Preliminary communication

New square-planar cationic Pt(II) complexes containing a methyl and an olefin in *cis* position

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Abstract

An effective method for the synthesis of square-planar cationic Pt(II) complexes containing a methyl and an olefin in *cis* position is described. The addition of Me_3OBF_4 to $[Pt(phen)(\eta^2\text{-}E\text{-}MeO_2CCH=CHCO_2Me)]$ affords the cationic olefin complex $[PtMe(phen)(\eta^2\text{-}E\text{-}MeO_2CCH=CHCO_2Me)]^+(BF_4^-)$. Dimethylfumarate is easily displaced by electron-rich olefins $RCH=CH_2$ (R = H, Ph, Me) and the products $[PtMe(phen)(\eta^2\text{-}RCH=CH_2)]^+(BF_4^-)$ can be isolated in good yield.

Keywords: Platinum; Alkyl; Olefin; Cationic complexes; Electrophilic attack

Cationic metallorganic d^8 complexes attract much attention owing to their reactivity and relevance in catalysis (several examples of the use of d^8 cationic complexes in stoichiometric and catalytic reactions can be found in Ref. [1]). Among these compounds olefin platinum(II) derivatives deserve great interest. In fact, square-planar hydrido complexes $[PtHL_2(\eta^2\text{-olefin})]^+$ are postulated as intermediates in migratory insertion/β-elimination processes and, for this reason, they have been extensively studied and characterized, both in solution (see for example Ref. [2]) and in the solid state [3,4]. Chloro-derivatives, e.g. $[PtCl(H_2NCH_2CH_2NH_2)(\eta^2\text{-}C_2H_4)]^+$ [5] have been widely investigated with regard to the facile nucleophilic attack on the coordinated alkene, which affords stable addition products [6,7]. Finally, an interesting insight into the stereochemistry of the platinum–olefin bond has been obtained by determining the crystal structures of several η^3-allyl complexes of formula $[Pt(\eta^3\text{-allyl})(PR_3)(\eta^2\text{-olefin})]^+$ [8].

In contrast, very scant data are available on cationic alkyl complexes of general formula *cis*-$[PtRL_2(\eta^2\text{-olefin})]^+$ (I). Previous literature concerns mainly *trans* derivatives [9] and rare examples of square-planar com-

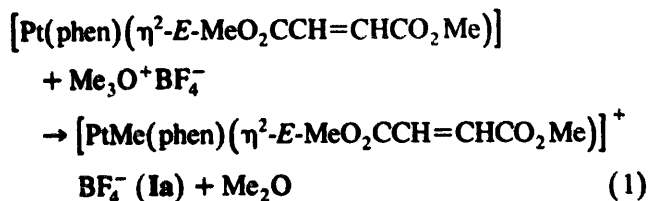plexes showing a *cis* arrangement of the hydrocarbyl ligands (e.g. $[PtMe(1,2\text{-}(Me_2As)_2C_6H_4)(\eta^2\text{-}C_2H_4)]^+$ [10] and $[PtMe(H_2NCH_2CH_2NH_2)(\eta^2\text{-}C_2H_4)]^+$ [11]) have been isolated (a *cis* arrangement of an axial methyl and an equatorial olefin can be found in cationic trigonal bipyramidal platinum(II) species, see Ref. [12]). These results are in contrast to the utmost importance of type I species. In fact, these complexes are strictly related to the reactive intermediates which occur in several processes promoted by platinum and other metals. For example, the insertion of alkenes into the Pt–C(aryl) [13] or the Pd–C(alkyl [14], aryl [15]) bonds is suggested to proceed via *cis*-$[MR(\eta^2\text{-olefin})L_2]^+$ species (M = Pd, Pt), and similar intermediates are invoked in palladium(II) catalyzed ethylene polymerization [16].

As part of our research dealing with olefin/hydrocarbyl complexes of Pd(II) [14,15,17] and Pt(II) [13,17], we have developed an effective method for the synthesis of type I complexes, which appears of fairly wide applicability.

The procedure adopted couples the known alkylating properties of trimethyloxonium salts (see for example Ref. [18]) with the ability of three-coordinate Pt(0) precursors of general formula $[Pt(N,N\text{-chelate})(\eta^2\text{-olefin})]$ to undergo electrophilic attack [19]. Thus, when a fresh deuteronitromethane solution of $Me_3O^+BF_4^-$ is

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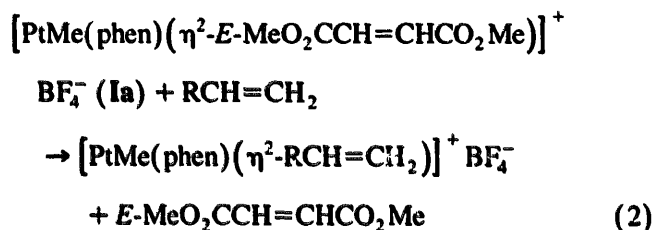allowed to react with one equivalent of [Pt(phen)(η^2-E-MeO$_2$CCH=CHCO$_2$Me)] (phen = 1,10-phenanthroline), reaction (1) takes place rapidly, as monitored through ^{1}H NMR spectroscopy.

$$[Pt(phen)(\eta^2\text{-}E\text{-MeO}_2CCH=CHCO_2Me)]$$

$$+ \, Me_3O^+BF_4^-$$

$$\rightarrow [PtMe(phen)(\eta^2\text{-}E\text{-MeO}_2CCH=CHCO_2Me)]^+$$

$$BF_4^- \, (Ia) + Me_2O \tag{1}$$

The NMR spectrum of the mixture also reveals that **Ia** is fluxional (Table 1). The two halves of phen are equivalent and the signal of the olefin protons is broad. This is also shifted upfield from that of free dimethylfumarate, which clearly indicates that the olefin is coordinated to platinum through the C=C double bond. Furthermore, the signal pertaining to traces of water also broadens. A fast dissociative equilibrium of the olefin, which may involve water, could account for the high symmetry of the NMR spectrum. It is conceivable that the dynamic process is due to the labile coordination of the electron-poor dimethylfumarate in the four-coordinate Pt(II) complex, in which the presence of electron-withdrawing alkenes is strongly disfavored for electronic reasons [20]. With this in mind, we note that **Ia** represents a rare example of a square-planar platinum(II) complex bearing an electron-withdrawing alkene (for examples of square-planar Pt(II) complexes which contain olefins with electron-withdrawing substituents, see Refs. [21–23]).

We were not able to obtain single crystals of the complex, but could isolate it in fairly pure form as a beige solid by adding toluene to the reaction mixture (1). [A typical preparation is as follows: Me$_3$OBF$_4$ (0.037 g, 0.25 mmol) dissolved in 1.5 ml of nitromethane is added to solid [Pt(phen)(η^2-E-MeO$_2$CCH=CHCO$_2$Me)] (0.13 g, 0.25 mmol) [19]. The resulting orange solution is filtered through Celite and complex **Ia** is crystallized by slow addition of toluene. The beige microcrystals are washed with toluene (1 × 3 ml), n-pentane (2 × 5 ml) and dried under vacuum (yield 0.10 g, 65%).]

Dimethylfumarate in **Ia** is readily displaced by ethylene or by an alkene bearing electron-donor substituents. Thus, when the reaction mixture (1) is treated with RCH=CH$_2$ (R = H, Me, Ph), the ^{1}H NMR spectrum shows free dimethylfumarate and the quantitative formation of complexes **Ib–d** (reaction (2)).

$$[PtMe(phen)(\eta^2\text{-}E\text{-MeO}_2CCH=CHCO_2Me)]^+$$

$$BF_4^- \, (Ia) + RCH=CH_2$$

$$\rightarrow [PtMe(phen)(\eta^2\text{-}RCH=CH_2)]^+ \, BF_4^-$$

$$+ \, E\text{-MeO}_2CCH=CHCO_2Me \tag{2}$$

Ib: R = H; **Ic**: R = Ph; **Id**: R = Me

Addition of toluene to the reaction mixture allows the isolation in good yield of the three complexes as

Table 1
Selected NMR and analytical data for type 1 complexes

	NMR					Anal. Found (Calc.)		
		^{1}H [a]		^{13}C [b]		C	H	N
	2- and 9-H-phen [c]	olefin	Pt–Me [d]	olefin	Pt–Me [e]			
Ia [f]	9.47 (d, 2H)	5.33 (br, 2H)	1.10 (75, 3H)			37.00	2.97	4.66
						(36.73)	(3.08)	(4.51)
Ib	9.20 (50, d, 1H)	4.54 (br, 4H)	0.93 (71, 3H)	71.3 (2C)	−6.7 (673, 1C)	35.45	3.10	5.28
	8.67 (14, d, 1H)					(35.66)	(2.99)	(5.55)
Ic	9.16 (53, d, 1H)	6.62 (dd, 1H)	0.77 (73, 3H)	95.8 (1C)	−2.6 (705, 1C)	43.58	3.41	4.71
	8.66 (15, d, 1H)	4.88 (d, 1H)		(1C) [g]		(43.39)	(3.29)	(4.82)
		4.53 (d, 1H)						
Id	9.17 (58, d, 1H)	5.41 (m, 1H) [h]	0.92 (73, 3H)	96.0 (1C)	−5.2 (702, 1C)	36.72	3.25	5.64
	1H [i]	4.45 (m, 1H)		67.2 (1C)		(37.01)	(3.30)	(5.40)
		4.26 (m, 1H)						

[a] At 270 or 200 MHz and 298 K; in CD$_3$NO$_2$, CHD$_2$NO$_2$ (δ = 4.33 ppm) as internal standard. Abbreviations: br, broad signal; d, doublet; dd, double doublet; m, multiplet; no attribute, singlet.
[b] At 67.9 or 50.3 MHz and 298 K; in CD$_3$NO$_2$, ^{13}CHD$_2$NO$_2$ (δ = 62.81 ppm) as internal standard.
[c] $^3J_{\text{H-H}}$ (Hz) in parentheses.
[d] $^2J_{\text{Pt-H}}$ (Hz) in parentheses.
[e] $^1J_{\text{Pt-C}}$ (Hz) in parentheses.
[f] At 60 MHz.
[g] Overlapped by the solvent signal.
[h] $^2J_{\text{H-H}}$ ca. 80 Hz.
[i] Overlapped by other phenanthroline signals.

light colored microcrystalline solids. [A typical preparation is as follows: to a fresh nitromethane solution of **Ia** prepared as described above is added an excess of the appropriate olefin. The product is crystallized by slow addition of toluene, washed with toluene (1 × 3 ml), *n*-pentane (2 × 5 ml) and dried under vacuum (yield 70–80%).] These are soluble in nitromethane and are stable in solution as well as in the solid state.

The NMR spectroscopic features of **Ib–d** (Table 1) deserve some comment. The olefin protons resonate in a range considered typical for square-planar platinum(II) complexes. For example, in the spectrum of **Ib** a broad signal at 4.54 ppm clearly pertains to ethylene protons in a square-planar arrangement. [Typical ^{1}H values (δ) for Pt(II) ethylene compounds are: 5.4 (free); 4.8–4.4 (four-coordinate complexes); 3.7–1.7 (trigonal bipyramidal complexes) [17].]
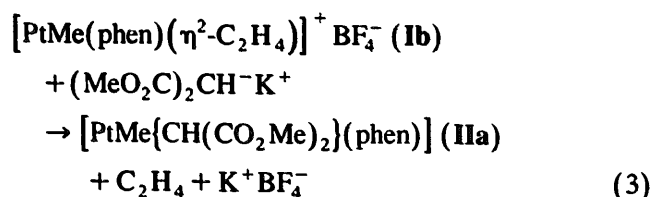
The protons of ethylene and styrene do not couple to ^{195}Pt, while the propylene protons do. [This holds true for dilute solutions ($C < 10\,\mathrm{mg\,ml^{-1}}$). The ^{1}H NMR spectrum of **Id** at a higher concentration, which is necessary in order to run the ^{13}C NMR spectrum, does not show coupling between the propylene protons and ^{195}Pt, obviously due to an increased exchange rate between two different metal centers.] This result may be due to a fast olefin exchange, which is inhibited when the coordinated alkene has better donor features. This is in agreement with the above quoted influence of the donor properties of the alkene on the strength of the platinum–olefin bond [20].

The two halves of phen are not equivalent. Protons in position 1 and 10 couple to ^{195}Pt to a different extent (for example, for **Ib** $^3J_{P_1-H} = 50$ and 14 Hz). Given the higher *trans* influence of methyl relative to ethylene [9], the smaller value can be attributed to the hydrogen nucleus close to the N atom which is *trans* to methyl.
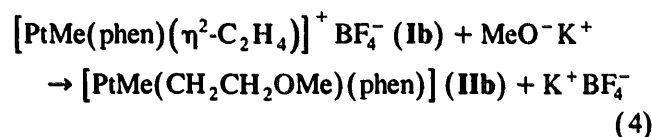
Some aspects of the reactivity of **Ib** have also been investigated. Ethylene does not insert into the Pt–Me bond even after several hours at 60 °C in deuteronitromethane in the presence of acetonitrile. This result confirms that Pt(II)–alkyl bonds are not easily involved in olefin migratory insertion [10].

The course of the reactions between **Ib** and nucleophiles is related to the nature of the latter species. More precisely, a soft carbanion, i.e. $(MeO_2C)_2CH^-$, does not attack the coordinated ethylene, but simply substitutes it. The reaction has been performed by adding **Ib** to a THF suspension of $(MeO_2C)_2CHK$ [24], and the product [PtMe{CH(CO$_2$Me)$_2$}(phen)] (**IIa**) has been isolated in high yield after work-up of the reaction mixture (reaction (3)). [Selected ^{1}H NMR data (at 200 MHz and 298 K; in CDCl$_3$, CHCl$_3$ ($\delta = 7.26$ ppm) as internal standard and elemental analyses are as follows. **IIa**: δ 4.35 ($^2J_{P_1-H} = 135$ Hz, 1H, Pt–CH), 3.60 (6H, OMe), 1.41 ($^2J_{P_1-H} = 80$ Hz, 3H, Pt–Me) ppm. Anal. Found:

C, 41.11; H, 3.59; N, 5.16. C$_{18}$H$_{18}$N$_2$O$_4$Pt Calc.: C, 41.46; H, 3.48; N, 5.37%.]

$$[PtMe(phen)(\eta^2\text{-}C_2H_4)]^+ BF_4^- \; (\mathbf{Ib})$$
$$+(MeO_2C)_2CH^-K^+$$
$$\rightarrow [PtMe\{CH(CO_2Me)_2\}(phen)]\;(\mathbf{IIa})$$
$$+ C_2H_4 + K^+BF_4^- \qquad (3)$$

By contrast, reaction of **Ib** with KOH in methanol affords the addition product **IIb** (reaction (4)). [Selected ^{1}H NMR data (at 200 MHz and 298 K; in CDCl$_3$, CHCl$_3$ ($\delta = 7.26$ ppm) as internal standard; abbreviations: app d, apparent doublet; no attribute, singlet) and elemental analyses are as follows. **IIb**: δ 3.70 (app d, 2H, Pt–CH$_2$CH_2), 3.43 (3H, OMe), 2.23 ($^2J_{P_1-H} = 90$ Hz, app d, 2H, Pt–CH$_2$), 1.30 ($^2j_{P_1-H} = 85$ Hz, 3H, Pt–Me) ppm. Anal. Found: C, 43.01; H, 3.98; N, 6.46. C$_{16}$H$_{18}$N$_2$OPt Calc.: C, 42.76; H, 4.04; N, 6.23%.]

$$[PtMe(phen)(\eta^2\text{-}C_2H_4)]^+ BF_4^-\;(\mathbf{Ib}) + MeO^-K^+$$
$$\rightarrow [PtMe(CH_2CH_2OMe)(phen)]\;(\mathbf{IIb}) + K^+BF_4^- \qquad (4)$$

This reactivity is different from that of the corresponding chloro-derivative [PtCl(H$_2$NCH$_2$CH$_2$NH$_2$)-$(\eta^2\text{-}C_2H_4)]^+$, in which the olefin is attacked by both nucleophiles [6,7]. It is possible to interpret this difference assuming that the platinum atom in **Ib** is softer than in [PtCl(H$_2$NCH$_2$CH$_2$NH$_2$)(η^2-C$_2$H$_4$)]$^+$. Thus, in the case of **Ib** a soft nucleophile, e.g. $(MeO_2C)_2CH^-$, may display a greater affinity for the metal center than for the coordinated ethylene.

Further investigations on type **I** complexes are in progress.

Acknowledgements

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