Journal of Organometallic Chemistry, 174 (1979) 237—245

STUDIES ON THE REACTIONS OF BIS(ACETYLACETONATO)PLATINUM(II) WITH LEWIS BASES

V *. REACTIONS OF β-DICARBONYL COMPOUNDS WITH CENTRAL CARBON-BONDED ACETYLACETONATO COMPLEXES OF PLATINUM(II) AND PALLADIUM(II)

TAKASHI ITO and AKIO YAMAMOTO

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227 (Japan)

(Received January 18th, 1979)

Summary

Central carbon-bonded acetylacetonato complexes of platinum(II) and palladium(II) [M(acac)(γ-acac)PPh_3], I (M = Pt and Pd), reacted with β-dicarbonyl compounds (Hdik) to give three types of complexes according to the nature of the β-dicarbonyl compounds employed; dimethyl malonate and methyl and ethyl acetoacetates yielded [M(acac)(γ-dik)PPh_3], II, whereas dibenzoylmethane afforded [M(dik)(γ-acac)PPh_3], IV, exclusively. The reaction of benzoylacetone with I afforded a mixture of [M(dik)(γ-dik)PPh_3], III, and IV. The selectivity of the reaction seems to be correlated with the enol- or keto-favoring character of the respective β-dicarbonyl compounds.

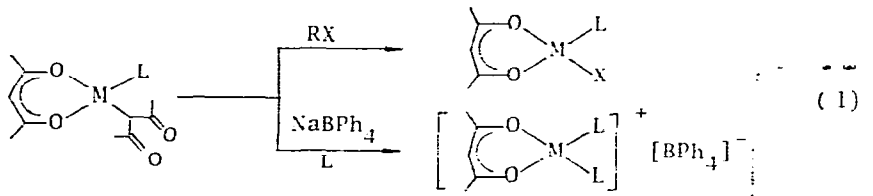
Introduction

Since the first finding of the central carbon-bonded acetylacetonato complex of platinum(IV) by Hazell et al. [1], many transition metal complexes possessing a C-bonded β-diketonato ligand have been reported for Pt^{IV} [2—5], Pt^{II} [6—15], Pd^{II} [16—18], Ir^{III} [19], and Au^{III} [20], and their structures have been investigated by X-ray analysis and spectroscopy. However, the reactivity of such complexes having a metal—carbon bond has scarcely been studied. Previously we have reported that the Pt—C bond of [Pt(acac)(γ-acac)PPh_3] **,

* Part IV see ref. 15;

** For the sake of brevity, all β-dicarbonyl compounds dealt with in the present study are generically named as β-diketones and the following abbreviations are used throughout the paper: dik = β-diketonato, acac = 2,4-pentanedionato (acetylacetonato), dmm = dimethylmalonato, mac = 1-methoxy-1,3-butanedionato (methyl acetoacetato), eac = 1-ethoxy-1,3-butanedionato (ethyl acetoacetato), bac = 1-phenyl-1,3-butanedionato (benzoylacetonato), dbm = 1,3-diphenyl-1,3-propanedionato (dibenzoyl methanato). The prefix γ- denotes the central C-bonded mode of coordination of each β-diketone. Thus, the above abbreviations without suffix γ- refer to the respective β-diketonato ligands coordinated to the metal through two oxygen atoms in their enol form.

Ia, is cleaved on treatment with either an organic halide, or $NaBPh_4$ (in the presence of PPh_3), to give $[Pt(acac)X(PPh_3)]$ or $[Pt(acac)(PPh_3)_2]BPh_4$, respectively [13]. A similar reaction has been observed for the Pd analog of Ia, $[Pd(acac)(\gamma\text{-acac})PPh_3]$ Ib, [13,16].



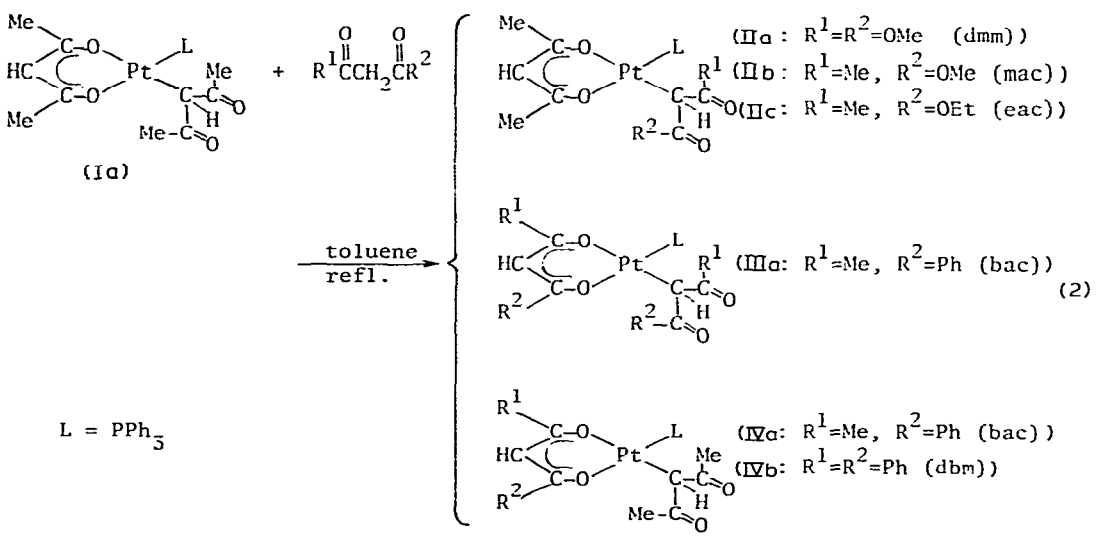
M = Pt (Ia) and Pd (Ib)

L = PPh_3

These results suggested that the γ-acac ligand is more labile than the chelate acac ligand towards electrophilic attack. We have studied the reactions of complexes Ia and Ib with a series of β-diketones and found that some β-diketones replaced the chelated acac ligand selectively, leaving the γ-acac ligand intact. Thus, three kinds of products, i.e., $[Pt(acac)(\gamma\text{-dik})PPh_3]$, $[Pt(dik)(\gamma\text{-dik})PPh_3]$, and $[Pt(dik)(\gamma\text{-acac})PPh_3]$, were obtained, depending on the nature of the β-diketones employed.

Results and discussion

The reaction of the γ-acac complex of Pt^{II}, $[Pt(acac)(\gamma\text{-acac})PPh_3]$ Ia, which was prepared in situ from $[Pt(acac)_2]$ and PPh_3 in toluene, with an excess of β-diketone at 110° C afforded new β-diketonato complexes of types II, III and IV. In these reactions, the type of the product was found to depend on the β-diketone employed, as shown in eq. (2).



L = PPh_3

Dimethyl malonate (Hdmm) and β-keto esters, such as methyl and ethyl acetoacetates (Hmac and Heac, respectively), replaced the C-bonded acac ligand

TABLE 1

PHYSICAL AND MICROANALYTICAL DATA FOR THE ISOLATED COMPLEXES

Complex [a]	Color	M.p. (°C) [b]	Analysis, found (calcd.)(%)	
			C	H
[Pt(acac)(γ-dmm)PPh$_3$] IIa	White	194—196	49.4(48.9)	4.4(4.3)
[Pt(acac)(γ-mac)PPh$_3$] IIb	Cream	185—186	50.3(50.1)	4.4(4.4)
[Pt(acac)(γ-eac)PPh$_3$] IIc	Pale yellow	180—182	50.1(50.8)	4.5(4.6)
[Pt(dbm)(γ-acac)PPh$_3$] IVb	Yellow	232—236	59.1(58.5)	4.4(4.1)
[Pd(acac)(γ-eac)PPh$_3$] IId	Yellow	150—152	57.9(58.4)	5.4(5.2)

[a] For abbreviations for the ligands, see footnote on p. 237. [b] Melting points (with decomposition) were measured on a hot stage with samples in small capillaries sealed under vacuum and are uncorrected.

in Ia selectively to give type II complexes, [Pt(acac)(γ-dik)PPh$_3$]. On the other hand, the reaction of dibenzoylmethane (Hdbm) with Ia afforded IV exclusively as a result of selective replacement of the chelate acac ligand in Ia with dbm. In the case of benzoylacetone (Hbac), complex III, in which both the chelate and the C-bonded acac ligands were replaced by the benzoylacetonato group, was obtained together with the type IV complex. Complex IIIa was isolated, although analytically impure, as a white powder by washing the mixture of IIIa and IVa carefully with Et_2O (see Experimental).

The palladium complex analogous to Ia, [Pd(acac)(γ-acac)PPh$_3$], Ib, behaved similarly and the type II complex [Pd(acac)(γ-eac)PPh$_3$], IId, was obtained on reaction of Ib with Heac at room temperature, whereas a mixture of types III and IV ([Pd(bac)(γ-bac)PPh$_3$], IIIb, and [Pd(bac)(γ-acac)PPh$_3$], IVc) was obtained by the reaction of Ib with Hbac.

The resulting complexes II—IV are not sensitive to air in the solid state but slowly deteriorate in solution in air. They are soluble in tetrahydrofuran (THF), hot toluene and chlorinated hydrocarbons, such as chloroform and dichloromethane, from which they are recrystallized to give white to yellow crystals. Analytical and physical properties of the isolated complexes IIa, IIb, IIc, IId, and IVb are listed in Table 1. Decomposition points of complexes II and IV are higher than those of the parent complexes Ia (148—153°C) [13] and Ib (142°C) [16].

Table 2 compares the characteristic IR absorptions of the complexes obtained in the present study. Band assignments were made by comparison with those reported for complex Ia [13] which is also included in Table 2. Although IR data do not afford decisive evidence to support the structures, ^{1}H NMR spectroscopic data of these complexes, which are summarized in Table 3, provide the principal basis for the structural assignments.

Assignment of the ^{1}H NMR signals in complexes II was straightforward and was made by comparing them with those reported for I [13,16], since the chemical shifts of the chelated acac ligand were scarcely altered on the change of γ-dik ligand. The coupling constants (^3J(PtH)) between the methine proton attached to the platinum-bonded carbon atom in the γ-dik ligand and ^{195}Pt in complexes II and Ia decreased in the order Ia (γ-acac) > IIb (γ-mac) > IIc (γ-eac) > IIa (γ-dmm). The result indicates that the replacement of the methyl group(s) in

TABLE 2

CHARACTERISTIC IR ABSORPTIONS (cm^{-1}) OF β-DIKETONATO COMPLEXES (KBr DISC)

Complex [a]	C-bonded β-dik			O-bonded β-dik	
	Ester		Ketone	$\nu(C{=}O) + \nu(C{=}C)$	$\nu(Pt{-}C)$
	$\nu(C{=}O)$	$\nu(COC)$	$\nu(C{=}O)$		
[Pt(acac)(γ-acac)PPh_3] [b] Ia			1685	1575	445
			1650	1550	
				1525	
[Pt(acac)(γ-dmm)PPh_3] IIa	1740	1215		1580	450
	1715	1130		1560	
				1520	
[Pt(acac)(γ-mac)PPh_3] IIb	1735	1200	1690	1580	450
	1715	1140	1675	1565	
				1520	
[Pt(acac)(γ-eac)PPh_3] IIc	1710	1215	1680	1585	450
		1145		1565	
				1520	
[Pd(acac)(γ-eac)PPh_3] IId	1705	1145	1670	1585	440
		1220		1560	
				1515	
[Pt(bac)(γ-bac)PPh_3] IIIa			1670	1590	460
				1555	
				1525	
[Pt(dbm)(γ-acac)PPh_3] IVb			1685	1580	[c]
			1665	1515	
				1470	

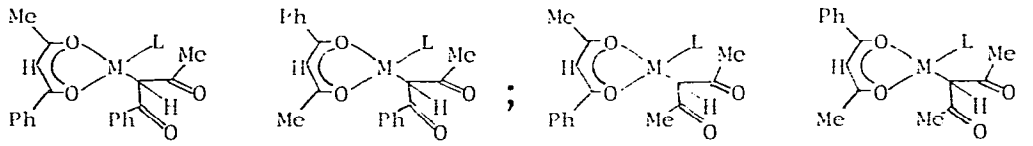
[a] Abbreviations for ligands are as shwon in the footnote on p. 237. [b] Data quoted from ref. 13. [c] Uncertain.

the γ-acac ligand with alkoxy group(s) gives rise to a decrease in the relative covalent character of the Pt—C bond in [Pt(acac)(γ-dik)PPh_3] [21,22].

The methylene signals of the ethoxy group in the γ-eac ligand in complex IId at room temperature consisted of two sets of quartets which separated each other by 2.0 Hz. The separation between the two quartets was larger at lower temperature (4.5 Hz at —20° C) and collapsed to a single quartet at 80° C. This splitting of the methylene signal is not due to long range coupling with phosphorus nucleus since the splitting survived in the ^{31}P irradiation experiment. The restricted rotation around the Pd—C bond and/or the methine carbon—carbonyl carbon bond in IId at the lower temperature, presumably resulting from the steric bulk of PPh_3, may have made the two methylene protons magnetically nonequivalent. A similar phenomenon was observed for IIc, the platinum analog of IId, although the chemical shifts of the γ-methine doublet (with ^{195}Pt satellite bands) of γ-eac and of the methylene quartets in question are so close to each other in the case of IIc that an accurate analysis of the spectrum at room temperature in this region was prevented.

A cream-colored powder obtained by the reaction of Ia with a 2 to 10 molar excess of Hbac showed a very complicated but reproducible ^1H NMR spectrum, the overall feature of which resembled that of the product obtained by the

reaction between Ib and Hbac. A careful analysis of the observed spectrum suggested that the powder contained two types of complexes: one is of type III in which both acac and γ-acac ligands in I are replaced by bac and γ-bac, respectively, the other a type IV complex in which only the chelated acac ligand is replaced by bac. The ratio of the two components was 1/4 (IIIa/IVa) for the platinum and 2/3 (IIIb/IVc) for the palladium complexes. Each component consisted of equivalent amounts of geometrical isomers; the *cis* isomer in which PPh_3 ligand is situated in *cis* position with respect to the methyl group in bac (*cis*(Me, L)) and the *trans* isomer with the methyl group in bac situated *trans* to the PPh_3 ligand (*trans*(Me, L)).



M = Pt *cis*(Me,L)-IIIa *trans*(Me,L)-IIIa *cis*(Me,L)-IVa *trans*(Me,L)-IVa

M = Pd *cis*(Me,L)-IIIb *trans*(Me,L)-IIIb *cis*(Me,L)-IVc *trans*(Me,L)-IVc

The assignment of each signal in the ^1H NMR spectrum of the mixtures was achieved by referring to the ^1H NMR data of the reported related complexes such as [Pd(eac)(γ-eac)PPh_3] [18] and [Pd(bac)$_2$] [23]. Furthermore, comparison of the ^1H NMR spectrum of the isolated mixture of *cis*- and *trans*- IIIa (see Experimental) aided the assignment of the rest of the complexes in a product mixture. An anionic Pt^{II} complex with a structure similar to IIIa, [PtX(bac)-(γ-bac)]$^-$ (X = Cl or Br), has been reported, but the geometric isomerization of this anionic Pt^{II} complex could not be solved [8] since no NMR data could be obtained due to its poor solubility. Since starting [Pd(acac)$_2$] was recovered unexchanged when [Pd(acac)$_2$] and 3 mol of benzoylacetone were heated under reflux in benzene in the absence of PPh_3, the coordination of PPh_3 ligand to the acetylacetonato complex is found to play an essential role in the displacement of chelated acac ligand.

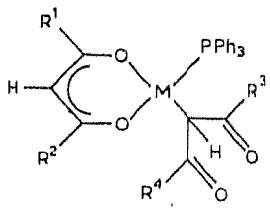
In order to clarify the factors governing such selectivity in the replacement of the acetylacetonato ligands in complex I with the β-diketoneto ligands, ^1H NMR spectra of the free β-diketones in C_6D_6 (2.0 *M*, 23°C) were examined. A great difference in the keto/enol ratio of each β-diketone was observed and the diketones may be divided into two categories: one is a highly keto-predominant type such as Hdmm (keto %, 100), Hmac (88), and Heac (86), and the other is rich in the enol form such as Hacac (enol %, 85), Hbac (94) and Hdbm (97). Hdmm, Hmac and Heac, which exist almost exclusively as the keto-form in the solution, can replace the γ-acac ligand of I to give type II complexes either by a direct attack of the carbanion (dik$^-$) to the metal center or by the process involving the ionic intermediate in which the β-diketonate anion is coordinated to the complex in the outer sphere [24].

On the other hand, Hdbm, which is almost exclusively in the enol form in solution, may replace the chelated acac ligand by the process in which reversible M—O bond scission [14] is involved.

Benzoylacetone, which is mainly in its enol form but has a certain proportion (ca. 6%) of the keto form might afford a type III complex in addition to

TABLE 3

^{1}H NMR DATA FOR COMPLEXES [M(dik)(γ-dik)PPh$_3$] [a]



Complex						dik			γ-dik				
	M	R^1	R^2	R^3	R^4	R^1	R^2	HC	R^3	R^4	HC—^3J(PH)		^2J(PtH)
IIa	Pt	Me	Me	OMe	OMe	1.52	1.98	5.43	3.43		3.72 ds	5	96
IIb	Pt	Me	Me	Me	OMe	1.53	2.01	5.46	2.28	3.48	3.89 ds	7	105
IIc	Pt	Me	Me	Me	OEt	1.52	2.00	5.44	2.29	1.11 t [b] 3.95 q [b,c]	3.85 ds	6	101
IId	Pd	Me	Me	Me	OEt	1.51	2.01	5.27	2.36	1.12 t [b] 3.98 q [b,c]	3.42 d	6	—
IVb	Pt	Ph	Ph	Me	Me	*o*-7.1 m *m*-7.4 m *p*-8.1 m		6.89	2.31		4.21 ds	6	110
IIa	Pt	Me	Ph [d]	Me	Ph	1.57	[f]	6.07	2.54	[f]	4.83 ds	6	113
		Ph	Me [e]	Me	Ph	[f]	2.09	6.10	2.56	[f]			
IVa	Pt	Me	Ph [d]	Me	Me	1.73	[f]	6.18	2.10		4.13 t [g]	6	[h]
		Ph	Me [e]	Me	Me	[f]	2.18	6.23	2.29				
IIIb	Pd	Me	Ph [d]	Me	Ph	1.53	[f]	5.97	2.62	[f]	4.42 d	6	—
		Ph	Me [e]	Me	Ph	[f]	2.13	6.01	2.58	[f]			
IVc	Pd	Me	Ph [d]	Me	Me	1.69	[f]	6.07	2.24		3.67 t [g]	6	—
		Ph	Me [e]	Me	Me	[f]	2.16	6.11	2.27				

[a] 100 MHz, in $CDCl_3$ at room temperature unless otherwise stated. Chemical shifts are in δ values (ppm) with respect to internal $(CH_3)_4Si$ and coupling constants are in Hz. Signals due to PPh_3 ligand which appear as multiplets at ca. 7.4 ppm (*m*- and *p*-protons) and ca. 7.8 ppm (*o*-) are omitted for clarity. Multiplicity abbreviations are: ds, doublet with satellite bands due to ^{195}Pt; t, triplet; q, quartet; d, doublet; m, multiplet; signals without multiplicity symbols are singlets. Each signal had a signal intensity which meets the value required by the assignment. [b] ^3J(HH) = 7 Hz. [c] Data taken at 80°C (see text). [d] *cis*-Isomer in which the methyl group of bac ligand is situated in the *cis* position with respect to PPh_3. [e] *trans*-Isomer in which bac-Me is trans to PPh_3. [f] Signals are not discernible from PPh_3 signals. [g] Apparent triplet consisted of two sets of doublet. [h] Not clear.

IV by further reaction of IV, the primary product of the reaction between I and the enol tautomer of Hbac, with the keto-Hbac.

Experimental

All reactions were carried out under atmosphere of nitrogen or argon. Solvents were dried and purified. [Pt(acac)(γ-acac)PPh_3], Ia, and [Pd(acac)-(γ-acac)PPh_3], Ib, were prepared in situ from PPh_3 and [$Pt(acac)_2$] [25] and [$Pd(acac)_2$] [26], respectively, as reported previously [13,16]. Commercially available β-diketones were used without further purification.

IR spectra were recorded on a Hitachi model 295 spectrometer as KBr disks. ^1H NMR spectra were measured on a JNM-PS-100 spectrometer by Mr. Y. Nakamura of our Laboratory. The carbon/hydrogen microanalyses were performed by Mr. T. Saito of our Laboratory using a Yanagimoto CHN Autocorder Type MT-2. Analytical results and melting points of the isolated products are listed in Table 1.

Preparation of [Pt(acac)(γ-dmm)PPh_3], IIa

A mixture of [$Pt(acac)_2$] (0.20 g, 0.51 mmol), PPh_3 (0.14 g, 0.54 mmol) and toluene (5 ml) was stirred at room temperature for 4 h to give a clear yellow solution. To the solution was added 1.0 ml (8.7 mmol) of dimethyl malonate and the mixture was heated under reflux for 7 h. The resulting pale yellow solution was concentrated in vacuo to ca. 1 ml to afford a white precipitate. Addition of 10 ml of hexane yielded a sticky white solid, which was collected by decantation. Rinsing the solid several times with hexane afforded a white powder, which was filtered, washed with hexane and dried in vacuo. The off-white powder thus obtained (0.28 g, 76% on the basis of the amount of [$Pt(acac)_2$] used) was spectroscopically pure. Recrystallization from hot tetrahydrofuran gave fine white crystals.

The other type II complexes of platinum, [Pt(acac)(γ-mac)PPh_3], IIb, (80%), and [Pt(acac)(γ-eac)PPh_3], IIc, (80%) were obtained essentially in the same manner as described for IIa using methyl acetoacetate and ethyl acetoacetate, respectively, in place of dimethyl malonate. In these cases, however, addition of hexane to the concentrated reaction mixture (red solution) gave a red oil instead of a sticky solid, as in the case of IIa. Repeated digestion of this oil with hexane afforded a cream to pale yellow powder which was recrystallized from hot toluene.

Preparation of [Pd(acac)(γ-eac)PPh_3], IId

To the heterogeneous system consisting of [$Pd(acac)_2$] (0.22 g, 0.72 mmol) and benzene (5 ml), PPh_3 (0.20 g, 0.75 mmol) was added to afford a clear orange-yellow solution, to which 1.0 ml (7.7 mmol) of ethyl acetoacetate was added. The mixture was stirred at room temperature for 8 h to give an orange solution. The solvent was evaporated in vacuo to leave an orange oily material. Digestion of the residue with hexane afforded yellow fine crystals which were filtered, washed with hexane and dried in vacuo (0.38 g, 89%). The crude product, whose purity was satisfactory on the basis of its IR spectrum, could be recrystallized from 1/3 mixture of THF and Et_2O to give yellow crystals.

Preparation of [Pt(dbm)(γ-acac)PPh_3], IVb

The mixture of [$Pt(acac)_2$] (0.35 g, 0.89 mmol), PPh_3 (0.26 g, 0.98 mmol) and toluene (10 ml) was stirred at room temperature for 3 h to give a yellow solution. To the solution was added 1.00 g (4.45 mmol) of dibenzoylmethane. Heating the mixture under reflux for 3 h afforded a pale orange solution. After cooling, the system was concentrated in vacuo to ca. 1 ml to leave a yellow oil. Repeated digestion of the oil with hexane afforded a yellow powder, which was filtered, washed well with hexane and dried in vacuo. The crude product thus obtained (0.70 g, 100%) was recrystallized from a 1/1 mixture of hot THF and acetone to give yellow prisms.

Reaction of [$Pt(acac)_2$] with benzoylacetone was carried out similarly to give a cream powder consisting of [Pt(bac)(γ-bac)PPh_3], IIIa, and [Pt(bac)-(γ-acac)PPh_3], IVa in 0.22/0.78 ratio. Changing the reactant composition from 2 through 5 to 10 (benzoylacetone/Pt) did not affect the ratio of the products significantly. In one case, repeated, rigorous washing of the product mixture with Et_2O (in which IVa dissolves more than IIIa) afforded, though analytically not pure enough, a small amount of white powder. The IR and ^1H NMR spectra of this product were consistent with a 1/1 mixture of *cis*(Me, L)- and *trans*(Me, L)-IIIa.

Reaction of [Pd(acac)(γ-acac)PPh_3], Ib, with benzoylacetone

On stirring a mixture consisting of [$Pd(acac)_2$] (0.31 g, 1.0 mmol), benzoylacetone (0.50 g, 3.0 mmol), PPh_3 (0.27 g, 1.0 mmol) and benzene (5 ml) at room temperature for 13 h, a clear red solution resulted. Solvent was evaporated off in vacuo to leave an oily orange material which was dissolved in 5 ml of Et_2O. The orange solution was kept at −20°C for a week to allow a yellow microcrystalline solid to precipitate. This was filtered, washed with Et_2O and dried in vacuo. The crude product (0.29 g) was reprecipitated from THF/hexane to give a pale yellow powder, whose ^1H NMR spectrum suggested that it consisted of complexes IIIb and IVc in 2/3 ratio.

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