium structure very close to the T_d structure. It is equally likely that a larger integration grid and tighter SCF convergence would eliminate these tiny imaginary frequencies.

The other 36 functionals show two distinct imaginary frequencies. For one method (M06-2X), the corresponding modes are both of triply degenerate t_1 symmetry. For the remaining 35 DFT methods, the two modes corresponding to the imaginary vibrational frequencies are of t_1 and a_2 symmetry.

Returning to reality, we ask the question, “Is the T_d structure of $Co_4(CO)_{12}$ a genuine minimum?” Our answer: probably yes. The ordering of the $\Delta E(T_d - C_{3v})$ values as a function of DFT method is very roughly similar for $Ir_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Co_4(CO)_{12}$. Since only the methods with negative ΔE values predict the known energetic order for $Ir_4(CO)_{12}$, those methods should also be most reliable for $Co_4(CO)_{12}$. All of the methods (except M06-L) with $\Delta E(T_d - C_{3v}) < 22\text{ kcal/mol}$ have small imaginary vibrational frequencies, which would

either (a) disappear with increasing size of the integration grid or stricter SCF convergence or (b) settle at an equilibrium geometry very close to tetrahedral.

Perhaps more surprising, three of the methods (M06-2X, M05-2X, and BHandHLYP) conclude that even the C_{3v} structure is not a minimum. It seems clear that all three of these methods have too much exact exchange, which is known to create problems for transition-metal systems.

d. Comparison with Dixon and Coworkers. For $Ir_4(CO)_{12}$, the most reliable theoretical prediction of $\Delta E(T_d - C_{3v})$ is -4.0 kcal/mol , the aug-cc-pVTZ(-PP) CCSD(T) result of Chen, Dyer, Gates, Katz, and Dixon.¹⁶ Their CCSD(T) computations were carried out assuming the SVWN5 equilibrium geometries predicted with the smaller basis set, aug-cc-pVDZ(-PP). The Dixon result is consistent with the experimental conclusion that the T_d structure is the global minimum. Dixon also reported second-order perturbation theory (MP2) results where the wrong energetic ordering was found. In Dixon’s research, the MP2 method predicted the T_d structure to lie about 5 kcal/mol above the C_{3v} structure.

Two direct comparisons with Dixon’s research are possible. First is their SVWN5 prediction that the T_d structure lies 7.7 kcal/mol above the C_{3v} structure. We predict $\Delta E(\text{SVWN})$ to be 7.7 kcal/mol with our cc-pVDZ(-PP) basis but only 5.9 kcal/mol for our larger cc-pVTZ(-PP) basis. Secondly, with his B3LYP/aug-cc-pVDZ(-PP)-optimized geometries, Dixon’s prediction for $\Delta E(T_d - C_{3v})$ is -1.9 kcal/mol . In the present research, we predict values of -2.3 and -3.6 with the cc-pVDZ(-PP) and cc-pVTZ(-PP) basis sets, respectively. Thus, the agreement with Dixon’s earlier paper is satisfactory where direct comparisons can be made.

Our Hartree–Fock predictions are also worth mentioning: $\Delta E(T_d - C_{3v}) = 18.7\text{ kcal/mol}$ for $Co_4(CO)_{12}$, 22.0 kcal/mol for $Rh_4(CO)_{12}$, and -23.0 kcal/mol for $Ir_4(CO)_{12}$ with the cc-pVTZ(-PP) basis set including the ZPVE corrections. Although the $T_d - C_{3v}$ energy ordering is correct, the magnitude of the true $T_d - C_{3v}$ energy difference for $Ir_4(CO)_{12}$ is almost certainly smaller than 23 kcal/mol.

CONCLUSIONS

A wide range of DFT methods has been used to predict the energy differences between the triply bridged (C_{3v}) and all-terminal (T_d) structures of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$. All of the methods agree that the cobalt and rhodium systems have triply bridged global minimum structures. However, there is much disagreement among the DFT methods concerning whether the T_d structure is a genuine minimum for $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. All of the methods show the iridium system to be the one that is most likely to have an all-terminal global minimum structure. However, only 21 of the 45 DFT methods predict the experimentally known T_d structure⁹ of $Ir_4(CO)_{12}$ to lie energetically below the C_{3v} structure. The $\Delta E(T_d - C_{3v})$ predictions by the different DFT methods show variations of 14.4 kcal/mol (Co), 13.6 kcal/mol (Rh), and 14.6 kcal/mol (Ir). Reliable gas-phase experimental $\Delta E(T_d - C_{3v})$ values are needed. Without such definitive experiments it is difficult to recommend a particular DFT method to provide guidance to transition-metal force field parameters. It is certain that many of the DFT methods fail for the energetic ordering of the two $Ir_4(CO)_{12}$ isomers, and many of the DFT methods have errors of at least 5 kcal/mol in $\Delta E(T_d - C_{3v})$ for $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. The use of DFT

results to parametrize force fields for molecular systems including transition metals should be done with caution.

■ ASSOCIATED CONTENT

■ Supporting Information

Cartesian coordinates of the $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{Ir}_4(\text{CO})_{12}$ structures with the B3LYP and $\omega\text{B97X-D}$ methods and vibrational frequencies for $\text{Ir}_4(\text{CO})_{12}$ with the M06 method using different integration grids. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: yxlu@ecust.edu.cn.

*E-mail: ccq@uga.edu.

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Notes

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