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# Substitution reactions of NN chelating atoms of organoplatinum (II) complexes with phosphorous donor reagents

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#### ABSTRACT

Substitution reactions of the chelate 2,2'-bipyridine ligand in the organoplatinum(II) complexes of general formula [PtR<sub>2</sub>(NN)] (NN = 2,2'-bipyridine, and R = CH<sub>3</sub>, **1**, or R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, **1**') by the P donor reagents L, L = P(O<sup>-i</sup>Pr)<sub>3</sub> or PPh<sub>3</sub> or L<sub>2</sub> = dppm, bis(diphenylphosphino)methane, to form the complexes *cis*-[R<sub>2</sub>PtL<sub>2</sub>] were studied. Each of the complexes **1** and **1**' has an MLCT band in the visible region which was used to easily follow kinetics of the related ligand substitution reactions by UV–Vis spectroscopy. Although the complex **1** or **1**' contains two *cis* Pt–C bonds, the involved substitution reaction followed a normal associative mechanism. The reaction rates were found to be dependent on concentration and nature of the entering group, while independent of the presence of excess free NN leaving group. Reaction of the complex **1** with P(O<sup>-i</sup>Pr)<sub>3</sub> proceeded some 20 times faster than similar reaction with the complex **1**'. The  $\Delta H^{\dagger}/\Delta S^{\dagger}$  compensation plot gives a straight line suggesting operation of the same mechanism involving all the entering nucleophiles.

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#### 1. Introduction

Organoplatinum complexes propose extensive scope for different studies including design of catalysis for organic synthesis and exploring new therapeutic agents, in which substitution reactions play an important role. Thus, for example a key concept in designing anticancer complexes is optimization of their chemical reactivity in ligand substitution reactions to allow facile attack on the target site (e.g., DNA) yet avoid attack on other sites associated with unwanted side effects [1,2]. Ligand substitution reactions on square planar platinum(II) complexes have been extensively studied [2-8] and are usually interpreted in terms of an associative process, which implies the formation of 18e five-coordinated intermediates [9,10]. However, to the best of our knowledge, such reactions have not been studied on reactions during which a neutral chelate ring opening is taken place in organoplatinum complexes. On the other hand, chelate ring closure reactions in the complexes  $[Pt(bph)(S(CH_3)_2)_2]$ (bph = 2, 2'-biphenyl dianion) and  $[PtPh_2(S(CH_3)_2)_2]$ , each bearing two Pt-C bonding, with reagents potentially having bidentate chelate donor abilities such as bipyridine, phenanthroline or 1,2-(diphenylphosphino)ethane, have been investigated and shown to occur through a dissociative path [11]. The ligand dissociation step is facilitated by the strong trans-influence of the alkyl or arvl group, which weakens the M–L bonds, while the alternative associative mechanism is less favored because the electron-rich platinum center is resistant to nucleophilic attack [11]. Previously. we have investigated the substitution reactions involving the binuclear organoplatinum(II) complex cis,cis-[(CH<sub>3</sub>)<sub>2</sub>Pt(µ-NN)(µdppm)Pt(CH<sub>3</sub>)<sub>2</sub>], in which dppm = bis(diphenylphosphino)methane and NN = phthalazine, with different phosphorus nucleophiles L,  $L = P(O^{-i}Pr)_3$  or PPh<sub>3</sub>, or  $L_2 = dppm$ , using UV–Vis spectroscopy, suggesting to proceed *via* the normal associative pathway [5]. In this work, we present substitution reactions of the chelate ligand NN of  $[PtR_2(NN)]$  (NN = 2,2'-bipyridine, and R = CH<sub>3</sub>, **1**, or  $R = p-CH_3C_6H_4$ , **1**') by monodentate and bidentate phosphine ligands using UV-Vis spectroscopy.

The phosphine reagent PPh<sub>3</sub> has a higher  $\sigma$ -donor ability than the phosphite reagent P(O<sup>-i</sup>Pr)<sub>3</sub>, and therefore when the lone pair of electrons of PPh<sub>3</sub> entering ligand is binding to the low lying platinum 6 p<sub>z</sub> orbital to form the initial transition state containing the square—pyramidal metallic center, it is better able to cope with the electron density already present in the same direction from the filled metal 5dz<sup>2</sup> orbital [4]. In contrast, however, PPh<sub>3</sub> has a Tolman angle (145°) greater than that of P(O<sup>-i</sup>Pr)<sub>3</sub> (130°) making nucleophilic attack of the former on the metallic center harder than that of P(O<sup>-i</sup>Pr)<sub>3</sub>. Both these steric and electronic effects would influence





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rate of the substitution reactions of these monodentate phosphines with Pt(II) complexes [3,5]. Besides, it has previously been described for the reaction of  $[Pt(p-CH_3C_6H_4)(ppy)S(CH_3)_2]$  with PPh<sub>3</sub> or dppm [8] that the complex reacted faster with PPh<sub>3</sub> than with dppm. This

has been attributed to the domination of electronic factor over steric factor. Thus, although cone angle of the attacking part of dppm, i.e. Ph<sub>2</sub>PCH<sub>2-</sub>, is smaller than that of PPh<sub>3</sub>, when one of the dppm phosphorus atoms is reacting with the complex to form the



**Fig. 1.** Changes in the UV–Vis spectrum during the reaction of complex [Me<sub>2</sub>Pt(NN)], **1**,  $(3 \times 10^{-4} \text{ M})$  and P(O–<sup>i</sup>Pr)<sub>3</sub> (0.015 M) in acetone at T = 25 °C: (a) initial spectrum (before adding P(O–<sup>i</sup>Pr)<sub>3</sub>) and (b) spectrum at t = 10 s; successive spectra were recorded at intervals of 1 min.



**Fig. 2.** Absorbance–time curves for the reaction of complex **1** with  $P(O^{-i}Pr)_3$  (0.015–0.116 M,  $[P(O^{-i}Pr)_3]$  increases reading downward) in acetone at 25 °C.



**Fig. 3.** Plots of first-order rate constants  $(k_{obs}/s^{-1})$  for the reaction of complex **1** with  $P(O^{-i}Pr)_3$  in acetone at different temperatures *vs.* concentration of  $P(O^{-i}Pr)_3$ .

related penta-coordinate intermediate  $[Pt(p-CH_3C_6H_4)(ppy) S(CH_3)_2(\eta^1-dppm)]$ , the other rather electronegative free phosphorus atom withdraws electron from the connecting phosphorus atom making it having a lower  $\sigma$ -donor ability than PPh<sub>3</sub>.

#### 2. Results

## 2.1. Reaction of the organoplatinum(II) complexes with P-donor ligands

Reactions of the diorganoplatinum(II) complexes [PtR<sub>2</sub>(NN)] (NN = 2,2'-bipyridine, and R = CH<sub>3</sub>, **1**, or R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, **1**') with 2 equiv of L nucleophile (L = P(O<sup>-1</sup>Pr)<sub>3</sub> or PPh<sub>3</sub>, or L<sub>2</sub> = bis(diphenylphosphino)methane, dppm) proceeded as described in Scheme 1 by displacement of the NN chelating ligand in each case with L to form the complexes **2**, almost quantitatively in pure form. In the reaction involving substitution of dppm, it is suggested that the intermediate product [Pt(CH<sub>3</sub>)<sub>2</sub>(η<sup>1</sup>–dppm)<sub>2</sub>] is formed first and then it would dissociate rapidly in solution to give the final product, identified as complex **2c** [12]. When the complexes **1** and **1**' were reacted with a large excess of L or L<sub>2</sub>, the same products **2** were isolated with effectively no further reactions.

The complexes **2** and **2**'**a** were identified by comparison of their <sup>1</sup>H NMR spectra with those of the authentic samples [6,12].

#### 2.2. Kinetic study of the substitution reactions

As was mentioned above, reactions of the complexes  $[PtR_2(NN)]$ , **1** or **1**', with 2 equiv of phosphorus nucleophiles proceeded *via* 



Fig. 4. Eyring plots for the reaction of complex 1 with: (a) PPh\_3; (b) dppm; (c)  $P(O-{}^iPr)_3$  in acetone.

displacement of the chelate bipyridine ligand to give the final complexes **2**. The complexes **1** and  $\mathbf{1}'$  contain a band in the visible region which is ascribed to the  $5d_{\pi}(Pt) \longrightarrow \pi^*(imine)$  MLCT band and is believed to be responsible for the color of the complex [5,8]. This was used to monitor the reactions of complexes with donor nucleophiles in order to investigate the kinetics of reactions by using UV–Vis spectroscopy, as will be described below. Typically, the reaction of complex  $[Pt(CH_3)_2(NN)]$ , **1**, and  $P(O^{-i}Pr)_3$  is described. As can be seen in Fig. 1, the complex 1 has a maximum absorption band at 475 nm and upon reaction of the reddish complex 1 with the phosphorus donors, L, the color is gradually faded away and eventually an almost colorless solution is obtained. Thus, an excess of L was used at 25 °C and the disappearance of the MLCT band at  $\lambda = 475$  nm in acetone solution was used to monitor the reaction. The time-dependence curves of the spectra of the reaction in acetone are shown in Fig. 2. Thus, the pseudo-first order rate constants  $k_{obs}$  were evaluated by nonlinear least-squares fitting of the absorbance-time profiles to the monophasic first order equation (Eq. (1)):

$$A_t = A_{\infty} + (A_0 - A_{\infty})(\exp(-k_{obs}t))$$
<sup>(1)</sup>

The reactions followed good first order kinetics (Fig. 2). Graphs of these first-order rate constants against the concentration of the nucleophile L gave good straight line plots passing through origin, showing a first-order dependence of the rate on the concentration of L (Fig. 3). The slope in each case gave the second-order rate constant, and the results are collected in Table 1. The same method

#### Table 1

Second-order rate constants ( $10^2 k_2/L \text{ mol}^{-1} \text{ s}^{-1}$ )<sup>a</sup> and activation parameters ( $\Delta H^{\ddagger}$  in kJ mol<sup>-1</sup>,  $\Delta S^{\ddagger}$  in J K<sup>-1</sup> mol<sup>-1</sup>)<sup>b</sup> for reaction of the complex [PtR<sub>2</sub>(2,2'-bipyridine)], (R = Me, **1** and R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, **1**') with the nucleophile L (L = PPh<sub>3</sub> and P(O-<sup>i</sup>Pr)<sub>3</sub>) or L<sub>2</sub> = dppm) in acetone.

Reagent	Complex	15 °C	25 °C	30 °C	35 °C	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$P(O-^{i}Pr)_{3}$	1	21.0(0.0)	38.7(0.1)	50.9(0.2)	66.4(0.3)	40.2(0.5)	-118(1.8)
$PPh_3$	1	27.0(0.2)	56.3(0.4)	76.1(0.7)	110.2(0.5)	49.0(1.1)	-85(3.8)
dppm	1	22.2(0.1)	46.0(0.4)	61.4(0.3)	88.3(0.5)	48.1(1.2)	-90(4.2)
P(O <sup>-i</sup> Pr) <sub>3</sub>	1′	0.93(0.01)	1.9(0.0)	2.4(0.0)	3.3(0.0)	50.0(1.3)	-127(4.3)

<sup>a</sup> Second-order rate constant values, and associated errors, are given based on 95% confidence limits from least-squares regression analysis.

<sup>b</sup> Obtained from the Eyring equation.



was used at other temperatures, and activation parameters were obtained from the Eyring equation (see Eq. (2) and Fig. 4) and the data are given in Table 1. In Eq. (2),  $k_B$  is the Boltzmann constant, h is the Planck constant, R is the gas constant and  $\ln(k_B/h)$  has a value of 23.76.

$$\ln(k_2/T) = \ln(k_B/h) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT$$
(2)

We also measured the rate constant of the reactions in the presence of excess free bipyridine (NN) and found no change in the rate constants. Thus, for example, rate constant ( $k_2$ ) for the reaction of [Pt(CH<sub>3</sub>)<sub>2</sub>(NN)], **1**, with excess P(O<sup>-i</sup>Pr)<sub>3</sub> at 25 °C is 38.7(0.1) × 10<sup>-2</sup> L mol<sup>-1</sup> s<sup>-1</sup> (see Table 1), and that for the same reaction in the presence of excess NN was measured to be 38.1(0.1) × 10<sup>-2</sup> L mol<sup>-1</sup> s<sup>-1</sup>.

#### 3. Discussion

The above studies led us to propose the associative mechanism shown in Scheme 2. A simple second-order rate law (Eq. (3)) was clearly obtained with absolutely no sign of any dissociative or solvolytic paths.

$$-d[\text{complex } \mathbf{1}]/dt = k_{\text{obs}}[\text{complex } \mathbf{1}]; k_{\text{obs}} = k_2[L]$$
(3)

The rather large negative values of  $\Delta S^{\ddagger}$  (see Table 1) for all the reactions strongly confirm the associative mechanism. A further support for the proposed associative mechanism comes from the fact that the rate of the reactions is dependent on the nature of the entering group (see Table 1), but independent of presence of excess free NN leaving group. The following trend was observed for rates of reactions of the phosphorus donors with complex **1**:PPh<sub>3</sub> > dppm > P( $O-^{i}Pr$ )<sub>3</sub>. Rate of the reaction of complex **1** with PPh<sub>3</sub> in acetone at 25 °C is 1.5 times faster than the corresponding rate with  $P(O-iPr)_3$  at the same condition due to lower  $n_{Pt}^0$  value of  $P(O-Pr)_3$  as compared with that of the PPh<sub>3</sub> [5]. This trend is similar to that observed for the reaction of  $cis, cis-[(CH_3)_2Pt(\mu-$ NN)( $\mu$ -dppm)Pt(CH<sub>3</sub>)<sub>2</sub>] with corresponding phosphorus nucleophiles [5]. An opposite trend has been seen for the substitution reactions of the complex [Pt(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(ppy)(S(CH<sub>3</sub>)<sub>2</sub>)], with phosphorus nucleophiles [8]. The complex 1 has two Pt–C bonds that should labilize the Pt-C bond significantly to enable a dissociative substitution mechanism. However, the in plane bipyridine ligand can cause a significant  $\pi$ -back bonding with the metal center, which will decrease the electron density on the metal center and make it more electrophilic to enable an associative attack by the entering ligands. We therefore suggest that as shown in Scheme 2, the first mole of L has an associative nucleophilic attack on the platinum(II) center of complex **1**, and so the first step, which is rate determining, is proceeded *via* the usual five coordinated transition states with a square pyramid and a trigonal bipyramid geometries, **3** and **4**, respectively, to give the intermediate **5**. The second mole of L completely replaces the NN ligand by a rate which is much faster than the rate of replacement of the first L.

The  $\Delta H^{\ddagger}/\Delta S^{\ddagger}$  compensation plot for reactions of complex **1** with P-donor nucleophiles in acetone is shown in Fig. 5. A good straight line is obtained and this may be taken as an evidence for operation of the same mechanism (associative, second-order) in this series of reactions.

The kinetic of the substitution reaction involving the chelate ring opening of  $[(p-CH_3C_6H_4)_2Pt(NN)]$ , **1**', with  $P(O-^iPr)_3$  was investigated similarly at different temperatures. The reaction followed a second order rate law (Fig. 6). This reaction occurs nearly 20 times slower than the similar reaction for complex **1**, due to



Fig. 5. The  $\Delta H^{\ddagger}/\Delta S^{\ddagger}$  compensation plots of reaction of complex 1 with the P-donor nucleophiles in acetone.



**Fig. 6.** Plots of first-order rate constants  $(k_{obs}/s^{-1})$  for the reaction of  $[(p-CH_3C_6H_4)_2Pt(NN)]$  complex with  $P(O-^iPr)_3$  in acetone at different temperatures *vs.* concentration of  $P(O-^iPr)_3$ .

more steric effect of p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, indicative of associative mechanism.

#### 4. Conclusion

The substitution reactions of the organoplatinum(II) complexes [PtR<sub>2</sub>(NN)], (R = CH<sub>3</sub>, **1**, R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, **1**'), with different phosphorus nucleophiles L, L = P(O<sup>-i</sup>Pr)<sub>3</sub> or PPh<sub>3</sub>, or L<sub>2</sub> = dppm, were investigated using UV–Vis spectroscopy and suggested to proceed *via* the normal associative pathway. Observation of the large negative entropies of activation, the significant dependency of the rate on both concentration and nature of the entering nucleophile, L (Table 1), and independency of the rate in presence of excess free NN leaving group, supported the proposed mechanism.

In the reaction involving the CH<sub>3</sub> complex [Pt(CH<sub>3</sub>)<sub>2</sub>(NN)], **1**, in acetone solvent, the nucleophile PPh<sub>3</sub> is reacted slightly faster than  $P(O^{-i}Pr)_3$  (by a factor of nearly 1.5); for example the reaction rates involving PPh<sub>3</sub> and P(O $-^{i}$ Pr)<sub>3</sub> at 25 °C are 56.3  $\times$  10<sup>-2</sup> L mol<sup>-1</sup> s<sup>-1</sup> and 38.7  $\times$  10<sup>-2</sup> L mol<sup>-1</sup> s<sup>-1</sup>, respectively. Thus, it could be concluded that in these two types of phosphorous donors the steric and electronic effects compensate each other causing their reaction rates with complex **1** being close to each other. Also, as has been reported previously, the reaction rates for cyclometalated complex  $[Pt(p-CH_3C_6H_4)(ppy)S(CH_3)_2]$ , in which ppy = deprotonated 2phenylpyridyl [8], with PPh<sub>3</sub> and P( $O^{-i}Pr$ )<sub>3</sub> at 25 °C (in CH<sub>2</sub>Cl<sub>2</sub>) are close to each other but with PPh<sub>3</sub> (169.8 L mol<sup>-1</sup> s<sup>-1</sup>) reacting slightly slower than P(O<sup>-i</sup>Pr)<sub>3</sub> (197.7 L mol<sup>-1</sup> s<sup>-1</sup>). A slight discrepancy in the trends of reaction rates with PPh<sub>3</sub> and  $P(O-iPr)_3$ in these two types of reactions can be related to the solvent effect on these reagents. The latter reagent is expected to be more polar than PPh<sub>3</sub> and so its interaction, as compared to PPh<sub>3</sub>, with acetone solvent molecules (used in the present study) is more pronounced than that with CH<sub>2</sub>Cl<sub>2</sub> solvent molecules (used in the reference 8) slightly affecting the reaction rates. It is also interesting to notice that the reactions of PPh<sub>3</sub> and  $P(O-^{i}Pr)_{3}$  with the cyclometalated complex [Pt(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(ppy)S(CH<sub>3</sub>)<sub>2</sub>] [8], proceed some 8000-10,000 times faster as compared to those studied at the present work involving the complex  $[(p-CH_3C_6H_4)_2Pt(NN)]$ , 1', containing bipyridine ligand. We attribute this rather huge difference to the following factors:

- i) The types of ancillary ligands present in the complexes, i.e. 2 N ligands in the complex 1' as compared to one N and one S ligands in the cyclometalated complex [Pt(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(ppy) S(CH<sub>3</sub>)<sub>2</sub>]. S-donor ligand has weaker  $\sigma$ -donor ability than Ndonor ligand and also the former ligand forms a better  $\pi$ -back bonding, as compared to N-donor ligand, with the metallic center. Both these effects would significantly increase the positive charge density on the platinum center in the complex [Pt(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(ppy)S(CH<sub>3</sub>)<sub>2</sub>] as compared to that in the complex 1' causing the former complex being significantly more prone to substitution reactions than the latter complex.
- ii) The lower steric influence around the Pt center of the complex  $[Pt(p-CH_3C_6H_4)(ppy) S(CH_3)_2]$ , as compared to that in the complex  $[(p-CH_3C_6H_4)_2Pt(NN)]$ , **1**′, would also help in increasing the related rates of the former complex. Both complexes have one  $p-CH_3C_6H_4$  ligand, but the other aromatic ligand in complex  $[Pt(p-CH_3C_6H_4)(ppy)S(CH_3)_2]$  is involved in cyclometalation and so is expected to be oriented coplanar with the square–planar geometry, creating less steric influence when compared with the aromatic ligand  $p-CH_3C_6H_4$  in complex **1**′, that is expected to be perpendicular to plane of the square–planar geometry.

The complex [Pt(CH<sub>3</sub>)<sub>2</sub>(NN)], **1**, reacted faster with PPh<sub>3</sub> than with bis(diphenylphosphino)methane, dppm; for example the reaction rates involving PPh<sub>3</sub> and dppm at 25 °C are  $56.3 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup> and  $46.0 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup>, respectively. This observation confirms the assumption suggested previously (see the Introduction).

The substitution reactions of the complex  $[(p-CH_3C_6H_4)_2-Pt(NN)]$ , **1**', with P(O–<sup>i</sup>Pr)<sub>3</sub> are generally proceeded much slower, by a factor of nearly 20, than those involving the complex **1**; for example the reaction rates involving complex **1** and complex **1**' at 25 °C are  $38.7 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup> and  $1.9 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup>, respectively. We believe that in this case the higher steric effect of *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> ligands in the complex **1**' (considering that these aromatic ligands stay perpendicular to the plane of the related square–planar complex), as compared to that of CH<sub>3</sub> ligands in complex **1**, is greatly influential in decreasing the rate of reactions. All these observations comply well with the proposed associative mechanism.

#### 5. Experimental

The <sup>1</sup>H NMR spectra of the complexes were recorded in CDCl<sub>3</sub> solutions on a Bruker Avance DPX 250 MHz spectrometer and TMS (0.00) was used as external reference. Kinetic studies were carried out by using a Perkin–Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. The [Pt(CH<sub>3</sub>)<sub>2</sub>(NN)], **1**, was made as described in the literature [13]. The final products complexes **2** were fully identified according to their <sup>1</sup>H NMR spectra reported earlier [6,12].

#### 5.1. Kinetic study

In a typical experiment, a solution of complex **1** in acetone (3 ml,  $3 \times 10^{-4}$  M) in a cuvette with a 1 cm path length was thermostated at 25 °C and a known excess of P(O<sup>-i</sup>Pr)<sub>3</sub> (50 µl, 4.37 M) was added using a micro syringe. After rapid stirring, the absorbance at  $\lambda = 475$  nm was monitored with time. The same reaction was performed in the presence of excess NN ligand (10 equiv,  $3 \times 10^{-3}$  M).

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#### References

- M. Frezza, Q.P. Dou, Y. Xiao, H. Samouei, M. Rashidi, F. Samari, B. Hemmateenejad, J. Med. Chem. 54 (2011) 6166-6176.
- F. Wang, A. Habtemariam, E.P.L. vander/Geer, R. Fernandez, M. Melchart, R.J. Deeth, R. Aird, S. Guichard, F.P.A. Fabbiani, P. Lozano-Casal, I.D.H. Oswald, [2] D.I. Jodrell, S. Parsons, P.J. Sadler, Proc. Natl. Acad. Sci. 102 (2005) 18269–18274.
- [3] M.L. Tobe, J. Burgess, Inorganic Reaction Mechanism, Longman, Essex, UK, 1999. [4] D.T. Richens, Chem. Rev. 105 (2005) 1961–2002.

- [5] S.J. Hoseini, S.M. Nabavizadeh, S. Jamali, M. Rashidi, J. Organomet. Chem. 692 (2007) 1990-1996.
- [6] A.R. Esmaeilbeig, H.R. Samouei, M. Rashidi, J. Organomet. Chem. 693 (2008) 2519-2526.
- [7] M. Rashidi, S.M. Nabavizadeh, A. Zare, S. Jamali, R.J. Puddephatt, Inorg. Chem. 49 (2010) 8435-8443.
- [8] S.M. Nabavizadeh, H.R. Shahsavari, M. Namdar, M. Rashidi, J. Organomet. Chem. 696 (2011) 3564–3571.
- [9] R.G. Wilkins, Kinetics and Mechanisms of Reactions of Transition Metal Complexes, VCH, Weinheim, Germany, 1991.
- F. Basolo, Coord. Chem. Rev. 154 (1996) 151–161.
   M.R. Plutino, L.M. Scolaro, R. Romeo, A. Grassi, Inorg. Chem. 39 (2000) 2712– 2720 (and references therein).
- [12] F.S.M. Hassan, D.M. McEwan, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1985) 1501-1506.
- [13] J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643-1648.