

Supporting Information for
Theoretical Study on Internal Alkyne/Vinylidene
Isomerization in Group 8 Transition Metal Complexes

Miho Otsuka,[†] Noriko Tsuchida,^{,†,§} Yousuke Ikeda,[‡] Natacha Lambert,[‡] Rina
Nakamura,[‡] Yuichiro Mutoh,^{‡,¶} Youichi Ishii,[‡] and Keiko Takano^{*,†}*

[†]*Department of Chemistry and Biochemistry, Graduate School of Humanities and
Sciences, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan;*

[‡]*Department of Applied Chemistry, Faculty of Science and Engineering, Chuo
University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan*

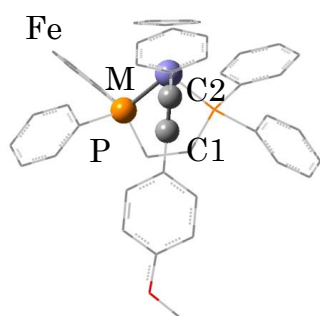
E-mail: takano.keiko@ocha.ac.jp

Contents	Page
Dihedral angles $\gamma(\text{PMC2C1})$ of the reactant structures	S2
Energy profiles and geometries for scan calculations on the Fe complexes	S4
Transition state (TS) structures	S6
Comparison of reactivity between Ph migration and Ar migration	S8
Natural bond orbitals and orbital energies for the orbital interaction between LP(M) and BD*(C1-C2) in the reactant	S10
Solvation effect on energy profiles	S12

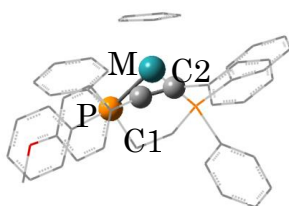
Dihedral angles $\gamma(\text{PMC2C1})$ of the reactant structures

For the Fe complexes, the dihedral angles of path 2 are in the range from 38.9 to 42.2 degrees. In contrast, those of path 3 for the Ru and Os complexes are in -27.6 to -40.8 degrees.

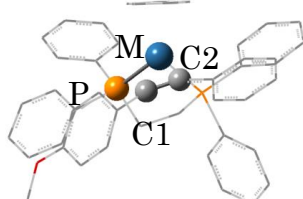
Table S1. Dihedral angles $\gamma(\text{PMC2C1})$ of the reactant structures for each path in the group 8 transition metal complexes ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$). C1 and C2 are connected with the triple-bonded carbon, and C2 denotes the carbon closer to the Cp ring. The reactant structures in the case of $\text{R} = \text{OMe}$ (Ph migration, path 2P or 3P) are shown.



Ru



Os



R	metal	Ar migration		Ph migration	
		path	$\gamma(\text{PMC2C1})$	path	$\gamma(\text{PMC2C1})$
OMe	Fe	1	-72.0	1	N/A
		2P	40.4	2P	40.3
		2A	40.4	2A	42.2
	Ru	1	-77.2	1	N/A
		3P	-38.0	3P	-40.8
		3A	-38.3	3A	-37.9
	Os	1	-78.0	1	N/A
		3P	-33.3	3P	-34.1
		3A	-33.2	3A	-36.0
CO_2Et	Fe	1	-71.3	1	N/A
		2P	39.9	2P	38.9
		2A	40.4	2A	40.4
	Ru	1	-76.3	1	-75.9
		3P	-38.9	3P	-38.8
		3A	-38.6	3A	-40.6
	Os	1	-77.5	1	N/A
		3P	-27.6	3P	-30.0
		3A	-30.6	3A	-36.7
Cl	Fe	1	-71.5	1	N/A
		2P	40.1	2P	40.1
		2A	40.9	2A	40.9
	Ru	1	-76.6	1	-76.7
		3P	-36.8	3P	-36.7
		3A	-38.0	3A	-38.1
	Os	1	-77.4	1	N/A
		3P	-34.5	3P	-34.4
		3A	-30.9	3A	-34.6

Energy profiles (kcal/mol) and geometries for scan calculations on the Fe complexes

Rotation barriers of alkyne on the Fe complexes were calculated to be 9.3 kcal/mol for R = OMe and 9.4 kcal/mol for R = CO₂Et, respectively (Figure S1), and these values are lower than the activation energies (ΔG_R^\ddagger) of path 1 which has a perpendicular type as a reactant (OMe, 17.6 kcal/mol; CO₂Et, 17.6 kcal/mol) (Table 1).

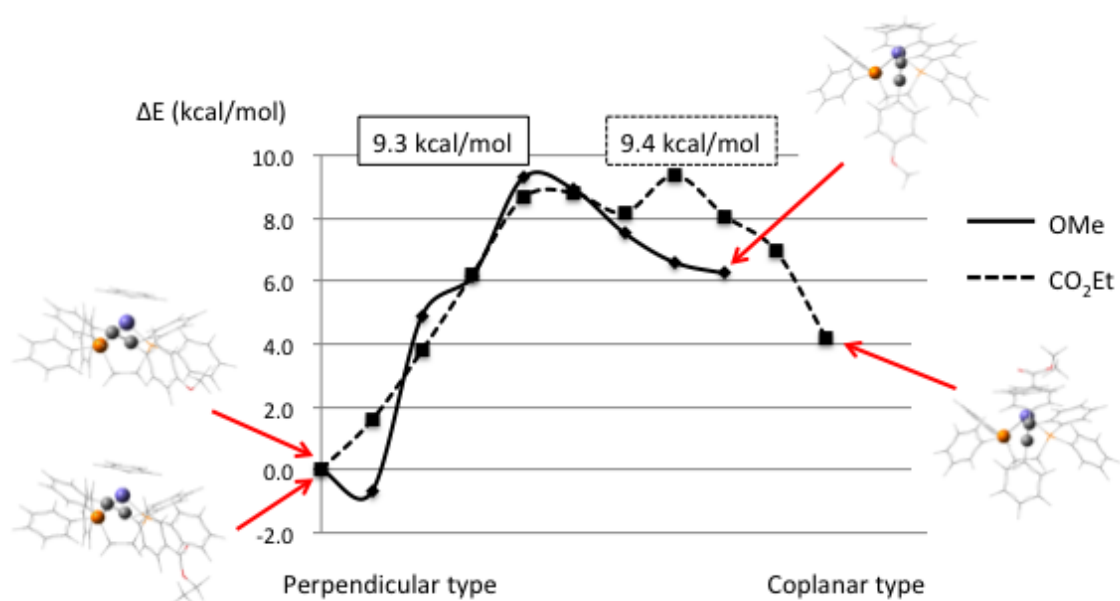


Figure S1. Energy profiles and geometries for scan calculations from the perpendicular type to the coplanar type on the Fe complexes. To clarify the conformation change, the atoms that are related to the rotational angle are shown as balls and sticks. Solid and dashed lines are, respectively, for R = OMe and CO₂Et.

Transition state (TS) structures

Table S2 lists selected structural parameters and imaginary frequencies in the transition state (TS). The values of α (C1–C2–C3) show the migration angles, where “C3” corresponds to a migrating carbon atom (Scheme 5, TS). A comparison of the angles α (C1–C2–C3) in each substituent (R) suggests that the α values do not depend on the kind of pathway and metal, but on the migrating group (Ar or Ph). The migrating angles α of Ar/Ph migration for R = OMe are 96° – 104° / 72° – 76° , respectively. The angles α of Ph migration, which has an advantage in the activation energy, are smaller than those of Ar migration for any metals. In contrast, Ar migration has smaller α values for R = CO₂Et. Furthermore, the absolute values of the difference between the migration angles α of Ar migration and Ph migration are smaller than those in the case of R = OMe. The angles α of the TS for Ar and Ph migrations are comparable for R = Cl. These results indicate that the difference in migrating angles α between Ar migration and Ph migration is closely related to that of the experimental migration aptitude.

Table S2. Selected structural parameters of TS structures in degree or angstrom and imaginary frequencies in cm^{-1} for each substituent (R = OMe, CO_2Et , and Cl). C3 is a carbon of the migrating group.

R	metal	path	Ar migration					Ph migration						
			$\alpha(\text{C1-C2-C3})$	d(C1-C2)	d(C2-M)	d(M-P)	freq (cm ⁻¹)	path	$\alpha(\text{C1-C2-C3})$	d(C1-C2)	d(C2-M)	d(M-P)	freq (cm ⁻¹)	
OMe	Fe	1	99.3	1.28	2.04	2.25	86i	1	N/A					
		2P	96.3	1.28	2.03	2.23	81i	2P	72.7	1.28	1.93	2.23	226i	
		2A	99.8	1.28	2.03	2.23	81i	2A	72.1	1.28	1.95	2.22	238i	
	Ru	1	97.8	1.28	2.10	2.30	91i	1	N/A					
		3P	98.2	1.28	2.11	2.29	65i	3P	73.6	1.28	2.02	2.30	259i	
		3A	96.1	1.28	2.09	2.29	78i	3A	73.0	1.28	2.03	2.30	248i	
	Os	1	98.9	1.29	2.11	2.32	100i	1	N/A					
		3P	104.0	1.28	2.14	2.30	69i	3P	75.6	1.28	2.03	2.31	253i	
		3A	96.4	1.29	2.09	2.31	75i	3A	75.6	1.28	2.05	2.30	220i	
CO ₂ Et	Fe	1	84.4	1.28	1.98	2.24	69i	1	N/A					
		2P	79.5	1.28	1.97	2.23	129i	2P	93.5	1.28	2.00	2.23	66i	
		2A	82.0	1.28	1.96	2.23	98i	2A	88.8	1.28	2.00	2.22	78i	
	Ru	1	85.0	1.28	2.07	2.30	71i	1	95.5	1.28	2.10	2.30	55i	
		3P	81.5	1.28	2.06	2.29	116i	3P	89.2	1.28	2.06	2.29	81i	
		3A	80.8	1.28	2.04	2.30	140i	3A	91.9	1.28	2.09	2.29	55i	
	Os	1	95.1	1.28	2.11	2.31	34i	1	N/A					
		3P	90.4	1.28	2.08	2.30	33i	3P	91.2	1.29	2.07	2.31	75i	
		3A	83.8	1.28	2.05	2.31	103i	3A	98.8	1.28	2.11	2.30	46i	
Cl	Fe	1	95.1	1.28	2.02	2.24	34i	1	N/A					
		2P	84.6	1.28	1.99	2.23	85i	2P	88.3	1.28	1.98	2.23	62i	
		2A	89.4	1.28	1.98	2.23	52i	2A	85.4	1.28	1.99	2.23	77i	
	Ru	1	92.2	1.28	2.09	2.30	39i	1	90.6	1.28	2.08	2.30	43i	
		3P	85.1	1.28	2.07	2.29	79i	3P	85.3	1.28	2.05	2.29	91i	
		3A	85.2	1.28	2.05	2.30	89i	3A	85.8	1.28	2.07	2.29	71i	
	Os	1	96.8	1.29	2.11	2.31	52i	1	N/A					
		3P	96.5	1.29	2.11	2.30	32i	3P	87.2	1.28	2.06	2.31	81i	
		3A	88.0	1.28	2.06	2.31	70i	3A	98.8	1.28	2.11	2.30	28i	

Comparison of reactivity between Ph migration and Ar migration in terms of orbital interactions

Table S3 lists the orbital interaction energies between C4-C6 or C4 as a donor and C1 as an acceptor. As already discussed in our previous study for the Ru complexes,¹² the reason why a group with lower nucleophilic reactivity is preferred as a migrating group for the nucleophilic reaction is explained by comparison of two types of orbital interaction energies: entry 1-6 in Table 2 and entry 7-12 in Table S3. For Ph migration for R = OMe, the energy of charge transfer from the donor (C2-C3) on the phenyl side to the acceptor C1 is 207.0 - 232.0 kcal/mol (entry 1, in Table 2) and much larger than the interaction energy of 55.8 - 65.9 kcal/mol (entry 7 in Table S3) from the donor (C4-C6) in the aryl group to the acceptor C1 carbon. Thus, the strong interaction between the migrating phenyl group and the accepting carbon atom to be migrated causes the phenyl migration. In contrast, the stability derived from Ar migration (26.4 - 44.0 kcal/mol, entry 2 in Table 2,) is much lower than that from Ph migration (207.0 - 232.0 kcal/mol, entry 1 in Table 2). Furthermore, for Ar migration, the interaction energies between the Ph group (C4), which stays at the C1 site as a donor, and C1 as an acceptor are quite large (246.2 - 256.2 kcal/mol, entry 8 in Table S3). These strong interactions between the Ph group and the acceptor carbon (C1) prevent the Ar group from migrating to the C1 carbon. As for the complex with R = CO₂Et, entry 4 is dominant. The large values of 118.1 - 144.3 kcal/mol correspond to the strong interaction between C2-C3 as an electron donor and C1 as an electron acceptor. There is only a small difference between the Ph and Ar migrations for the case of R = Cl, which is consistent with the experimental results. These results revealed that the charge transfer energies between an aromatic ring and a CC triple bond reflect the migratory aptitude.

Table S3. Orbital interaction energies between C4-C6 or C4 as a donor and C1 as an acceptor for TS structures.

R	migration group	R ¹	R ²	entry	donor	acceptor	metal	$\Delta E_{i \rightarrow j}$ (kcal/mol)	$E_i - E_j$ (a.u.)	F(i,j)
OMe	Ph	H	OMe	7	C4-C6	C1	Fe	55.8	0.15	0.11
					C4-C6	C1	Ru	60.2	0.34	0.14
					C4-C6	C1	Os	65.9	0.35	0.15
	Ar	OMe	H	8	C4	C1	Fe	256.2	0.18	0.21
					C4	C1	Ru	249.1	0.19	0.22
					C4	C1	Os	246.2	0.19	0.22
CO ₂ Et	Ph	H	CO ₂ Et	9	C4-C6	C1	Fe	79.7	0.37	0.16
					C4-C6	C1	Ru	83.3	0.38	0.16
					C4	C1	Os	240.0	0.19	0.22
	Ar	CO ₂ Et	H	10	C4-C6	C1	Fe	76.2	0.35	0.15
					C4-C6	C1	Ru	71.9	0.36	0.15
					C4-C6	C1	Os	80.0	0.37	0.16
Cl	Ph	H	Cl	11	C4-C6	C1	Fe	59.6	0.35	0.13
					C4-C6	C1	Ru	79.5	0.37	0.16
					C4-C6	C1	Os	101.2	0.39	0.18
	Ar	Cl	H	12	C4-C6	C1	Fe	91.4	0.36	0.17
					C4-C6	C1	Ru	81.7	0.37	0.16
					C4-C6	C1	Os	88.7	0.37	0.17

Natural bond orbitals and orbital energies for the orbital interaction between LP(M) and BD*(C1-C2) in the reactant

In the case of $M = \text{Fe}$, the overlap is remarkably small compared with the other metal cases, which leads to the small orbital interaction (Figure S2). This should be related to different reactant structures, namely, coplanar (Fe) and perpendicular (Ru and Os) (Figure 1). Planes of LP(M) and BD*(C1-C2) are parallel for the Ru and Os complexes, whereas those are perpendicular for the Fe complex.

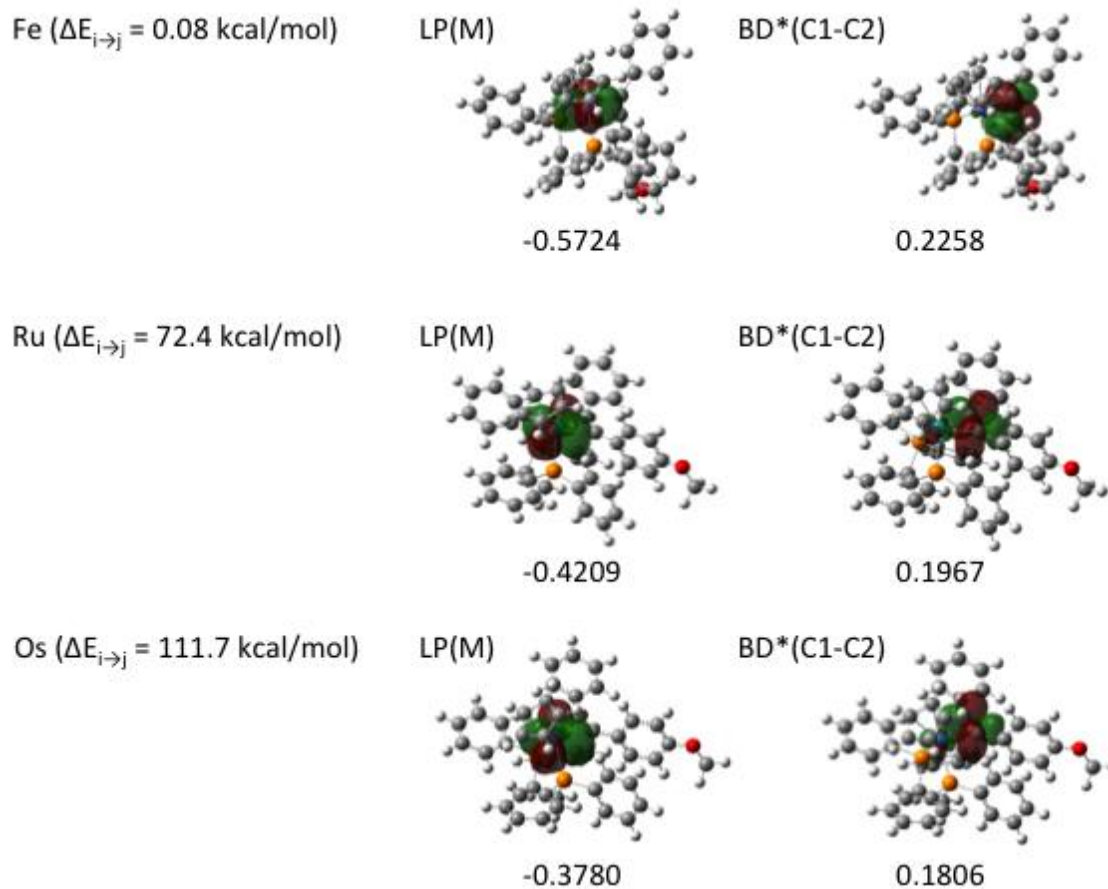


Figure S2. Natural bond orbitals and orbital energies (a.u.) for the orbital interaction between LP(M) and BD*(C1-C2) in the case of R = OMe (Table 3). The orbital energy differences and overlaps are as follows: Fe (0.80, 0.008); Ru (0.62, 0.191); Os (0.56, 0.224) (Table 3), although the values for M = Fe are not listed in Table 3 because the interaction energy is too small.

Solvent effect on energy profiles

To evaluate the solvent effect on energy profiles, single-point energy calculations (B3PW91/SDD+6-31G(d)) with polarizable continuum model (PCM) were performed. Benzene ($\epsilon = 2.2706$) for the Fe and Os complexes and dichloroethane ($\epsilon = 10.125$) for the Ru complex were applied as the solvent model under the same condition as the experiment. The relative energies and energy barriers are listed in Table S4. Geometry change of the complex due to the solvent was assessed for the Ru complex with a OMe group. It was confirmed that the solvent effect on the geometry is quite small.

Table S4. The relative energies to the most stable reactant complex (E_R , E_{TS} , E_P) and energy barriers (kcal/mol) ($\Delta E_R^\ddagger = E_{TS} - E_R$) for each path of the group 8 transition metal complexes at the B3PW91/SDD+6-31G(d) with solvent effect using the PCM method.

R	metal	path	Ar migration				path	E _R	Ph migration			
			E _R	E _{TS}	E _P	ΔE _R [‡]			E _{TS}	E _P	ΔE _R [‡]	
OMe	Fe	1	0.0	20.8	-7.4	20.8	1		N/A			
		2P	5.8	17.2	-6.8	11.4	2P	5.8	13.5	-7.7	7.7	
		2A	6.0	15.6	-7.7	9.5	2A	5.9	16.1	-7.0	10.2	
	Ru	1	0.0	24.4	-7.0	24.4	1		N/A			
		3P	0.3	21.3	-6.7	21.0	3P	0.4	17.9	-7.1	17.6	
		3A	0.1	19.3	-6.9	19.2	3A	0.1	17.9	-6.7	17.8	
	Os	1	0.9	26.8	-9.7	25.9	1		N/A			
		3P	0.4	23.6	-9.9	23.2	3P	0.4	18.5	-10.0	18.1	
		3A	0.1	20.3	-9.6	20.3	3A	0.0	21.0	-9.9	21.0	
CO ₂ Et	Fe	1	0.0	21.7	-7.2	21.7	1		N/A			
		2P	7.1	19.5	-6.9	12.4	2P	7.0	18.1	-7.4	11.1	
		2A	7.2	16.9	-7.4	9.7	2A	7.2	20.4	-7.4	13.2	
	Ru	1	0.0	25.9	-7.0	25.9	1	0.1	27.6	-6.6	27.6	
		3P	0.7	24.5	-6.3	23.9	3P	0.4	23.1	-7.2	22.7	
		3A	0.4	22.0	-7.0	21.6	3A	1.1	25.6	-6.6	24.5	
	Os	1	0.7	27.8	-10.2	27.0	1		N/A			
		3P	0.6	25.2	-10.0	24.5	3P	0.0	23.4	-10.4	23.4	
		3A	0.3	22.3	-10.5	22.0	3A	0.0	26.5	-10.2	26.5	
Cl	Fe	1	0.0	21.2	-7.1	21.2	1		N/A			
		2P	6.9	18.7	-7.2	11.8	2P	6.9	16.7	-7.2	9.8	
		2A	7.4	16.4	-7.1	9.0	2A	7.4	19.2	-7.1	11.8	
	Ru	1	0.2	25.4	-6.8	25.2	1	0.0	25.9	-6.8	25.9	
		3P	0.3	23.2	-6.8	22.9	3P	0.3	21.4	-6.8	21.1	
		3A	0.5	21.0	-6.8	20.5	3A	0.5	23.6	-6.8	23.1	
	Os	1	0.7	27.4	-10.6	26.6	1		N/A			
		3P	0.0	24.2	-10.3	24.2	3P	0.0	21.8	-10.6	21.8	
		3A	0.3	21.7	-10.1	21.4	3A	0.2	24.9	-10.2	24.6	