



Chelate ring closing and opening behavior in cyclopentadienyl cobalt(III) complexes with pendant nitrogen functional group

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ARTICLE INFO

Article history:

Received 25 September 2009
Received in revised form 4 November 2009
Accepted 6 November 2009
Available online 11 December 2009

Keywords:

Kinetic studies
Chelation
Substitution
Cyclopentadienyl cobalt(III) complexes
DFT calculations

ABSTRACT

Kinetic studies were performed for the chelate ring closing and opening process of cyclopentadienyl cobalt(III) complexes having a pendant N-functional group with an amine, piperidine or pyridine moiety in the side chain. The metal–nitrogen bond energy was measured. The rate of chelation by such pendant N-functionalized side chains in diiodomonocarbonyl cobalt(III) reaction intermediates is determined by the electronic density on the donor atom and the strength of the forming chelated bond. The steric factor around the donor atom plays a secondary role. On the basis of the enthalpies and entropies obtained from the kinetic studies, the process of chelate ring closing in diiodomonocarbonyl cobalt(III) reaction intermediates is via an associative pathway involving loss of CO, while the chelate ring opening process in the resulted chelators is via a metal–nitrogen bond cleavage, solvation then metal–phosphorus bond formation pathway during substitution of PPh₃. The chelator with the most rigid arm of picolyl shows a smallest steric hindrance for incoming PPh₃ compared to the other two analogues.

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1. Introduction

The hemilability of hybrid ligands in metal complexes has gained much interest because of the fact that the ligands can undergo a reversible metal chelate ring opening process through rupture of the weakest coordinative bond, yielding a coordinatively unsaturated complex. The formation of such coordinatively unsaturated complexes occurs via subtle control of the ligands coordinated to the metal center. The concept of ligand hemilability is useful in explaining the properties of metal complexes and in designing new systems for molecular activation, homogeneous catalysis, functional materials, or small-molecule sensing [1–4]. Although the interplay between electronic and steric properties has long been recognized as essential in determining the chemical or physical properties of a complex, predictions of reactivity can be very difficult, generally because of the small energy differences involved. Each metal may react differently towards the same ligand while different ligands can completely modify the chemistry of a given metal [5–9].

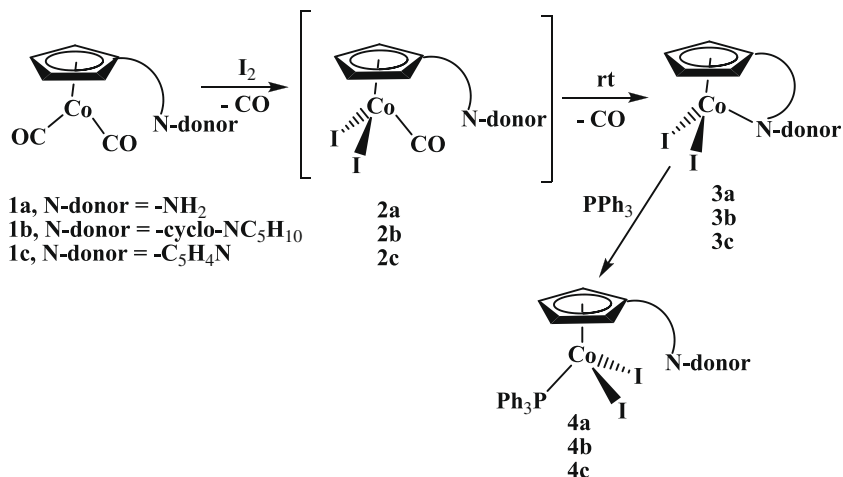
Despite the intense interest in the hemilabile properties of ligands in complexes, there have been relatively few quantitative studies on such chelate ring opening and closing processes [10–14]. It is important to obtain quantitative results in order to gain a better understanding of ligand hemilability. In this purpose, the kinetic study can be used to evaluate the reversible metal chelate ring

opening and closing process. We are studying the properties of metal complexes with nitrogen atom in the functional group attached to a cyclopentadienyl ring. Since cyclopentadienyl ligand can stabilize metal in various oxidation states and the nitrogen atom can form metal–nitrogen bond with intermediate strength, a complex bearing such bidentate ligand must show some hemilability. In our study, we chose amine, piperidine and pyridine, respectively, as the different N-functional groups, where the electronic and steric effects around the donor ligand were altered. Thus bidentate ligands of C₅H₄C₂H₄NH₂, C₅H₄C₂H₄NC₅H₁₀ and C₅H₄CH₂NC₅H₄ were synthesized. It was found that with such bidentate ligands, the binding ability of the donor nitrogen to the metal center was greatly altered and the chemical activity of these complexes varied greatly [15]. This might be attributed to small changes in electronic and steric effects around the donor by different substituent on it. The goal of this paper is to elucidate the mechanism of chelate ring opening and closing process in cobalt complexes with such pendant chelatable functional groups via kinetic study.

2. Results and discussion

The studied chelate ring opening and closing process is depicted in Scheme 1. The N-functional groups in the pendant side chain of the metal complexes involved in this process are amine, piperidine and pyridine, respectively. The synthesis of the corresponding cobalt dicarbonyl compounds (η^5 -C₅H₄C₂H₄NH₂)Co(CO)₂ (**1a**), (η^5 -C₅H₄C₂H₄NC₅H₁₀)Co(CO)₂ (**1b**) and (η^5 -C₅H₄CH₂NC₅H₄)Co(CO)₂ (**1c**) were described in elsewhere [15]. It is known that the

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Scheme 1.

chelators were formed via the diiodomonocarbonyl complexes (vide infra) when its precursor dicarbonyl metal complexes were oxidized by iodine. When iodine was added to the tetrahydrofuran solutions of these dicarbonyl compounds, a strong carbonyl absorption band at higher frequencies compared to the two-carbonyl stretching frequencies of their precursors appeared and then decreased. This was the strong evidence of the existence of monocarbonyl reaction intermediates. The changing of this characteristic IR-active CO absorption band is a sign of the intramolecular displacement of the remaining carbonyl ligand by the pendant amino functional group. And the lifetime or the stability of such corresponding monocarbonyl reaction intermediates **2a**, **2b** and **2c** were compared with the persistence of this CO absorption band [15–17]. The CO stretching frequencies in tetrahydrofuran were similar to that obtained in dichloromethane reported previously [15]. The decay of this absorption band showed the pattern of the first-order reaction, and the plots of $\ln A(\nu_{\text{CO}})$ versus time showed linear relationship (Fig. 1). The observed rates of chelation, $k(\text{chel})_{\text{obs}}$, were obtained from the slope of the linear regression and the activation parameters were obtained from the temperature dependent $k(\text{chel})_{\text{obs}}$ values by Eyring plots. These data were listed in Table 1.

Comparing the data listed in Table 1, it is found that the rate of chelation in **2b** is about five times faster than the corresponding

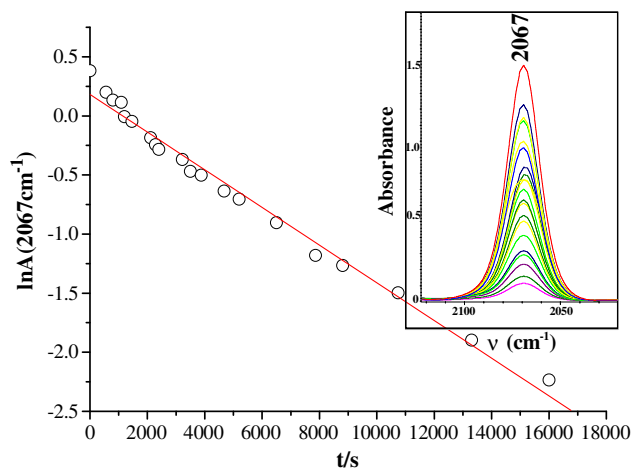


Fig. 1. Plot of $\ln A$ vs. time at $\nu = 2067 \text{ cm}^{-1}$ for the chelation of complex **2b** in THF at $T = 36.0 \text{ }^\circ\text{C}$.

value of **2a** in temperatures ranging from room temperature to about $45 \text{ }^\circ\text{C}$, although the pendant piperidine moiety in **2b** should have much larger steric hindrance around the donor nitrogen atom than the dangled amine moiety in **2a**. The rate of chelation of **2c** was found to be even faster and could not be measured by our simple method. The value of the enthalpy of activation for the chelate ring closure found for **2b** ($54.1 \pm 5.8 \text{ kJ/mol}$) was still a little bit larger than that of **2a** ($45.2 \pm 1.6 \text{ kJ/mol}$), indicating a larger energy barrier during the process of forming the corresponding chelator ($\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NC}_5\text{H}_{10}\text{)}\text{CoI}_2$ (**3b**) compared to ($\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NH}_2\text{)}\text{CoI}_2$ (**3a**). This result agrees with the conclusion that **3b** has a larger steric resistance compared to **3a** deduced from their crystal structures and the COSY spectrum [15–17]. Our results are also consistent with the thermal property of some other d^6 metal carbonyl complexes during chelate ring closure [18–20]. It was found that the chelate ring closure in the reaction of $\text{M}(\text{CO})_5\text{L} \rightarrow \text{M}(\text{CO})_4\text{L} + \text{CO}$, where L was N-substituted bidentate ligands, depended significantly on the extent of steric hindrance about the aliphatic nitrogen atom of the ligand. The rates of chelation were found to be about 12–44 times faster when the donor group is an isopropyl substituted imine compared to an amine depending on the different metal involved. Pyridine was found to have a larger affinity to the metal compared to amine. Changing donor group from amine to pyridine should increase the rate of metal–nitrogen bond formation. A similar trend in the values of the enthalpy of activation depending on the substituent on the donor atom were also found in these d^6 metal carbonyl complexes during the procedure of chelate ring closure [21–27]. The fastest rate of chelation found for **2c** is consistent with these literature results.

The differences in the rates of chelation of these monocarbonyl reaction intermediates can be attributed to the differences in electronic properties of the donor nitrogen in the pendant side chain. The slower rate of chelation observed for **2a** compared to **2b** can be attributed to the weaker σ -donor ability of the amine nitrogen towards the hard metal center of cobalt(III). When the two hydrogen atoms of the amine nitrogen are replaced by an alkyl group such as in piperidine, the electronic density at the nitrogen is increased as does its donor ability. The ability of the nitrogen in displacing the remaining carbonyl group from the pendant side chain and forming a new metal–nitrogen bond should be enhanced and the rate of chelation increased as we observed for **2b**. Obviously steric hindrance plays a secondary role during the chelation [18]. As for **2c**, the nitrogen atom is in an aromatic ring system. The moderate π -acceptor property of the picolyl moiety in the pendant side chain facilitates the formation of a partial double bond

Table 1
Temperature dependence of $k(\text{chel})_{\text{obs}}$ and the activation parameters for the chelation of the monocarbonyl reaction intermediates.

2a		2b		2c	
T (K)	$10^5 \times k(\text{chel})_{\text{obs}}/\text{s}^{-1}$	T (K)	$10^5 \times k(\text{chel})_{\text{obs}}/\text{s}^{-1}$	T (K)	$k(\text{chel})_{\text{obs}}/\text{s}^{-1\text{a}}$
299.0	1.60(0.21)	300.0	8.17(0.42)	299.5	>0.02
304.1	2.36(0.46)	303.9	8.56(0.18)		
309.4	3.04(0.38)	309.2	15.9(0.5)		
313.2	3.87(0.50)	315.1	21.4(1.5)		
318.5	5.34(0.61)	318.7	29.0(1.6)		
$\Delta H^\ddagger = 45.2 \pm 1.6$ kJ/mol		$\Delta H^\ddagger = 54.1 \pm 5.8$ kJ/mol			
$\Delta S^\ddagger = -185 \pm 5$ J/K mol		$\Delta S^\ddagger = -144 \pm 19$ J/K mol			

^a This value represents a lower limit since $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{NC}_5\text{H}_4)\text{CoI}_2$ is formed immediately following oxidation on the experimental timescale. The spectrum was taken 2 min after the addition of iodine to the THF solution of **1c**, only a very small absorbance of M–CO corresponding to **2c** was found, thus $k(\text{chel})_{\text{obs}} > 0.02$.

between the metal and nitrogen when the pyridine plane is perpendicular to the Cp plane and bisects the CpCoI_2 moiety as is found in **2c** [28–30]. This effect combined with less steric hindrance as well as shorter chain in the functionalized arm of **2c** leads to the fastest rate of chelation observed among the three reaction intermediates [31].

It seems that the observed rate of chelation is consistent with two possible mechanisms: a mechanism in which dissociation of CO is followed by chelate ring closing or a mechanism in which the chelate ring forms and then CO dissociates. The later involves a 20-electron species but it can be readily avoided by the coordination of the cyclopentadienyl ring changing from η^5 - to η^3 . In such a mechanism, dissociation of the CO should be the rate-limiting step.

It is known that CO is a good ligand for cobalt(I) complex, but is not good for cobalt(III). As a d^6 metal, cobalt(III) has less electron density to feedback to CO and therefore the metal–CO bond is weaker than that in cobalt(I) complexes. However, monocarbonyl cobalt(III) compounds have been reported as stable complexes even when there is a weak competitive donor functional group such as ether, ester or multiple bonds in a pendant side chain [32–40]. When a nitrogen atom is included in the pendant side chain as in our case, since it is a better donor than oxygen or multiple bonds, the CO was thermally substituted by the amino functional group and metal chelators were formed under mild conditions. The large negative values of the entropy of activation found for **2a** (-185 ± 5 J/K mol) and **2b** (-144 ± 19 J/K mol) support that the chelate ring closure might occur via an associative mechanism.

The associative pathway with a relatively small enthalpy of activation (about 50 kJ/mol) suggests a ring slippage process might be involved in order to avoid an unfavorable 20-electron configuration [41–46]. In 1984, Basolo reported the substitution of d^6 metal complexes, indenylmanganesetricarbonyl, by triphenylphosphine can proceed solely via associative pathways with enthalpy of activation about 66–81 kJ/mol and entropy of activation about -109 to -151 J/K mol under elevated temperature [44]. Three years later, Wakatsuki reported that in the replacement of coordinated 1,5-cyclooctadiene (cod) ligand in $[(\text{C}_5\text{H}_4\text{X})\text{Co}(\text{cod})]$ with norbornadiene in acetonitrile solution, the mechanism changed from dissociative in nature to a dominant associative transition state when the substituent X changed from H to CHO and COCF_3 [47]. The authors attributed this mechanism change to the increasing of positive charge on the metal by the electronic withdrawing effect of the CHO and COCF_3 substituent on the metal through-space, thus enhancing the attack of a nucleophile. A dissociative process in chelate ring closing process usually exhibits larger enthalpy of activation and positive entropy of activation [47,48]. So the dissociative mechanism in chelate ring closing process in **2a**, **2b** and **2c**, which bearing a larger positive charge on metal than Co(I), can thus be excluded and the chelation takes place via an associative transition state is not surprising.

Ligand substitution was also studied to compare the strength of the chelate metal–nitrogen bond in chelators **3a**, **3b** and $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{NC}_5\text{H}_4)\text{CoI}_2$ (**3c**), respectively. All these chelators were stable in acetonitrile solution as there were no detectable absorbance change of the pure compounds after several hours of incubation at 40 °C. With triphenylphosphine as the substituent, kinetic studies of these chelators under pseudo first-order reaction conditions were performed. The concentrations of PPh_3 was varied from 15 to more than 300 times larger than the metal concentration, in some trials even 1000 times larger. In all cases, good isosbestic points were observed in the UV–vis spectra of the reaction mixtures during substitution. For example, the inset in Fig. 2 shows a typical spectral change observed for the reaction of **3b** (1.93×10^{-4} M) and PPh_3 (0.0250 M) in CH_3CN at 35.3 °C. The increased band of absorption at 358 nm was assigned to the MLCT transition and the decreased absorption band at 550 nm was assigned to the d – d transition. The final spectrum of the kinetic experiment was identical to the electronic spectrum of the authentic sample of $(\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NC}_5\text{H}_{10})\text{CoI}_2\text{PPh}_3$. Hence only one product, a monophosphine substituted derivative, was formed in the reaction and no long lifetime intermediates were observed during the substitution [49]. A plot of $\ln(A - A_\infty)$ versus time at $\lambda = 550$ nm for the substitution of **3b** by PPh_3 shows a good linear relationship in Fig. 2. The observed linear relationship indicates that the substitution is first order to the metal complex. The substitution of **3b** by PPh_3 was also run in chloroform. The rate constant $k(\text{subs})_{\text{obs}}$ is obtained from the slope of the linear relationship of each trial. The averages of three trials are listed in Table 2. The

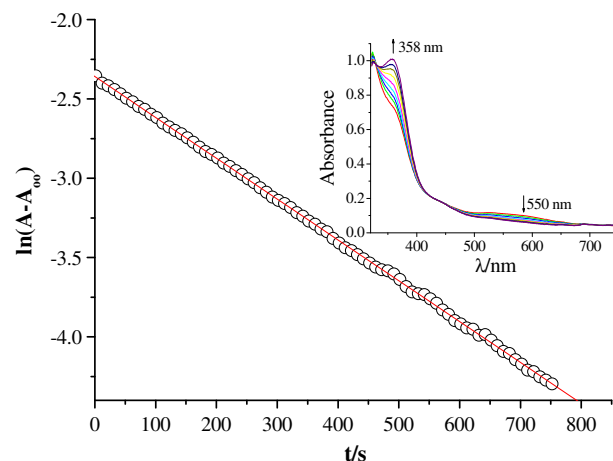


Fig. 2. Plot of $\ln(A - A_\infty)$ vs. time at $\lambda = 550$ nm for the substitution of complex **3b**, diiodo- $\eta^5\text{-}\eta^1\text{-2-N-piperidinoethylcyclopentadienylcobalt(III)$, with triphenylphosphine in CH_3CN at 35.3 °C. Inset. The isosbestic points as found in the UV–vis spectrum.

standard deviations of the averages are given in parentheses. The data from different temperatures ranging from about 21–41 °C at fixed ligand concentration are given in Table 3.

Since a ring slippage mechanism is suggested during the chelate ring closure process, it might also involve in the ring opening process during ligand substitution. Because the dependence of $k(\text{subs})_{\text{obs}}$ by two different solvents was observed, a solvated reaction intermediate might involve in the rate-determining step. Thus a possible mechanism for the reaction of these chelators and PPh₃ is illustrated by Scheme 2. Path D represents the dissociative process involving a solvated ring opened reaction intermediate, path A represents the associative ones involving a ring slippage mechanism. Applying the steady-state assumption for these two intermediates I_5 and I_3 separately yields the rate expression of Eqs. (1) and (2):

$$k(\text{subs}, D)_{\text{obs}} = \frac{k_1 k_2 [\text{L}]}{k_{-1} + k_2 [\text{L}]}, \quad (1)$$

$$k(\text{subs}, A)_{\text{obs}} = \frac{k_3 k_4 [\text{L}]}{k_{-3} + k_4}. \quad (2)$$

They represent the contributions to $k(\text{subs})_{\text{obs}}$ in substitution from path D or path A, respectively. However, if both paths contribute to the reaction would lead to the rate expression of Eq. (3):

$$k(\text{subs})_{\text{obs}} = \frac{k_1 k_2 [\text{L}]}{k_{-1} + k_2 [\text{L}]} + \frac{k_3 k_4 [\text{L}]}{k_{-3} + k_4}. \quad (3)$$

In the plot of $k(\text{subs})_{\text{obs}}$ versus PPh₃ concentration, we see the data points deviate from linearity at higher ligand concentrations and exhibited a tendency toward saturation limiting. A typical plot of $k(\text{subs})_{\text{obs}}$ versus PPh₃ concentration is shown in Fig. 3. If the substitution is mainly via an associative process, then Eq. (3) can be simplified by omitting the first term and reduced to Eq. (2). Thus $k(\text{subs})_{\text{obs}}$ should be proportional to the ligand concentration and show linear relationship. However, this is not consistent with our observations. By contraries, our plot is consistent with Eq. (1), which is obtained by ignoring the second term in Eq. (3). In this case, if the rate constant for the reversion to starting material, k_{-1} , which can be assumed similar to the size of the rate constant of chelation we obtained from its monocarbonyl reaction intermediate, is comparable in size to the rate constant for the reaction with PPh₃, k_2 , considering the concentration of PPh₃ we used in the reaction, there will be a competition for the intermediate. That will result in a dependence of the observed rate constant on PPh₃ concentration as Fig. 3 shows.

The reciprocal plots of $1/k(\text{subs})_{\text{obs}}$ versus $1/[\text{PPh}_3]$ show good linear relationship in the whole range of ligand concentrations with a non zero interception (Fig. 4). The reciprocal expression of Eq. (3) does not show a simple relationship with the reciprocal of ligand concentration. But if the value of k_3 is too small, one can

Table 3

Temperature dependence of $k(\text{subs})_{\text{obs}}$ and the activation parameters for the substitution of the chelators.

3a , [Co] = 2.15×10^{-4} M, [PPh ₃] = 0.0523 M		
$\lambda = 540$ nm (<i>d-d</i> band)		
Temp./K	$10^3 \times k(\text{subs})_{\text{obs}}/\text{s}^{-1}$	$10^3 \times k_1/\text{s}^{-1}$
294.4	1.35(0.32)	4.21
298.8	1.72(0.39)	5.35
303.6	2.14(0.30)	6.66
308.4	3.18(0.38)	10.1
314.0	4.72(0.62)	14.7
$\Delta H_1^\ddagger = 47 \pm 3$ kJ/mol		
$\Delta S_1^\ddagger = -131 \pm 11$ J/K mol		
3b , [Co] = 1.93×10^{-4} M, [PPh ₃] = 0.0250 M		
$\lambda = 550$ nm (<i>d-d</i> band)		
Temp./K	$10^3 \times k(\text{subs})_{\text{obs}}/\text{s}^{-1}$	$10^3 \times k_1/\text{s}^{-1}$
294.2	1.44(0.30)	2.45
298.2	1.95(0.35)	3.31
302.2	2.31(0.16)	4.20
308.5	3.19(0.24)	5.43
314.7	5.58(1.00)	9.50
$\Delta H_1^\ddagger = 46 \pm 4$ kJ/mol		
$\Delta S_1^\ddagger = -139 \pm 13$ J/K mol		
3c , [Co] = 8.27×10^{-5} M, [PPh ₃] = 0.0250 M		
$\lambda = 530$ nm (<i>d-d</i> band)		
Temp./K	$10^3 \times k(\text{subs})_{\text{obs}}/\text{s}^{-1}$	$10^3 \times k_1/\text{s}^{-1}$
293.7	0.547(0.12)	0.746
297.2	0.768(0.22)	1.05
301.7	1.61(0.48)	2.20
307.4	2.43(0.66)	3.30
313.0	4.58(0.86)	6.24
$\Delta H_1^\ddagger = 82 \pm 5$ kJ/mol		
$\Delta S_1^\ddagger = -27 \pm 17$ J/K mol		

ignore the contribution from path A, thus Eq. (3) can be reduced to Eq. (1), which gives a simple reciprocal expression with a non zero interception as Eq. (4):

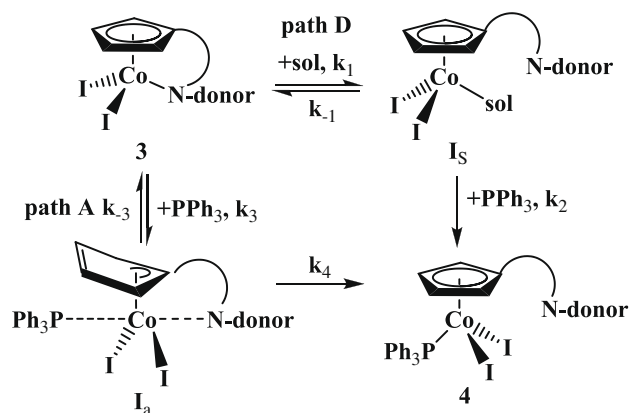
$$\frac{1}{k(\text{subs})_{\text{obs}}} = \frac{k_{-1}}{k_1 k_2} \cdot \frac{1}{[\text{L}]} + \frac{1}{k_1}. \quad (4)$$

Since PPh₃ is a ligand with large core angle, the formation of I_3 requires large activation energy to overcome the steric hindrance and strain in chelated structure caused by ring slippage, ignore the contribution from path A is reasonable. If one try to ignore the contribution from path D, then Eq. (3) will be reduced to Eq. (2). Its reciprocal expression would have a zero interception and is not consistent with our experimental results. Although we cannot exclude the contribution of path A in the substitution process,

Table 2

$k(\text{subs})_{\text{obs}}$ for the chelators in substitution reaction with different ligand concentration from the *d-d* band.

3a (in acetonitrile)	3b (in acetonitrile)	3c (in acetonitrile)	3b (in chloroform)
[Co] = 2.15×10^{-4} M $T = 308.4$ K	[Co] = 1.93×10^{-4} M $T = 302.2$ K	[Co] = 8.27×10^{-5} M $T = 307.4$ K	[Co] = 1.71×10^{-4} M $T = 302.2$ K
[PPh ₃]/M	[PPh ₃]/M	[PPh ₃]/M	[PPh ₃]/M
$10^3 \times k(\text{subs})_{\text{obs}}/\text{s}^{-1}$	$10^3 \times k(\text{subs})_{\text{obs}}/\text{s}^{-1}$	$10^3 \times k(\text{subs})_{\text{obs}}/\text{s}^{-1}$	$10^3 \times k(\text{subs})_{\text{obs}}/\text{s}^{-1}$
0.215	0.0250	0.0250	0.00469
0.157	0.0171	0.0185	0.00667
0.110	0.0128	0.0132	0.01370
0.0523	0.00831	0.00726	0.02347
0.0256	0.00290	0.00208	
$10^3 \times k_1 = 10.8(0.7)$	$10^3 \times k_1 = 4.21(0.13)$	$10^3 \times k_1 = 2.81(0.04)$	$10^3 \times k_1 = 3.60(0.35)$
$k_{-1}/k_1 k_2 = 12.2(0.3)$	$k_{-1}/k_1 k_2 = 4.96(0.04)$	$k_{-1}/k_1 k_2 = 2.91(0.02)$	$k_{-1}/k_1 k_2 = 3.73(0.20)$
$k_2/k_{-1} = 7.55$	$k_2/k_{-1} = 48.0$	$k_2/k_{-1} = 122$	$k_2/k_{-1} = 74.4$



Scheme 2.

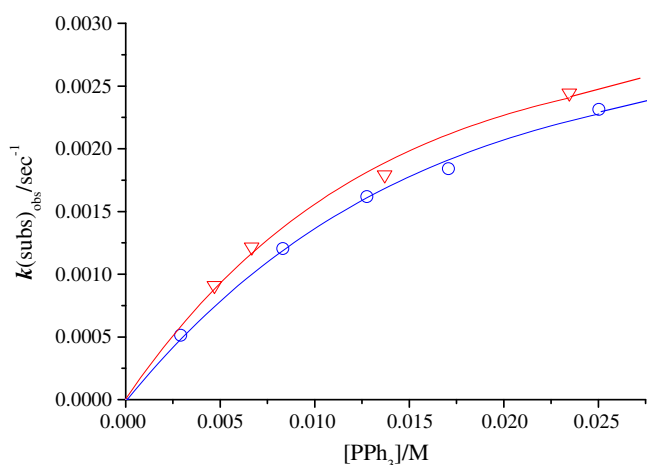


Fig. 3. Plot of $k(\text{subs})_{\text{obs}}$ vs. $[\text{PPh}_3]$ for **3b** at 29.0 °C in different solvents (circles were data point from acetonitrile, triangles were from chloroform). Both plots show clearly the deviation from linear relationship.

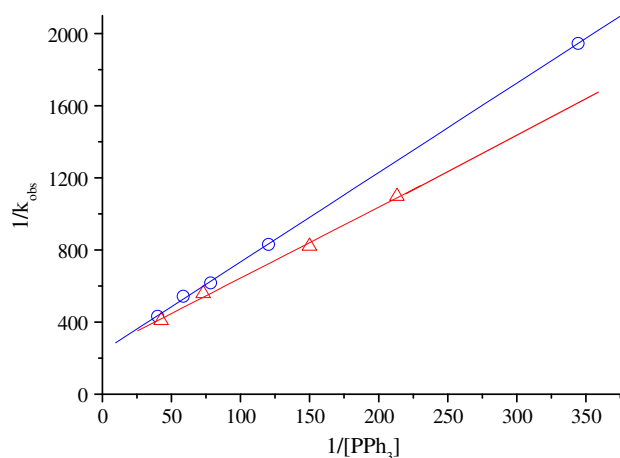


Fig. 4. Plots of $1/k(\text{subs})_{\text{obs}}$ vs. $1/[\text{PPh}_3]$ for **3b** at 29.0 °C which show good linear relationships and non zero intercepts with $R^2 \geq 0.997$. Circles are data from acetonitrile and triangles are data from chloroform.

it is logical to assume that the dominant process of the substitution is via path D. According to Eq. (4), our experimental data gave satisfactory correlation coefficients ($R^2 \geq 0.997$). From the plots of $1/k(\text{subs})_{\text{obs}}$ versus $1/[\text{PPh}_3]$, we obtained k_1 from the intercepts and

k_{-1}/k_1k_2 from the slopes (Table 2). Assuming the change of the competitive ratio of k_2/k_{-1} in the temperature range of our reaction is small [50,51], the activation parameters of ΔH_1^\ddagger and ΔS_1^\ddagger can be calculated from the temperature dependent k_1 via Eyring plot. All the calculated kinetic parameters are listed in Table 3.

Since bond breaking is a slow process compared to chelation or substitution, k_1 should be the rate-determining step. The obtained enthalpy of activation ΔH_1^\ddagger should include two contributions: the Co–N bond energy of the chelator and the released solvation energy to form a ring opened reaction intermediate I_S . It was reported that a metal–solvent bond in a coordinatively unsaturated cyclopentadienyl metal carbonyl compound is about 8 kJ/mol [52–54]. Thus the energy needed to break the chelated bond might be about 54 kJ/mol estimated from the summation of ΔH_1^\ddagger (about 46 kJ/mol for **3a** and **3b**) and the solvation energy from Yang's data. This value is similar to the values of ΔH^\ddagger (45.2 ± 1.6 kJ/mol found for **2a** and 54.1 ± 5.8 kJ/mol found for **2b**, respectively) obtained in their chelate ring closing processes within experimental errors. All these values are very close to 50 kJ/mol, in accordance with the definition to a hemilabile bond given by Braunstein [55]. The value of ΔH_1^\ddagger obtained for **3c** was about 73% larger than the values obtained from **3a** and **3b**. This can be attributed to the partial double bond in **3c** and due to the loss of a perfect symmetric structure during substitution. Fig. 5 shows the results from the DFT calculation, demonstrating the delocalization of the electronic density of the HOMO orbital in **3c**. Besides the Co–N bond, a moderate π -interaction between cobalt(III) and the picolyl moiety must be ruptured during substitution, a relatively high enthalpy of activation is reasonable. Compared to the typical dissociative bond breaking process (~ 135 kJ/mol), the value of the enthalpy of activation, ΔH_1^\ddagger , found for **3a**, **3b** and **3c** is small [56].

The negative values of ΔS_1^\ddagger found suggest that the transition state involve a very strong solvation of the ring opened intermediate I_S rather than a coordinatively unsaturated species [54,57,58]. In this case, an outer-sphere complex with a loosely bound PPh_3 in the activated solvated ring opened intermediate is formed; at the same time, the solvent molecule is still bonded to the metal. This close association of the incoming ligand and the solvated ring opened reaction intermediate contributes a negative entropy value to the transition state. A similar mechanism was also found during the substitution of chelated cymantrene derivatives by phosphines and phosphates [57]. In that case, the value of the enthalpy of activation ΔH^\ddagger was found to be 94.1 kJ/mol and the entropy of activation ΔS^\ddagger was found -41 J/Kmol. Since it was reported that

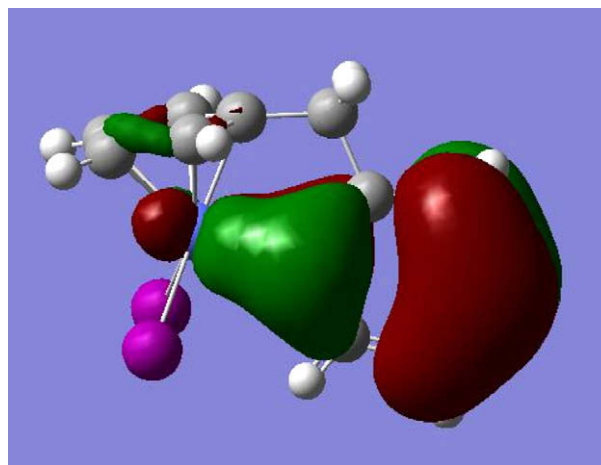


Fig. 5. Result from DFT calculations, showing the electronic density of the HOMO orbital in **3c**. The perfect symmetric structure facilitates the bondage between the cobalt(III) atom and the picolyl moiety through π -interaction.

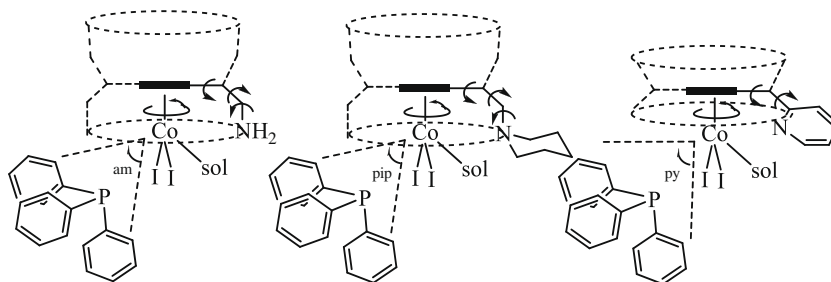


Fig. 6. The rotated Cp ring with its arm looks like a bell over the metal. Open space of the reaction intermediate with different pendant side chains show varying steric hindrance towards the incoming triphenylphosphine.

cyclopentadienyl dicarbonyl cobalt(I) derivatives had values of ΔH^\ddagger of about 66–77 kJ/mol for phosphine substitution via a ring slippage process [46], the contribution from the associative pathway to our substitution process cannot be totally ruled out.

The order of the value of k_1 is contrary to the order of $k(\text{chel})_{\text{obs}}$ found for **2a**, **2b** and **2c**. Since the rate constant k_1 describes the rupture of the chelated Co–N bond and the formation of a solvated reaction intermediate, the smallest k_1 value found for **3c** implies that the metal–nitrogen bond in **3c** is the most difficult one to rupture. The rate of chelate ring closing in coordinatively unsaturated metal complex is known as an ultrafast process and depends on the forming ring size [59–62]. The solvated ring opened reaction intermediate I_5 depicted in Scheme 2 are expected to be nearly identical in electronic property of the metal in spite of the different functional groups in their side chains. The effect of steric hindrance around the metal on k_{-1} should be similar as its effect on $k(\text{chel})_{\text{obs}}$. So the order of k_{-1} for the three chelators should be similar to what was found for their $k(\text{chel})_{\text{obs}}$. Thus, the competitive ratio of k_2/k_{-1} can be used to estimate the steric hindrance during the attack of the incoming nucleophile. **3c** is expected to have the largest k_{-1} since we found that the rate of chelation, $k(\text{chel})_{\text{obs}}$, for **2c** is the fastest one among the three analogues. Therefore the largest value of k_2/k_{-1} found for **3c** might imply the largest value of k_2 among the three analogues. Imagining the rapid rotation of Cp ring with its arm in a reaction intermediate, it looks like a bell hang over the metal (Fig. 6). The rigid methylene side chain with less rotational freedom might make the intermediate I_5 of **3c** showing largest open space for an incoming nucleophile compared to **3b** and **3a**. Triphenylphosphine is a ligand of large cone angle and is sensitive to steric influence during reactions [47,63]. The congested environment around the metal during substitution plays a larger influence on k_2 than the steric influence around the pendant nitrogen on k_{-1} . If this is true, then there might be a trend of angle of open space $\theta_{\text{am}} \sim \theta_{\text{pip}} < \theta_{\text{py}}$ in their structures as depicted in Fig. 6.

3. Conclusions

The results from this study clearly affirm that the Co(III)–N bond strength is in the range of hemilabile bond. The rate of chelation by a pendant N-functionalized side chain in diiodomonocarbonyl cobalt(III) reaction intermediates is determined by the electronic density on the donor atom and the strength of the forming chelated bond. The steric hindrance around the donor atom plays a secondary role. On the basis of entropies and enthalpies obtained by kinetic studies, the process of chelate ring closing by a hemilabile ligand in diiodomonocarbonyl cobalt(III) reaction intermediate is via associative pathway involving loss of CO. Although Co–N bond cleavage was found the rate-determining step in the substitution of triphenylphosphine to the chelators, ultrafast salvation occurs before the triphenylphosphine attack the metal. The solvated ring opened reaction intermediate with the rigid arm of

picolyl might have less steric hindrance for the incoming triphenylphosphine compared to the other two analogues.

4. Experimental

4.1. General

All manipulations were carried out under a purified nitrogen atmosphere using standard Schlenk techniques except where mentioned. All reagents were purchased from commercial sources (Acros organics or Lancaster Synthesis Ltd.) in the highest available purity and used as received. Solvents were purified by standard methods, distilled under nitrogen before use. Glassware was heated under vacuum and then flushed with N_2 prior to use.

4.2. Instrumentation

IR spectra were recorded on a Nicolet Avatar-360 FT-IR spectrometer with a 0.2 mm NaCl IR cell at a resolution of 2 cm^{-1} . UV–vis spectra were recorded on an Agilent diode-array model 8453 at a resolution of 1 nm. ^1H NMR spectra were recorded on a Bruker AVAVCE-DMX 500 NMR spectrometer or a JEOL ECA400 NMR spectrometer. The chemical shifts are reported in ppm referenced to tetramethylsilane.

4.3. Reagents

The dicarbonyl complexes of $(\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NH}_2)\text{Co}(\text{CO})_2$ (**1a**), $(\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NC}_5\text{H}_{10})\text{Co}(\text{CO})_2$ (**2a**), $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{NC}_5\text{H}_4)\text{Co}(\text{CO})_2$ (**3a**), chelators of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NH}_2)\text{CoI}_2$ (**3a**), $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NC}_5\text{H}_{10})\text{CoI}_2$ (**3b**), $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{NC}_5\text{H}_4)\text{CoI}_2$ (**3c**) and $\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NC}_5\text{H}_{10})\text{CoI}_2\text{PPh}_3$ are synthesized according to the literature method [15] and their identities confirmed by ^1H NMR and IR spectra.

4.4. Kinetic measurements

The rates of chelation were obtained by monitoring spectral changes of $\nu(\text{CO})$ in the IR region for diiodomonocarbonyl cobalt complexes $(\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NH}_2)\text{Co}(\text{CO})\text{I}_2$ (**2a**), $(\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{NC}_5\text{H}_{10})\text{Co}(\text{CO})\text{I}_2$ (**2b**) and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{NC}_5\text{H}_4)\text{Co}(\text{CO})\text{I}_2$ (**2c**) prepared in situ. In a typical experiment, the cobalt dicarbonyl compound was dissolved in tetrahydrofuran at a concentration of 0.25 M. The solution of cobalt dicarbonyl was kept in a thermostatic bath. A tetrahydrofuran solution with equal molar of iodine was placed in the same bath for at least 20 min before being added to the cobalt dicarbonyl solution. After rapid stirring, an aliquot of the reaction mixture was taken periodically and transferred to an IR cell. The IR cell was sealed with a Teflon stopper and flushed with N_2 prior to use. The reactions were followed by monitoring the decrease of the carbonyl absorption at

2073 cm^{-1} for **2a** and 2067 cm^{-1} for **2b** for more than 2 half-lives. Plots of $\ln A$ versus time were linear with a correlation coefficient > 0.995 . $k(\text{chel})_{\text{obs}}$ was obtained from the slope of the line determined by the least squares method with the program origin 7.0.

Rate data for the substitution of cobalt chelators by triphenylphosphine were obtained by monitoring spectral changes in both MLCT and $d-d$ transition bands in UV–vis regions. Stock solutions of the cobalt chelators and the ligand triphenylphosphine were prepared in acetonitrile or chloroform and sealed in serum bottles under N_2 atmosphere before use. The temperatures of the reaction were kept within 0.1 $^\circ\text{C}$ with an external circulation bath (Superthermostate model DC-2006 with XTT-7 controller, ethylene glycol coolant). The volumes of the ligand solutions were measured at room temperature and the concentrations at working temperature were corrected for volume expansion. The ligand concentrations were at least 15 times greater than that of the metal chelators to ensure pseudo first-order reaction conditions. Ligand solutions without cobalt chelators served as blanks during the kinetics measurements. In a typical experiment, the stock ligand solution was transferred into a rubber septum-stopped 1.0 cm quartz cuvette equipped with a small magnetic stirring bar and then placed in the cuvette holder of the spectrometer for 15–20 min before injecting the metal solution and initiating the collection of kinetic data. Rate constants were determined by monitoring the changes of the absorption of **3a** at 338 and 540 nm, **3b** at 358 and 550 nm, **3c** at 365 and 530 nm, respectively, in the absorbance range between 0 and 1.0. $k(\text{subs})_{\text{obs}}$ data were calculated by employing a linear least square computer program (Agilent' online workstation) or from $\ln(A_t - A_\infty)$ versus time plots with the program origin 7.0. The activation parameters ΔH^\ddagger and ΔS^\ddagger were obtained by Eyring plots from both the MLCT bands and $d-d$ transition bands. Since the results from the two regions match each other, only results from $d-d$ band were listed in tables.

4.5. DFT calculations

Single point calculations based on geometries from XRD data were performed using GAUSSIAN 03 (REVISION B.03) [64]. The B3LYP hybrid density functional method was employed in all the calculations [65–67], combining LanL2DZ basis set on I and 6-31G* basis set on Co, C, H, N and O [68,69].

Acknowledgments

Support for this work was provided by the National Natural Science Foundation of China, Grant No. 20471016 and also by Shanghai Leading Academic Discipline Project, Project No. B108.

References

- [1] C. Abu-Gnim, I. Amer, J. Mol. Catal. 85 (1993) L275–L278.
- [2] F. Fache, E. Schultz, M.L. Tommasino, M. Lemaire, Chem. Rev. 100 (2000) 2159–2232.
- [3] C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc., Dalton Trans. (2001) 2989–2995.
- [4] P. Braunstein, F. Naud, Angew. Chem., Int. Ed. 40 (2001) 680–699.
- [5] J. Andrieu, J.-M. Camus, P. Richard, R. Poli, L. Gonsalvi, F. Vizza, M. Peruzzini, Eur. J. Inorg. Chem. (2006) 51–61.
- [6] G. Marangoni, B. Pitteri, G. Annibale, M. Bortoluzzi, Eur. J. Inorg. Chem. (2006) 765–771.
- [7] C.L. Boyd, E. Clot, A.E. Guiducci, P. Mountford, Organometallics 24 (2005) 2347–2367.
- [8] D. Reddy, D. Jaganyi, Transition Met. Chem. 31 (2006) 792–800.
- [9] W.J. Knebel, R.J. Angelici, Inorg. Chem. 13 (1974) 627–631.
- [10] M. Bassetti, Eur. J. Inorg. Chem. (2006) 4473–4482.
- [11] T.C. Flood, J.K. Lim, M.A. Deming, Organometallics 19 (2000) 2310–2317.
- [12] L. Gonsalvi, H. Adams, G.J. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 124 (2002) 13597–13612.
- [13] H.C. Martin, N.H. James, J. Aitken, J.A. Gaunt, H. Adams, A. Haynes, Organometallics 22 (2003) 4451–4458.
- [14] J.M. Wilson, G.J. Sunley, H. Adams, A. Haynes, J. Organomet. Chem. 690 (2005) 6089–6095.
- [15] L. Li, S. Han, Q. Li, Z. Chen, Z. Pang, Eur. J. Inorg. Chem. (2007) 5127–5137.
- [16] P. Jutzi, M.O. Kristen, J. Dahlhaus, B. Neumann, H.G. Stammer, Organometallics 12 (1993) 2980–2985.
- [17] P. Jutzi, M.O. Kristen, B. Neumann, H.-G. Stammer, Organometallics 13 (1994) 3854–3861.
- [18] K.B. Reddy, R. Eldik, Organometallics 9 (1990) 1418–1421.
- [19] L. Chan, A.J. Lees, J. Chem. Soc., Dalton Trans. (1987) 513–517.
- [20] P.H. Wermer, C.B. Dobson, G.R. Dobson, J. Organomet. Chem. 311 (1986) C47–C50.
- [21] S. Zhang, V. Zang, G.R. Dobson, E. Van, Inorg. Chem. 30 (1991) 355–356.
- [22] G.R. Dobson, J.E. Cortes, Inorg. Chem. 28 (1989) 539–544.
- [23] S. Zhang, G.R. Dobson, Inorg. Chem. 29 (1990) 598–602.
- [24] K.J. Asali, Z. Van, J. Gideon, G.R. Dobson, Inorg. Chem. 27 (1988) 3314–3319.
- [25] G.R. Dobson, J.E. Cortes, Inorg. Chem. 27 (1988) 3308–3314.
- [26] G.R. Dobson, C.B. Dobson, S.E. Mansour, Inorg. Chim. Acta 100 (2) (1985) L7.
- [27] G.R. Dobson, S.E. Mansour, D.E. Halverson, E.S. Erikson, J. Am. Chem. Soc. 105 (1983) 5505–5506.
- [28] S. Ašperger, B. Cetina-Čizmek, Inorg. Chem. 35 (1996) 5232–5236.
- [29] C.R. Johnson, R.E. Shepherd, Inorg. Chem. 22 (1983) 3506–3513.
- [30] T. Uno, K. Hatano, T. Nawa, K. Nakamura, Y. Nishimura, Y. Arata, Inorg. Chem. 30 (1991) 4322–4327.
- [31] M.J. Schadt, N.J. Gresalfi, A.J. Lees, J. Chem. Soc., Chem. Commun. (1984) 506–508.
- [32] Z. Pang, X.F. Hou, Z.E. Huang, R.F. Cai, R.Y. Ruan, Synth. React. Inorg. Met. Org. Chem. 8 (2000) 1459–1476.
- [33] X.F. Hou, Z. Pang, Y.F. Xu, R.F. Cai, Z.E. Huang, Chin. J. Chem. 5 (2000) 733–739.
- [34] M. Enders, G. Ludwig, H. Pritzkow, Organometallics 20 (2001) 827–833.
- [35] C.D. Ontiveros, J.A. Morrison, Organometallics 5 (1986) 1446–1448.
- [36] R.F. Heck, Inorg. Chem. 4 (1965) 855–857.
- [37] R.B. King, Inorg. Chem. 5 (1) (1966) 82–87.
- [38] N.E. Schore, C.S. Ilenda, M.A. White, H.E. Bryndza, M.G. Maturro, R.G. Bergman, J. Am. Chem. Soc. 106 (1984) 7451–7461.
- [39] E.R. Evitt, R.G. Bergman, J. Am. Chem. Soc. 102 (1980) 7003–7011.
- [40] N.E. Schore, C. Ilenda, R.G. Bergman, J. Am. Chem. Soc. 98 (1976) 7436–7438.
- [41] M.E. Rerek, F. Basolo, J. Am. Chem. Soc. 106 (1984) 5908–5912.
- [42] D.L. Lichtenberger, S.K. Renshaw, F. Basolo, M. Cheong, Organometallics 10 (1991) 148–156.
- [43] M. Cheong, F. Basolo, Organometallics 7 (1988) 2041–2044.
- [44] L.N. Ji, M.E. Rerek, F. Basolo, Organometallics 3 (1984) 740–745.
- [45] M.E. Rerek, F. Basolo, Organometallics 2 (1983) 372–376.
- [46] Y. Wakatsuki, H. Yamazaki, T. Kobayashi, Y. Sugawara, Organometallics 6 (1987) 1191–1196.
- [47] D.J. Taube, R. van Eldik, P.C. Ford, Organometallics 6 (1987) 125–129.
- [48] G. Schmidt, H. Paulus, R. van Eldik, H. Elias, Inorg. Chem. 27 (1988) 3211–3214.
- [49] R.S. Drago, Physical Methods for Chemists, second ed., Saunders College Publishing, 1992.
- [50] C.L. Hyde, D.J. Darensbourg, Inorg. Chem. 12 (1973) 1286–1291.
- [51] W.D. Covey, T.L. Brown, Inorg. Chem. 12 (1973) 2820–2825.
- [52] J.K. Klassen, G.K. Yang, Organometallics 9 (1990) 874–876.
- [53] D.M. Hester, J. Sun, A.W. Harper, G.K. Yang, J. Am. Chem. Soc. 114 (1992) 5234–5240.
- [54] P.F. Yang, G.K. Yang, J. Am. Chem. Soc. 114 (1992) 6937–6938.
- [55] P. Braunstein, J. Organomet. Chem. 689 (2004) 3953–3967.
- [56] Z. Pang, R.F. Johnston, Polyhedron 18 (1999) 3469–3477.
- [57] M.J. Schadt, N.J. Gresalfi, A.J. Lees, Inorg. Chem. 24 (1985) 2942–2946.
- [58] R.H. Hill, M.S. Wrighton, Organometallics 6 (1987) 632–638.
- [59] T. Jiao, Z. Pang, T.J. Burkey, R.F. Johnston, T.A. Heimer, V.D. Kleiman, E.J. Heilweil, J. Am. Chem. Soc. 121 (1999) 4618–4624.
- [60] B.S. Creaven, A.J. Dixon, J.M. Kelly, C. Long, M. Poliakoff, Organometallics 6 (1987) 2600–2605.
- [61] G.R. Dobson, C.B. Dobson, S.E. Mansour, Inorg. Chem. 24 (1985) 2179–2184.
- [62] S. Zhang, I.H. Wang, P.H. Wermer, C.B. Dobson, G.R. Dobson, Inorg. Chem. 31 (1992) 3482–3488.
- [63] C.A. Tolman, Chem. Rev. 77 (1977) 313–348.
- [64] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., Gaussian Inc., Pittsburgh, PA, 2003.
- [65] A.D. Becke, Phys. Rev. A 38 (1988) 3098–3100.
- [66] C. Lee, W. Yang, R.D. Parr, Phys. Rev. B 37 (1988) 785–789.
- [67] N. Galland, Y. Hannachi, D.V. Lanzisera, L. Andrews, Chem. Phys. 255 (2000) 205–215.
- [68] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270–283.
- [69] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284–298.