Journal of Organometallic Chemistry, 216 (1981) 413—419
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PREPARATION AND CHARACTERIZATION OF NEW CYCLOPLATINATED CARBENE COMPLEXES

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(Received February 19th, 1981)

Summary

Reaction of iodotrimethylplatinum(IV) tetramer with bis(1,3-diphenyl-2-imidazolidinylidene) [$(Hdpim)_2$] gave a new dinuclear carbene complex, [$\{Pt(dpim)I\}_2$] (dpim = 1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2'-*C*), III, in 84% yield, which contains a cycloplatinated carbene structure. Some mononuclear derivatives, [Pt(dpim)(acac)], [$Pt(dpim)I\{P(OCHMe_2)_3\}$], [$Pt(dpim)(NCCH_3)_2]ClO_4$, and [Pt(dpim)(COD)]$ClO_4$ were prepared from III and characterized by means of elemental analysis, IR and NMR spectroscopy, and molar conductivity. An intermediate species, [$\{PtMeI(Hdpim)\}_2$], leading to III is discussed also.

Introduction

Transition-metal carbene species are frequently regarded as active intermediates in various homogeneous or heterogeneous catalytic reactions [1—3]. As model compounds for these species, many kinds of carbene complexes have been prepared and their structural and chemical properties studied [4—7]. An electron-rich olefin, bis(1,3-diphenyl-2-imidazolidinylidene) (I) is a useful carbenoid precursor which gives transition-metal carbene complexes [6—11]. In the present study, the olefin I reacted with iodotrimethylplatinum(IV) tetramer (II) in refluxing *m*-xylene to give a new dimeric complex which contained a cyclometallated carbene moiety. Previously, we reported the formation of an analogous (carbene)palladium(II) complex from the reaction of di-μ-chloro-bis-(3-t-butylthio-2-methoxy-2-methylpropyl-1-*C*,*S*)dipalladium(II) with I [6]. Platinum(IV)-carbene complexes with a similar five-membered chelate resulted from the reaction of *cis*-[$PtCl_2\{C(NHR)(NHPh)\}PEt_3$] with chlorine [12].

Results and discussion

Preparations and general properties

A mixture of the olefin I and iodotrimethylplatinum(IV) tetramer II was refluxed in *m*-xylene for 3 h. After washing the precipitate with dichloromethane, complex III was obtained as pale olive microcrystals. On the basis of elemental analysis, spectroscopic data, and the characterization of derivatives of III, this complex was determined to be a dinuclear cycloplatinated carbene complex, di-μ-iodo-bis(1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2′-*C*)diplatinum(II) $[\{Pt(dpim)I\}_2]$ (dpim = 1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2′-*C*). The new dimeric complex is very insoluble in common organic solvents.

Complex III reacted with thallium(I) acetylacetonate and with triisopropyl phosphite to yield mononuclear complexes, IV and V, respectively. Moreover, facile iodine abstraction from III with $AgClO_4$ in the presence of an excess of acetonitrile and 1,5-cyclooctadiene gave cationic complexes, VI and VII, respectively. Yields, elemental analyses, and some physical and spectroscopic properties of these complexes are summarized in Tables 1—3.

These carbene complexes, III—VII, showed two characteristic strong bands of $\nu\{C(aromatic)—N\}$ near 1280 and 1300 cm^{-1} and medium bands of $\nu\{C(carbene)—N\}$ in the range 1485—1515 cm^{-1}. Moreover, out of plane $\delta(CH)$ bending modes of both mono- and 1,2-di-substituted aromatic rings were observed, as shown in Table 2. Coordination of acetonitrile molecules in VI *via* the nitrogen atom to the metal center is confirmed by the increase in C≡N stretching frequencies, compared with the uncomplexed nitrile (2254 cm^{-1}). Ionic structures of VI and VII were ascertained both by their high molar conductivities in dichloromethane (See Experimental) and by detection of a T_2(ClO) stretching mode at ca. 1100 cm^{-1} without any significant splitting (Ta-

TABLE 1

YIELDS AND PROPERTIES OF THE CARBENEPLATINUM(II) COMPLEXES

Complex		Yield [a] (%)	M.p. [c] (°C)	Analysis: Found (calcd.) (%)		
				C	H	N
$[\{Pt(dpim)I\}_2]$	III	84 [b]	>300	33.07 (33.17)	2.35 (2.41)	4.96 (5.16)
[Pt(dpim)(acac)]	IV	49	246	47.45 (46.60)	4.04 (3.91)	5.44 (5.43)
$[Pt(dpim)I\{P(OCHMe_2)_3\}]$	V	17	184—186	38.13 (38.36)	4.69 (4.56)	3.55 (3.73)
$[Pt(dpim)(CH_3CN)_2]ClO_4$	VI	95	212—214 [d]	38.14 (38.17)	3.23 (3.20)	9.34 (9.37)
$[Pt(dpim)(COD)]ClO_4$ [e]	VII	52	142—147 [d]	42.87 (42.35)	4.00 (3.93)	4.17 (4.20)
$[\{PtMeI(Hdpim)\}_2]$	IX	17 [d]	~250 [b]	34.06 (34.36)	3.04 (3.06)	4.82 (5.01)

[b] Based on III, unless noted elsewhere. [b] Based on II. [c] All melting points are uncorrected. [d] With decomposition. [e] With a half molecule of CH_2Cl_2 as solvent of crystallization.

TABLE 2

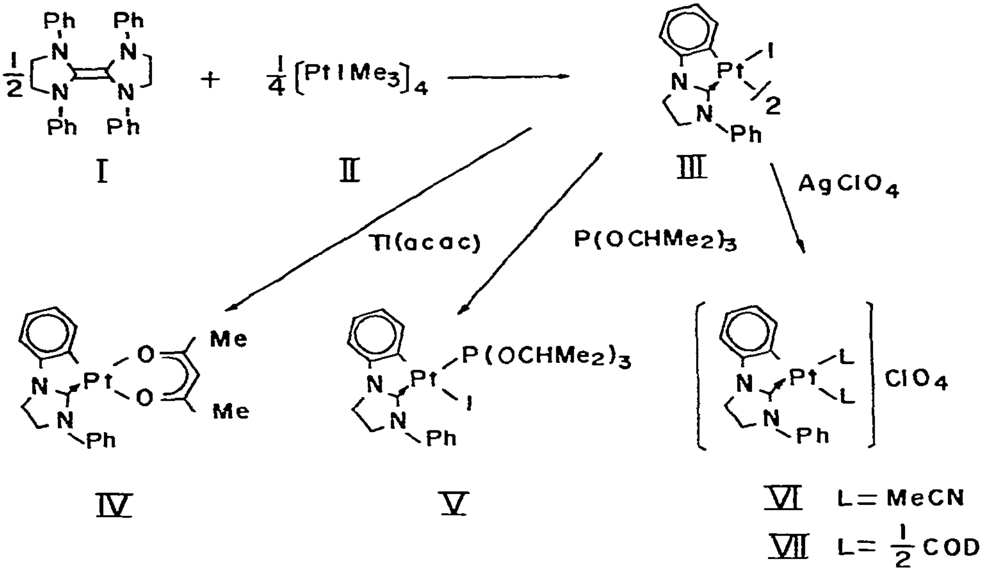
SELECTED IR DATA[a]

Complex	ν {C(carbene)—N}	$\nu(C_{\phi}—N)$[b]	δ(CH)[c]	Others
III	1489, 1501	1283, 1302	693, 748, 765	—
IV	1495	1278, 1299	685, 740, 758	1519, 1583 {ν(C=C) + ν(C=O)}
V	1490, 1505	1288, 1304	693, 760, 775	989 ν(P—O—C)
VI	1516	1289, 1307	695, 750, 775	2310, 2330 {ν(C≡N)} 1098 ν(Cl—O)
VII	1485, 1505	1283, 1299	696, 742, 767	1095 ν(Cl—O)
IX	1472, 1496	1283	688, 760	2940, 2883, 2802 {ν(CH)}[d]

[a] In cm^{-1}, in KBr disk. [b] ν {C(aromatic)—N}. [c] Out of plane δ(CH) bending modes of aromatic rings. [d] ν(CH)'s of Pt—CH_3 moieties. The band at 2883 cm^{-1} overlapped with the ν(CH) of the ethylene groups.

ble 2). The mass spectrum of IV showed a parent-ion pattern centered at *m/e* 515 in accord with the proposed structure.

SCHEME 1



^{13}C *NMR spectra*

The ^{13}C NMR spectra of the complex IV was observed in CD_2Cl_2, and enolate acac bidentate chelate exhibited five signals: two resonances at δ(C) 27.2 and 27.3 ppm for two methyl carbons, two at δ 184.4 and 185.7 ppm for two oxygen-bonding carbons, and one at δ 101.7 ppm for the methine carbon. The resonance at δ 101.7 ppm is flanked by satellites due to ^{195}Pt with coupling constant J(Pt—C) = 56 Hz. In addition, IV exhibited both a carbene carbon resonance (2-C) at δ 173.9 ppm and a resonance at δ 149.9 ppm for the platinum-substituted *o*-phenylene carbon (2′-C). The detection of the quaternary platinum-substituted carbon indicates, without doubt, that one phenyl group of the 1,3-diphenyl-2-imidazolidinylidene ligand was cycloplatinated.

The carbene carbon in the palladium analogue, (acetylacetonato)(1,3-diphenyl-2-imidazolidinylidenato-2-*C*,2'-*C*)palladium(II), VIII resonated at δ 192.1 ppm [6]. A similar upfield shift of the carbene resonance by replacement of Pd by Pt was reported for dihalo(carbene)(tertiary phosphine)metal(II) complexes [9].

Two resonances at δ 123.4 and 140.8 ppm are attributed to a N-substituted carbon (1'-C) of the *o*-phenylene group and to that (1''-C) of the unmetallated phenyl group. Unfortunately, the comparatively poor solubility of IV did not allow determination of *J*(Pt—C) for these quaternary carbon resonances. In addition, there are two other signals at δ 44.3 ppm [with satellites, $^3J(^{195}Pt—C)$ = 56 Hz] and at δ 27.7 ppm, assignable to two methylene carbons of the imidazolidinylidene ring. Three kinds of carbons in the unmetallated phenyl group resonated at δ 126.8 (for 2''- and 6''-C), 128.8 (for 3''- and 5''-C), and 127.4 ppm (for 4''-C).

^1H *NMR spectra*

In the ^{1}H NMR spectra of these platinum carbene complexes, four protons on a cyclometallated phenylene ring demonstrated a clearly distinguishable ABCD pattern (^3J = ca. 7.5 Hz, ^4J = ca. 1.5 Hz) in the range of δ 6.3—7.9 ppm, as shown in Table 3. This confirms unambiguously the cycloplatinated structure of the dpim moiety. A similar pattern was observed for analogous cyclopalladated carbene complexes [7]. Moreover, the ethylene protons (4 H) of the imidazolidinylidene ring in these cycloplatinated complexes showed a typic AA'BB' pattern in the range δ 3.5—4.5 ppm.

Reaction of III with a five-fold molar quantity of triisopropyl phosphite under THF reflux gave a pale olive powder. The ^{1}H NMR spectrum of the powder exhibited four doublets with the intensity ratio of 1 : 1 : 0.36 : 0.36 at δ 1.33,

TABLE 3

THE ^{1}H NMR DATA OF THE PLATINUM(II) COMPLEXES [a]

Complex	dpim moiety					Other [c]
	Cycloplatinated phenylene [b]			Phenyl (C_6H_5)	Ethylene NCH_2CH_2N	
	3' or 6'	4' and 5'	6' or 3'			
IV	6.43dd	6.79dt 7.00dt	— [d]	7.1— 7.7c [d]	3.56— 4.4m	1.31 (s, 3 H, Me) 1.97(s, 3 H, Me) 5.30 (s, H, CH)
V	6.53d	6.81t 7.10t	7.94d	7.1— 7.7b	3.6— 4.5c	1.33 (d, 18 H, Me) [f] 4.53—5.08 (c, 3 H, CH
VI [e]	6.54d	6.85t 7.11t	7.33d	7.46s	3.78— 4.5m	1.85 (s, 3 H, Me) 2.57 (s, 3 H, Me)
VII	6.73d	6.97t 7.21t	— [d]	7.58 bs [d]	3.8— 4.5c	2.0—2.8 (b, 8 H, CH_2) 5.07 (b, 2 H, CH) 6.06 (b, 2 H, CH)

[a] δ values from TMS, in CD_2Cl_2. Abbreviations used: b = broad, bs = broad singlet, c = complicated, d = doublet, m = an AA'BB' type multiplet, s = singlet. [b] Coupling constants: ^3J(HH) = ca. 7.5 Hz. ^4J(HH) = ca. 1.5 Hz. [c] Signal shape, proton number, and the assignment are given in the parentheses. [d] Overlapping with the other signals. [e] Measured at +40°C. [f] ^3J(HH) = 6 Hz.

1.23, 1.09 and 0.99 ppm (^3J(HH) = 6.3 Hz), respectively. The first signal corresponded to V. The second one was tentatively ascribed to the geometrical isomer of V, whereas the third and fourth signals were due to a cationic bis(triisopropyl phosphite)platinum(II) complex, since the intensities of these two signals were equal.

The ^{1}H NMR spectrum of VI in CD_2Cl_2 showed two singlets at δ 1.85 (3 H) and 2.57 (3 H) ppm for two acetonitrile ligands, even at 40°C. This result is in sharp contrast to that observed for the corresponding palladium complex, where two coordinated acetonitrile ligands showed only one singlet at 21°C due to an exchange process, and two separated singlets at —41°C [7]. The different behavior of the two metal complexes indicates that bonding between platinum and acetonitrile is stronger than that between palladium and acetonitrile.

The ^{1}H NMR spectrum of VI in CD_3CN showed only one signal at δ 1.93 ppm, indicating a fast exchange between the acetonitrile ligands and solvent molecules. In addition, cyclooctadiene complex VII in CD_3CN showed ^{1}H NMR signals of free cyclooctadiene, dissociated from platinum by solvent acetonitrile molecules. Similar lability of metal—olefin and metal—nitrile bonds was observed in analogous cyclopalladated carbene complexes [7].

An intermediate in the cycloplatination reaction

Iodotrimethylplatinum(IV) tetramer II does not decompose until about 195°C and is very stable even in refluxing *m*-xylene. However, coordination of the electron-rich olefin I to II and fragmentation of the olefin to form carbene-metal species might induce high electron density on platinum to bring about reductive elimination of ethane. From one run performed in refluxing toluene for 30 min, a gray powder was isolated, which was sparingly soluble in common organic solvents. The IR spectrum of this powder exhibited only two bands at 688 and 760 cm^{-1} in the range of 650 to 800 cm^{-1}, attributable to out of plane δ(CH) bending modes of monosubstituted aromatic rings. Other characteristic bands, such as ν(CH) of methyl groups, ν{C(aromatic)—N}, and ν{C(carbene)—N}, were detected as listed in Table 2. These data and elemental analysis (Table 1) indicate that the powder involves both a methyl group and a Hdpim moiety (Hdipm = 1,3-diphenyl-2-imidazolidinylidene), and is probably ascribed to a (carbene)methylplatinum(II) dimer, [{PtMeI(Hdpim)}$_2$] (IX).

From another run under toluene reflux for 3 h, only III was isolated, suggesting that IX is an intermediate leading to III. Upon continued heating in refluxing *m*-xylene, the methyl group in IX might abstract an *ortho*-proton from one phenyl ring attached to the 2-imidazolidinylidene ligand, yielding the cycloplatinated complex III together with methane evolution. Similar abstrac-

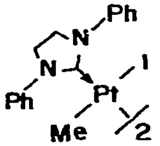


Fig. 1. Proposed structure of IX.

tion of the *ortho*-proton by an alkyl group was previously reported for the palladium carbene complex [6]. It is noted that the (carbene)methylplatinum(II) complex IX was isolated without the coordination of a tertiary phosphine or arsine or isocyanide, as compared with previously reported alkyl(carbene)platinum(II) complexes [13,14].

Concluding remarks

The cycloplatinated carbene complex III was obtained in high yield from the reaction of iodotrimethylplatinum(IV) tetramer II with the electron-rich olefin I, through the intermediate of [{PtMeI(Hdpim)}$_2$]. It is noteworthy that iodotrimethylplatinum(IV) tetramer is an effective starting material for the cycloplatination. Complex VII has carbene—platinum and olefin—platinum bonds, and may be regarded as a stable model compound for the active species of catalytic olefin metathesis.

Experimental

Materials and general procedures

Bis(1,3-diphenyl-2-imidazolidinylidene) I [15] and iodotrimethylplatinum(IV) tetramer II [16] were prepared by the respective literature methods. Solvents were dried by the standard methods and distilled. Preparative operations were performed under dry nitrogen. ^{13}C NMR spectra were recorded on a JEOL FX-90-Q spectrometer, using tetramethylsilane as an internal standard. IR, ^{1}H NMR, and mass spectra, melting points, and molar conductivities were measured according to the methods described in the previous paper [11].

Preparation of cyclometallated complex III

A mixture of I (0.96 mmol) and II (0.48 mmol) in *m*-xylene (70 ml) was refluxed for 3 h. The resulting solid was collected and washed successively with dichloromethane and diethyl ether to give pale olive microcrystals of [{Pt(dpim)I}$_2$] III.

Reaction of III with thallium acetylacetonate

A dichloromethane suspension (12 ml) containing the iodo-bridged dinuclear complex III (0.18 mmol) and thallium acetylacetonate (0.37 mmol) was heated under reflux for 5 h with stirring. After removal of solvent, the residue was recrystallized from benzene and hexane to yield yellow needles of [Pt(dpim)(acac)] IV.

Reaction of III with triisopropyl phosphite

Triisopropyl phosphite (0.37 mmol) was added to a THF solution (15 ml) of complex III (0.18 mmol), and the mixture was stirred at room temperature for 24 h. After removal of solvent under vacuum, the residue was recrystallized from benzene and hexane to afford yellow microcrystals of [Pt(dpim)I{P(OCHMe$_2$)$_3$}] V.

Reaction of III with acetonitrile in the presence of AgClO$_4$

A benzene solution (6 ml) of silver perchlorate (0.37 mmol) was added to acetonitrile suspension (6 ml) of complex III (0.18 mmol). After stirring for 24 h at room temperature, solvents were removed under vacuum and the residue was washed with benzene and diethyl ether. Yellow crystals of [Pt(dpim)-$(NCCH_3)_2]ClO_4$ VI were obtained by recrystallization from acetonitrile and diethyl ether. Molar conductivities of VI: 30 and 127 Ω^{-1} cm^2 mol^{-1} in 1.0 × 10^{-3} M CH_2Cl_2 and CH_3CN-solutions, respectively.

Reaction of III with 1,5-cyclooctadiene (COD) in the presence of $AgClO_4$

A benzene solution (5 ml) of silver perchlorate (0.37 mmol) was added slowly to a dichloromethane suspension (10 ml) of complex III (0.18 mmol) and 1,5-cyclooctadiene (3.7 mmol). The mixture was stirred for 2 h, and solvents were removed under a reduced pressure. Recrystallization of the residue from dichloromethane and diethyl ether gave orange microcrystals of $[Pt(dpim)(COD)]ClO_4$ VII. Molar conductivity; 44.5 Ω^{-1} cm^2 mol^{-1} in 1.0 × 10^{-3} M CH_2Cl_2 solution.

Isolation of the intermediate [{PtIMe(Hdpim)}$_2$] IX

Gray microcrystals of IX were prepared in a similar manner to the preparation of III, except that the reaction was performed under toluene reflux for 30 min.

Acknowledgements

The authors are grateful to Misses Yumi Kojima and Miho Sadauchi for their technical assistance.

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