Journal of Organometallic Chemistry, 433 (1992) 295–303
Elsevier Sequoia S.A., Lausanne
JOM 22521

Synthesis of molybdenum–triosmium cluster complexes: reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}CC_6H_4Me$

Joon T. Park, Jeong-Ju Cho
Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701 (South Korea)

Kang-Moon Chun and Sock-Sung Yun
Department of Chemistry, Chungnam National University, Taejon 305-764 (South Korea)

(Received September 6, 1991)

Abstract

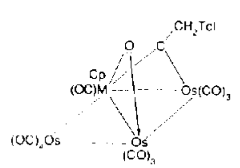
The reaction of $Cp(CO)_2Mo{\equiv}CTol$ ($Cp = \eta^5\text{-}C_5H_5$, Tol = $p\text{-}C_6H_4Me$) and $(\mu\text{-H})_2Os_3(CO)_{10}$ under mild conditions (5–20°C) produces three molybdenum–triosmium mixed-metal cluster compounds, $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (4, 65%) as a major product together with two minor products $CpMoOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-H})$ (5, 10%) and $CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-H})$ (6, 6%). Compounds 4, 5 and 6 have been isolated as crystalline solids and characterized by spectroscopic methods. Fluxionality of compound 4 has been examined by variable temperature ^{13}C NMR spectroscopy. Compound 5 in solution undergoes a degenerate metal framework rearrangement. ^1H NMR analysis of the tolyl methyl resonances of 5 for the rearrangement process gives $\Delta G_c^{\neq} = 15.2 \pm 0.2$ kcal/mol at the temperature of coalescence.

Introduction

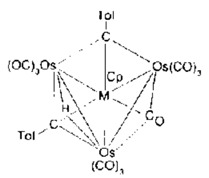
In the past years our research interest has been focused on the synthesis, characterization and reactivity of mixed-metal (group 6 and 8) cluster compounds [1]. Research in this area is stimulated by a belief that the presence of different metals in the cluster framework may result in drastically altered reactivity patterns compared to those of homometallic counterparts [2]. In previous work [1a–d], we have reported that the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ and $Cp(CO)_2W(CTol)$ ($Cp = \eta^5\text{-}C_5H_5$; Tol $= p\text{-}C_6H_4Me$) yields three tungsten–osmium mixed-metal clusters, $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (1) [1a,b], $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-H})$ (2) [1c] and $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$ (3) [1a,3], which exhibit a remarkable variety in structures and reactivities. We have extended our effort to the prepara-

Correspondence to: Dr. Joon T. Park, Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, South Korea.

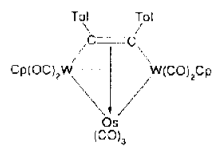
tion of molybdenum–triosmium mixed-metal clusters by coupling $(\mu\text{-H})_2Os_3(CO)_{10}$ with a molybdenum alkylidyne complex $Cp(CO)_2Mo(CTol)$. This approach has yielded three molybdenum–triosmium clusters: the major product $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**4**) and two minor products $CpMoOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-H})$ (**5**) and $CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-H})$ (**6**). A preliminary account of reactivity of **4** has been published [4]. In this paper a fully detailed report of the synthesis and spectroscopic characterization of compounds **4**, **5** and **6** is given. The complex $CpMoOs_3(CO)_{11}(\mu\text{-H})_3$ is, to our knowledge, the only previously reported molybdenum–triosmium cluster compound which was isolated in a low yield of 15% [5].



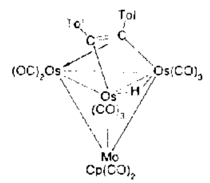
1 (M=W)
4 (M=Mo)



2 (M=W)
5 (M=Mo)



3



6

Experimental

General comments

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solvents were rigorously dried before use. The progress of the reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, Silica Gel 60 F-254, E. Merck). Preparative TLC was carried out using glass-backed silica gel plates (20 × 20 cm) prepared from silica gel G (Type 60, E. Merck). The method of Kaesz and co-workers [6] was used to prepare $(\mu\text{-H})_2Os_3(CO)_{10}$; $(\mu\text{-D})_2Os_3(CO)_{10}$ was prepared similarly, except that the compound was purified by crystallization instead of chromatography. Molybdenum alkylidyne complex $Cp(CO)_2Mo(CTol)$ was prepared as described in the literature [7].

Infrared spectra were obtained on a Nicolet 5-MX FT-IR spectrophotometer. Both ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were recorded by the staff of the Analytical Laboratory at Lucky Ltd. using a JEOL DX-300 mass spectrometer. All m/z values are referenced to ^{98}Mo and ^{192}Os. Microanalytical data were provided by the Analytical Laboratory of the Korea Research Institute of Chemical Technology.

Reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $Cp(CO)_2Mo(CTol)$

A cold (−30°C) dichloromethane solution of $Cp(CO)_2Mo(CTol)$ (199 mg, 0.623 mmol) was added to a dichloromethane solution of $(\mu\text{-H})_2Os_3(CO)_{10}$ (105 mg, 0.124 mmol) at 5°C. The reaction mixture (60 mL) was stirred at 5°C for 2 h and then slowly warmed to room temperature and stirred for 20 h. Evaporation of the solvent under vacuum and purification by preparative TLC (petroleum ether/dichloromethane, 4:1) provided dark red $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**4**, 91.5 mg, 0.078 mmol, 65%, $R_f = 0.36$), red $CpMoOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-H})$ (**5**, 15.1 mg, 0.0124 mmol, 10%, $R_f = 0.24$), and brown $CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-}H)$ (**6**, 8.6 mg, 0.0071 mmol, 6%, $R_f = 0.19$) isolated as crystalline solids.

$CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (4). ^1H NMR ($CDCl_3$, 25°C): δ 7.21–7.14 (AB pattern, 4H, C_6H_4); 5.30 (s, 5H, C_5H_5); 3.54–3.44 (AB pattern, $J = 13.3$ Hz, 2H, CH_2); 2.36 (s, 3H, CH_3). IR (CCl_4): ν(CO) 2095m, 2064s, 2032sh, 2022s, 2011s, 1978m cm^{-1}. MS (70 eV): m/z 1180 (M^+). Anal. Found: C, 25.84; H, 1.36. $C_{25}H_{14}O_{12}MoOs_3$ calc.: C, 25.60; H, 1.20%.

$CpMoOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-}H)$ (5). ^1H NMR ($CDCl_3$, −40°C): δ 7.30–6.97 (m, 8H, C_6H_4); 5.35 (s, 5H, C_5H_5); 2.39 (s, 3H, CH_3); 2.33 (s, 3H, CH_3); −21.5 (s, 1H, μ-H). IR(C_6H_{12}): ν(CO) 2092s, 2071vs, 2054vs, 2025m, 2012s, 2002s, 1991m, 1975m, 1718m cm^{-1}. MS (70 eV): m/z 1226 (M^+). Anal. Found: C, 30.21; H, 1.47. $C_{31}H_{20}O_{10}MoOs_3$ calc.: C, 30.54; H, 1.65%.

$CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-}H)$ (6). ^1H NMR ($CDCl_3$, 25°C): δ 6.29–6.79 (AB pattern, 8H, C_6H_4); 5.46 (s, 5H, C_5H_5); 2.28 (s, 6H, CH_3); −20.8 (s, 1H, μ-H). IR (C_6H_{12}): ν(CO) 2080m, 2063s, 2020vs, 2006w, 1985m, 1966m cm^{-1}. MS (70 eV): m/z 1226 (M^+). Anal. Found: C, 30.85; H, 1.77. $C_{31}H_{20}O_{10}MoOs_3$ calc.: C, 30.54; H, 1.65%.

Preparation of ^{13}C-enriched compound 4

Carbon-13-enriched $(\mu\text{-}H)_2Os_3(^*CO)_{10}$ (approx. 50% enrichment) [8] was utilized to prepare ^{13}C-enriched $CpMoOs_3(^*CO)_{11}[\mu_3\text{-}\eta^2\text{-}^*C(O)CH_2Tol]$ by a procedure similar to that described above.

Results and discussion

Reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with $Cp(CO)_2Mo(CTol)$

The reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with $Cp(CO)_2Mo(CTol)$ in dichloromethane under mild conditions affords three molybdenum–triosmium clusters: a triply-bridging acyl complex **4** (65%), a dialkylidyne complex **5** (10%), and an alkyne complex **6** (6%). Maximum yields have been obtained by using excess $Cp(CO)_2Mo(CTol)$ (approx. 6 equiv.). This is probably due to thermal decomposition of the unstable molybdenum alkylidyne complex before it can react with $(\mu\text{-}H)_2Os_3(CO)_{10}$. The structures of compounds **4**, **5** and **6** have been determined by comparing spectroscopic data of the complexes with those of known tungsten analogues, $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**1**) [1b], $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-}H)$ (**2**) [1b] and $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-}H)$ [1g]. Infrared spectra are essentially identical for both the tungsten and molybdenum analogues as shown in Fig. 1. A low frequency band at 1718 cm^{-1} in the carbonyl stretching region is observed in the IR spectrum of **5** which can be assigned to the semi-triply bridging carbonyl observed at 1703 cm^{-1} in the case of **2** [1b]. The identity of compound **6** was further confirmed by preparing the complex from the reaction of $CpMoOs_3(CO)_{12}H$ and di-*p*-tolylacetylene [9].

Monitoring the reaction by ^1H NMR reveals that three signals in the hydride region, at δ −5.50, −20.8 and −21.5, grow in as the reaction proceeds. Upon addition of carbon tetrachloride, the signal at δ −5.50 disappears. This implies that the resonance is due to $CpMo(CO)_3H$, which undergoes reaction with CCl_4 to give $CpMo(CO)_3Cl$ [10]. The two hydride resonances at δ −20.8 and −21.5 are

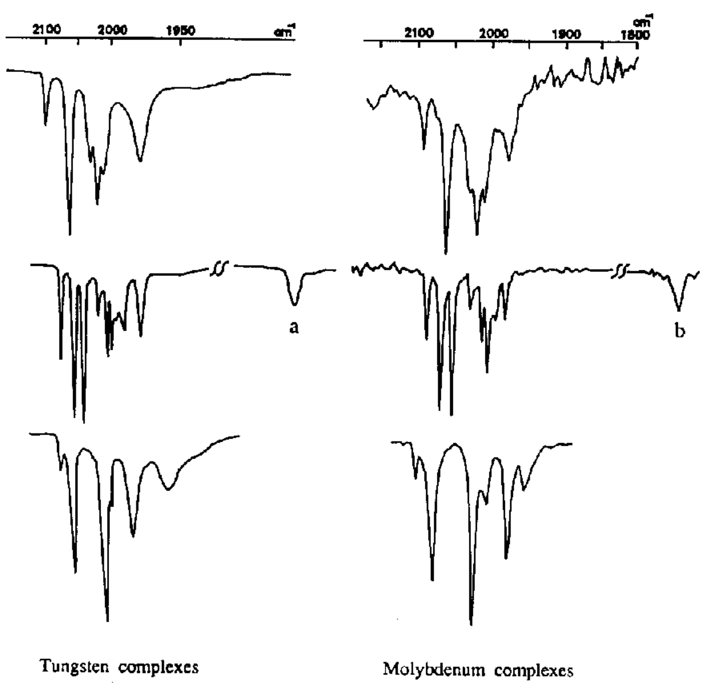


Fig. 1. IR spectra (CO region) of tungsten complexes 1 in carbon tetrachloride [1b], 2 in cyclohexane [2a] and $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-}H)$ in cyclohexane [1g], and molybdenum complexes 4, 5 and 6 in descending order. (a) Semi-triply bridging carbonyl of 2 at 1703 cm^{-1}. (b) Semi-triply bridging carbonyl of 5 at 1718 cm^{-1}.

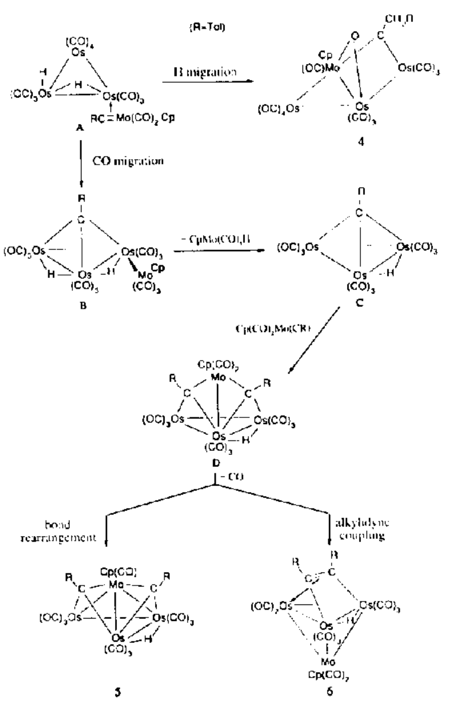
due to the formation of **6** and **5**, respectively. Consequently the overall stoichiometry for the formation of the three products is shown in eqs. 1–3.

$$(\mu\text{-H})_2Os_3(CO)_{10} + Cp(CO)_2Mo(CTol) \rightarrow CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol] \quad (1)$$

$$(\mu\text{-H})_2Os_3(CO)_{10} + 2Cp(CO)_2Mo(CTol) \rightarrow CpMoOs_3(CO)_{10}(\mu_3\text{-CTol})_2(\mu\text{-H}) + CpMo(CO)_3H + CO \quad (2)$$

$$(\mu\text{-H})_2Os_3(CO)_{10} + 2Cp(CO)_2Mo(CTol) \rightarrow CpMoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-H}) + CpMo(CO)_3H + CO \quad (3)$$

Likely reaction mechanisms for the formation of **4**, **5** and **6** are shown in Scheme 1. The common intermediate involved may be species **A**, a 1 : 1 adduct of the starting materials closely related to other adducts $H(\mu\text{-H})Os_3(CO)_{10}L$ (L = CO, PPh_3) between $(\mu\text{-H})_2Os_3(CO)_{10}$ and the donor molecule L [11]. Hydrogen migration to the alkylidyne carbon would initiate the formation of **4** whereas CO migration to the molybdenum would lead to species **B**. Complex **4** is formed by a 1 : 1 combination of the starting materials. The triply-bridging acyl carbon atom in **4** was observed to be enriched with carbon-13 when the compound was prepared from the reaction of $Cp(CO)_2Mo(CTol)$ with carbon-13-enriched $H_2Os_3(^*CO)_{10}$. The apparent sequence of steps for the formation of **4** would involve hydrogen



Scheme 1.

transfer from osmium to the alkylidyne carbon in the 1:1 adduct to form a benzyl group, migration of this group onto a carbonyl to form an acyl, and multiple coordination of the acyl. Reductive elimination of $CpMo(CO)_3H$ from **B** would form unsaturated species **C**. Shapley and co-workers in fact isolated and characterized the tungsten analogue of **B**, whose reactivity clearly indicated the formation of the unsaturated intermediate **C** by the reductive elimination of $CpW(CO)_3H$ from **B** [12]. However, no evidence of formation of the species **B** has been obtained in the present reaction. This may imply that the reductive elimination of $CpMo(CO)_3H$ is more facile in the molybdenum species **B** than that of $CpW(CO)_3H$ in the tungsten analogue. The coupling of an alkylidyne group with an alkyne to form an allyl ligand is well known in several cases [13]. Formation of compounds **5** and **6** can be rationalized in similar terms, utilizing the isolobal analogy [14] between C≡C and M≡C triple bonds. Coordination of the metalla-alkyne $Cp(CO)_2Mo{\equiv}CTol$ to **C** followed by coupling would lead to species **D**. Loss of carbon monoxide from **D** and subsequent metal framework rearrangement would give **5**, or subsequent coupling of the two alkylidyne moieties to an alkyne would afford **6**. The coupling of two alkylidyne groups into an alkyne ligand has been observed previously in the formation of **3** [1a,3] and in other related reactions by Stone [15]. The dialkylidyne complex **5** is an isomer of the alkyne complex **6**. The origin of both the benzylic hydrogens in **4** and the hydride ligand in **5** and **6** was confirmed by reaction of $Cp(CO)_2Mo(CTol)$ and $(\mu\text{-}D)_2Os_3(CO)_{10}$. The hydride migration appears to be a predominant pathway since compound **4** is the major product from the present reaction.

Fig. 2. Variable-temperature ^{13}C NMR spectra of $CpMoOs_3(^*CO)_{11}[\mu_3\text{-}\eta^2\text{-}^*C(O)CH_2Tol]$ [75 MHz, −10–30°C (CD_2Cl_2), 40–50°C ($CDCl_3$)].

The Wade–Mingos rule [16] predicts a tetrahedral cluster shape with 60 valence electrons (VE), and a triangular rhomboidal or "butterfly" arrangement with 62 VE. Both compounds **4** and **5** formally contain 62VE and therefore the four metal atoms adopt a triangular rhomboidal and a "butterfly" structure, respectively. Compound **6** with 60 VE has the expected tetrahedral structure of metal atoms.

Solution dynamics of 4

The limiting low-temperature spectrum (−10°C, CD_2Cl_2) of ^{13}C-enriched $CpMoOs_3(^*CO)_{11}[\mu_3\text{-}\eta^2\text{-}^*C(O)CH_2Tol]$ shows 12 carbonyl resonances at δ 231.4, 189.4, 189.0, 186.1, 184.3, 184.2, 180.8, 180.1, 177.9, 177.2, 175.2 and 172.8 as shown in Fig. 2. The most downfield signal at δ 231.4 is assigned to the carbonyl ligand *b* on the molybdenum atom. This resonance lies in the reported region for terminal carbonyls on a molybdenum atom containing a cyclopentadienyl ligand [6,17] and remains unchanged at higher temperatures. The remaining resonances can be assigned in groups on the basis of their variable temperature behavior and by consideration of carbon–carbon coupling constants.

As the temperature is raised to 10°C, the three resonances at δ 186.1, 180.8, 172.8 due to carbonyls *j*, *k* and *l* on the Os(1) atom become broad. Of these three signals, the resonance at δ 186.1 shows ^{13}C satellites ($^2J(CC) = 22.2$ Hz) in the spectrum at −10°C; it therefore is assigned to the carbonyl ligand *j* trans to the acyl carbon *a*. The acyl carbon resonates at δ 175.2 with the same coupling ($^2J(CC) = 22.2$ Hz) and remains sharp at higher temperatures. Thus the line broadening is due to localized threefold exchange at the Os(1) atom. Both signals at δ 189.4 and 189.0 exhibit an AB pattern of ^{13}C satellites ($^2J(CC) = 35.0$ Hz), characteristic of inequivalent trans axial carbonyl ligands, *c* and *f*. Increasing the temperature to 40°C, another set of three resonances at δ 189.0, 180.1 and 177.2 broaden to the same extent, while the resonance at δ 189.4 remains sharp. This result is due to localized threefold exchange at the $(CO)_4Os(3)$ center, as previously observed for the analogous center in $HOs_3(CO)_{10}(COCH_3)$ [18] and compound **1** [1b]. The resonances at δ 180.1 and 177.2 are therefore assigned to the two equatorial carbonyl ligands *d* and *e* on the Os(3) atom. The remaining three signals which become broad at the slowest rate are assigned to the three carbonyl ligands *g*, *h* and *i* on the Os(2) atom. It is apparent that the activation barriers for localized threefold carbonyl exchange in **4** increase as Os(1) < Os(3) < Os(2), which is similar in trend to **1** [1b].

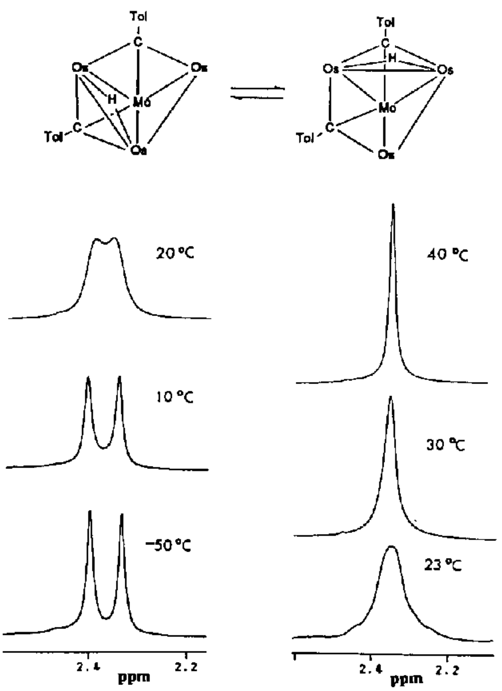


Fig. 3. Variable-temperature ^1H NMR spectra (300 MHz, $CDCl_3$) of methyl resonances of $CpMoOs_3(CO)_{10}(\mu_3\text{-CTol})_2(\mu\text{-H})$. The cyclopentadienyl and carbonyl ligands are omitted for clarity.

Solution dynamics of 5

It has been proposed that compound **2**, $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2(\mu\text{-H})$, undergoes a degenerate framework rearrangement which interchanges the two possible enantiomeric forms [1c] (see Fig. 3). This was viewed as breaking and making hydrogen-bridged metal–metal bonds. The variable-temperature ^1H NMR spectra of compound **5**, $CpMoOs_3(CO)_{10}(\mu_3\text{-CTol})_2(\mu\text{-H})$, also show two distinct methyl resonances at −50°C, arising from the tolyl moieties, which broaden at higher temperatures and coalesce at 23°C (300 MHz) as shown in Fig. 3. This indicates that the same framework rearrangement is also operative in compound **5**. Free energy of activation ($\Delta G_c^{\neq}$) for the fluxional process was derived from the coalescence temperature (T_c) and peak separation ($\delta\nu$) using the Eyring equation as given in eq. 4 [19].

$$\Delta G_c^{\neq} = 4.575 \times 10^{-3} T_c [9.972 + \log(T_c/\delta\nu)] \text{ kcal/mol} \quad (4)$$

The analysis gave $\Delta G_c^{\neq} = 15.2 \pm 0.2$ kcal/mol for the enantiomer-interchange process of **5**, which is comparable with the value of 15.7 ± 0.3 kcal/mol for **2** [1c].

Acknowledgment

We are grateful to the Korea Science and Engineering Foundation for financial support of this research.

References

1 (a) J.R. Shapley, J.T. Park, M.R. Churchill, C. Bueno and H.J. Wasserman, J. Am. Chem. Soc., 103 (1981) 7385; (b) J.T. Park, J.R. Shapley, M.R. Churchill and C. Bueno, Inorg. Chem., 22 (1983) 1579; (c) J.T. Park, J.R. Shapley, M.R. Churchill and C. Bueno, *ibid.*, 23 (1984) 4476; (d) J.R. Shapley, J.T. Park, M.R. Churchill, J.W. Ziller and L. Beanan, J. Am. Chem. Soc., 106 (1984) 1144; (e) J.T. Park, J.R. Shapley, M.R. Churchill and C. Bueno, *ibid.*, 105 (1983) 6182; (f) M.R. Churchill, C. Bueno, J.T. Park and J.R. Shapley, Inorg. Chem., 23 (1984) 1017; (g) J.T. Park, J.R. Shapley, M.R. Churchill and C. Bueno, Organometallics, 7 (1988) 2307; (h) J.T. Park and J.R. Shapley, Bull. Korean Chem. Soc., 11 (1990) 531.
2 (a) W.L. Gladfelter and G.L. Geoffroy, Adv. Organomet. Chem., 18 (1980) 207; (b) D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and E.N. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 6, Pergamon, Oxford, 1982, pp. 763–877.
3 (a) M.R. Churchill, C. Bueno and H.J. Wasserman, Inorg. Chem., 21 (1982) 640; (b) Y. Chi and J.R. Shapley, Organometallics, 4 (1985) 1900.
4 J.T. Park, K.M. Chun, S.S. Yun and S. Kim, Bull. Korean Chem. Soc., 12 (1991) 249.
5 L.Y. Hsu, W.-L. Hsu, D.-Y. Jan and S.G. Shore, Organometallics, 5 (1986) 1041.
6 S.A.R. Knox, J.W. Koepke, M.A. Andrew and H.D. Kaesz, J. Am. Chem. Soc., 97 (1975) 3942.
7 (a) E.O. Fischer, A. Schwanzer, H. Fischer, D. Neugebauer and G. Hüttner, Chem. Ber., 110 (1977) 53; (b) E.O. Fischer, T.L. Lindner, G. Hüttner, P. Friedrich, F.R. Kreisel and J.O. Besengard, *ibid.*, 110 (1977) 3397.
8 A.D. Clauss, M. Tachikawa, J.R. Shapley and C.G. Pierpont, Inorg. Chem., 20 (1981) 1528.
9 J.T. Park and K.M. Chun, unpublished results.
10 (a) T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1986) 104; (b) C.E. Coffey, J. Inorg. Nucl. Chem., 25 (1963) 179.
11 J.B. Keister and J.R. Shapley, Inorg. Chem., 21 (1982) 3304 and refs. therein.
12 Y. Chi, J.R. Shapley, M.R. Churchill and Y. Li, Inorg. Chem., 25 (1985) 4165.
13 (a) L.R. Beanan, Z. Abdul Rahman and J.B. Keister, Organometallics, 2 (1983) 1062; (b) J. Hein, J.C. Jeffery, P. Sherwood and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 2211.

14 F.G.A. Stone, in M.H. Chisholm (Ed.), Inorganic Chemistry: Toward the 21st Century, ACS Symp. Ser., 211 (1983) 383.
15 L. Busetto, M. Green, J.A.K. Howard, B. Hessner, J.C. Jeffrey, R.M. Mills, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1981) 1101.
16 (a) K. Wade, Chem. Ber., 11 (1975) 177; (b) K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 1; (c) D.M.P. Mingos and M.I. Forsyth, J. Chem. Soc., Dalton Trans., (1977) 610 and refs. therein.
17 (a) L.J. Todd and J.R. Wilkinson, J. Organomet. Chem., 77 (1974) 1.
18 P.D. Gavens and M.J. May, J. Organomet. Chem., 162 (1978) 389.
19 J. Sandström, Dynamic NMR Spectroscopy, Academic Press, London, 1982, p. 96.