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Homoleptic carbene complexes
VI. [☆]
Bis{1,1′-methylene-3,3′-dialkyl-diimidazolin-2,2′-diylidene}palladium chelate complexes by the free carbene route

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Abstract

1,1′-Methylene-3,3′-dialkyldiimidazolium salts have been deprotonated with *n*-butyllithium in the presence of palladium(II) iodide to give the percarbene complexes **1** (alkyl = Me) and **2** (alkyl = Et), each containing two bidentate 1,1′-methylene-3,3′-dialkyldiimidazolin-2,2′-diylidene chelate ligands. The X-ray structure analysis of **1** reveals a stereochemistry in which the two spiro-linked six-membered metallacycles adopt boat-like conformations strongly bending out of the PdC_4 coordination plane in opposite directions. The carbenoid imidazole rings, which are rotated by +42 and −43°, respectively, relative to this plane, break down into two tightly bound π-systems ($N \doteq 4C \doteq 4N$, C=C) connected by long C–N bonds.

Keywords: Carbene complexes; Free carbenes; Spiro-metallacycles

1. Introduction

The most efficient and convenient synthetic approach to carbene-rich metal complexes undoubtedly is that via nucleophilic additions to coordinated isocyanides. While the first homoleptic tetracarbene complexes of palladium and platinum were obtained from simple tetra(methylisocyanide)metal precursors and methylamine [2], it was through intramolecular cyclizations of and intermolecular cycloadditions to "functional" isocyanides in metal complexes that many new compounds of this type containing carbenoid imidazoles or imidazolines and up to six oxazolines as ligands have been prepared [3–5]. Aside from this, however, various synthetic procedures starting from preformed heterocycles have been developed [6a–f], of which Lappert's route via electron-rich olefins deserves particular attention [7]. From there, a first chelating dicarbene–rhodium(I) complex with a macrocyclic bis(imidazolidin-2-ylidene) type ligand had resulted [8]. Earlier, Wanzlick and Schönherr [9] had prepared bis(imidazolin-2-ylidene)mercury(II) by deprotonation of *N*,*N*′-diphenylimidazolium perchlorate and treatment of the intermediate product with mercury(II) chloride. A closely related approach, reactions of *N*,*N*′-dialkylated azolium salts with (basic) hydridocarbonylmetalates, was chosen by Öfele and co-workers to obtain a series of heterocyclic carbene derivatives of the hexacarbonyls of the Group 6 metals [10], and only recently extended to the preparation of chelating dicarbene complexes of chromium and tungsten [11]. Arduengo et al.'s discovery of the existence of stable free imidazol-2-ylidenes [12] now provided a plausible mechanism for the latter transformations and at the same time opened up a route to new carbene complexes of both main group elements and transition metals via isolated free carbenes [13–15].

Bidentate 1,1′-methylene-3,3′-dialkyldiimidazolin-2,2′-diylidenes were of interest to us for the intended preparation of chelating percarbene complexes of the late transition metals. Only a few compounds of this type are known [1], none with cyclic carbene ligands. Both types, however, can be regarded as preliminary

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[☆] For Part V, see Ref. [1].

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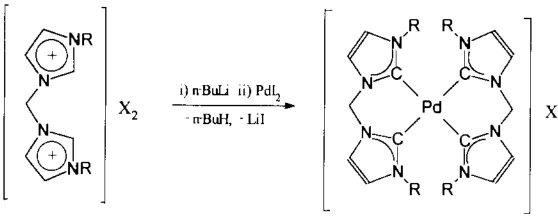
stages and, possibly, prerequisites for the construction of macrocyclic systems with C-encapsulated metal atoms ("C-porphyrins", "C-cages"), one of our long-term research objectives. Here we report on the synthesis and structural characterization of two percarbene complexes of palladium(II) with 1,1′-methylene-3,3′-dialkyldiimidazolin-2,2′-diylidenes as chelating ligands.

2. Results and discussion

In order to trap immediately a possibly formed free carbene (dicarbene) by metal coordination, the deprotonation of 1,1′-methylene-3,3′-dimethyldiimidazolium iodide with two equivalents of *n*-butyllithium was carried out in the presence of suspended palladium iodide. The colourless crystalline solid which was isolated in small amounts from the reaction mixture proved to be the hoped-for carbene chelate complex **1** (Eq. (1)). As expected, 1,1′-methylene-3,3′-diethyldiimidazolium tetrafluoroborate reacted similarly to give complex **2**. However, no reaction occurred between PtI_2 and the in situ-generated free dicarbene.



	R	X
1	Me	I
2	Et	BF_4

The ^1H NMR spectrum of **1** shows two doublets of equal intensity at δ 7.75 and 7.4 for the imidazole ring protons, two doublets at δ 6.75 and 6.48 for the methylene protons and a singlet at δ 3.4 for the methyl groups. The chemical shifts in the spectrum of **2** are similar (δ 7.85 and 7.6 for the ring protons and δ 6.6 and 6.55 for the protons of the methylene group between the rings) except for the protons of the ethyl group which give rise to two multiplets at δ 3.8 and 3.4 and a triplet at δ 1.1 ppm. Similar values have been observed for the imidazole protons in tetrakis(*N*-alkylimidazolin-2-ylidene)palladium complexes containing monodentate carbene ligands [4], while those of free 1,3-dimethylimidazol-2-ylidene [13] and *cis*-tetracarbonyl(1,1′-methylene-3,3′-dimethyldiimidazolin-2,2′-diylidene)chromium [11] were found at lower fields. A strong coordination effect comes out in the ^{13}C NMR signals of the carbene carbon atoms which in **1** and **2** like in $[Pd\{\overline{CN(R)CHCHN}H\}_4]^{2+}$ appear around 168 as against 215 ppm in 1,3-dimethylimidazol-2-ylidene [4,13]. The number of resonances in both the ^{13}C and ^1H NMR spectra is in accordance with a symmetrical structure of the complex cation in solution. The non-equivalence of the protons of the linking methylene groups, however, rules out a planar structure. Temperature-dependent NMR spectra up to 410 K show this non-equivalence to be preserved, i.e. the structure is rigid with respect to an equilibration of the geminal Hs by quickly passing through a planar arrangement. Inspections of models of **1** and **2** show that the *N*-alkyl groups cannot get past one another if the bischelate system is forced into planarity. This is in contrast to *cis*-tetracarbonyl(1,1′-methylene-3,3′-dimethyldiimidazolin-2,2′-diylidene)chromium, which is fluxional at room temperature [16]. The crowded ligand sphere in **2** seems even to hinder the free rotation about the N–Et axis, thus causing the two multiplets of the $CH_2(Me)$ groups.

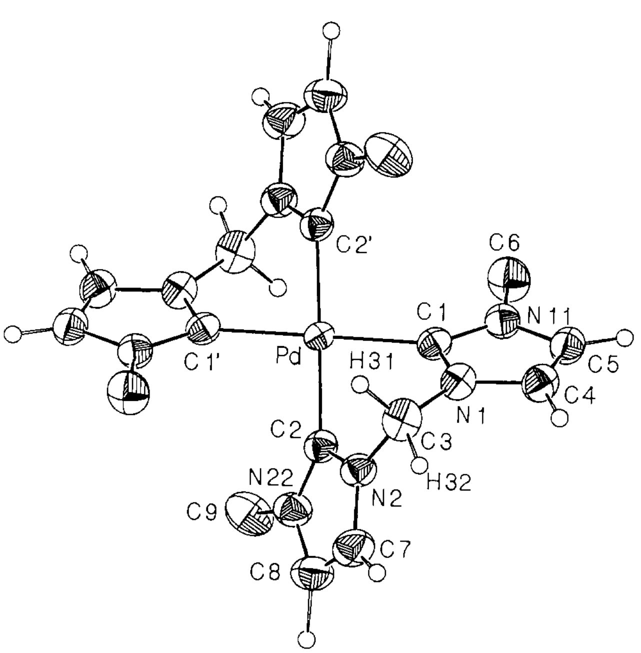


Fig. 1. ORTEP plot and labelling scheme of the cation of **1**. The thermal ellipsoids have been drawn to include 50% probability.

In the IR spectra of **1** and **2**, the stretching vibrations of the N ═ C ═ N groups are tentatively assigned to bands about 1570 cm^{-1}; as pointed out before, in aromatic ring systems this feature is not very characteristic and possibly strongly coupled to other ring vibrations [4].

Crystals of **1** suitable for an X-ray diffraction study were obtained from water/methanol. The structure of the complex cation is shown in Fig. 1. Coordinates of **1** are given in Table 1 and selected bond lengths and angles in Table 2. The asymmetric unit contains one half of the cation, one iodide and one molecule of water. The other part is generated by a center of symmetry which is occupied by the metal.

The heterocyclic rings are planar with the best planes

Table 1
Coordinates of **1**

Atom	x/a	y/b	z/c
Pd1	0.0000	1.0000	0.0000
I1	0.3383(1)	0.7177(1)	−0.2918(1)
C1	0.1954(5)	1.1084(5)	−0.0069(4)
C2	0.0805(5)	0.8093(5)	0.1740(4)
N1	0.2200(4)	1.0976(4)	0.1177(4)
N11	0.3100(4)	1.1918(4)	−0.1157(4)
N2	0.1268(4)	0.8382(4)	0.2754(4)
N22	0.1077(4)	0.6398(4)	0.2173(4)
C3	0.1281(6)	1.0069(6)	0.2628(5)
C4	0.3740(5)	1.1723(5)	0.0874(5)
C5	0.4297(5)	1.2303(5)	−0.0572(5)
C6	0.3444(6)	1.2294(6)	−0.2735(5)
C7	0.1808(6)	0.6905(6)	0.3819(5)
C8	0.1686(6)	0.5660(6)	0.3463(5)
C9	0.0829(7)	0.5446(6)	0.1383(6)
O1	0.2572(5)	1.1373(3)	0.4648(4)

as defined by the ring atoms deviating from the coordination plane by as much as +42° and −43°. This heavy bulging in opposite directions of the two chelate systems obviously serves the purpose of reducing the steric hindrance between the *N*-methyl groups (C6, C9′ and C9, C6′), thereby leading to the chemically inequivalent methylene protons H31 and H32 already observed in the NMR spectra. The six-membered ring which consists of the metal, the carbene carbon atoms, two adjacent nitrogens and the methylene group is reminiscent of a cyclohexane ring in a fixed boat conformation. Most remarkably, tetrakis(*N*-methylimidazoline-2-ylidene)palladium iodide can be viewed as forming comparable chelate rings in the solid state. Instead of the CH_2 bridge it is the iodide counteranion which connects two monodentate carbene ligands through (N)H ··· I ··· H(N) hydrogen bridges [4]. The much stronger covalent bonds in **1** cause a significant distortion of the expected square arrangement about palladium (81.8, 98.2) which allows the other angles to adopt more or less ideal values. The metal–carbene carbon bond lengths correspond to the sum of the covalent radii of Pd^{II} and $C(sp^2)$, i.e. these bonds have single bond character. Short C(carbene)–N distances, on the other hand, clearly indicate that carbene stabilization is exclusively committed to π-interaction between these atoms. As an obvious consequence, π-delocalization within the ring has partly been given up in favour of two rather localized π-systems, the NCN group and the transannular C–C double bond, which are held together by comparatively long bonds. Similar ring distortions have been established in the X-ray structures of monodentate imidazolin-2-ylidene complexes [4,6g,17] and imidazolin-2-ylidene–Lewis acid adducts [14,15], in addition to that of free 1,3-di(1-adamantyl)imidazolin-2-ylidene [12].

Table 2
Selected bond lengths (pm) and angles (°) of **1**

Pd1–C1	213.7(5)	C1–Pd–C2	81.8(2)
Pd1–C2	204.9(4)		
C1–N1	136.5(7)	Pd–C1–N1	122.2(2)
C1–N11	139.8(5)	Pd–C2–N2	122.4(4)
C2–N2	136.2(7)		
C2–N22	135.6(5)	C1–N1–C3	118.7(4)
N1–C3	148.5(5)	C1–N1–C4	112.9(3)
N1–C4	146.4(6)	C4–C5–N11	105.5(4)
N11–C5	145.0(8)	N11–C4–C5	106.9(5)
N11–C6	147.0(7)	C5–N11–C1	113.3(4)
N2–C3	144.9(7)		
N2–C7	139.8(5)	C2–N2–C3	121.6(3)
N22–C8	141.6(7)	C2–N2–C7	112.6(4)
N22–C9	148.3(9)	N2–C7–C8	105.2(5)
C4–C5	132.4(6)	C7–C8–N22	107.5(4)
C7–C8	133.7(9)	C8–N22–C2	110.5(5)

We had earlier speculated that this particular stereochemistry might be associated with a certain activation of the heterocycle by the carbene-like metal coordination. In fact, recent investigations of the chemistry of pentacarbonyl(4-aminoimidazolin-2-ylidene)chromium and -tungsten, products of four-component condensations with cyano complexes, revealed an unprecedented course of the oxidative removal of the heterocyclic ligand from the metal involving oxidation of the isolated C–C double bond [18].

3. Experimental details

The reactions were carried out in dried solvents under argon. *n*-Butyllithium (Aldrich) was used without further purification, 1,1′-Methylene-3,3′-dimethyldiimidazolium iodide and 1,1′-methylene-3,3′-diethyldiimidazolium tetrafluoroborate were prepared using literature methods [19]. NMR spectra were recorded on a Bruker WH 270 spectrometer. They were referenced internally using residual protic solvent resonances relative to tetramethylsilane. All chemical shifts are quoted in ppm and coupling constants in Hz. Signals are expressed as position, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant relative integration and assignment. IR (KBr) spectra were recorded on a Perkin-Elmer Model 983 spectrometer (intensity: vs = very strong, s = strong, m = medium, w = weak, br = broad). Mass spectra were obtained using a Varian CH 5 DF spectrometer. Signals are expressed as mass to charge at (m/z) and assignment (L = diimidazole ligand). Elemental analyses were carried out using a Heraeus CHN-Rapid. Melting points (Gallenkamp MFB 595) are uncorrected.

3.1. *Bis(1,1′-methylene-3,3′-dimethyldiimidazolin-2,2′-diylidene)palladium iodide (1)*

PdI_2 (0.72 g, 1.50 mmol) and 1,1′-methylene-3,3′-dimethyldiimidazolium iodide (1.50 g, 3.50 mmol) were suspended in 30 ml of *n*-hexane and cooled to −72°C. To this 2.3 ml of a 1.6 M solution of *n*-butyllithium in *n*-hexane (8 mmol) were added slowly. The reaction mixture was stirred for 1 h and then allowed to warm to room temperature within 6 h. The black solid was collected by filtration and extracted with methanol. The combined extracts were neutralized with HCl, and the solvent was removed in vacuo to leave a colourless solid. Recrystallization from methanol/water gave 0.13 g (0.18 mmol, 12%) of colourless crystals, m.p. 215°C (decomp.). Anal. Found: C, 28.94; H, 3.97; N, 15.18. Calc. for $C_{18}H_{24}I_2N_8Pd + 2\ H_2O$ (748.7): C, 28.88; H, 3.77; N, 14.97%. Mass spectrum (*m/z*): 585 (2%, $[PdL_2I]^+$); 545 (4%); 457 (5%, $[PdL_2]^+$); 282 (8%, $[PdL]^+$). ^{1}H NMR (DMSO-d_6): 7.8 (d, ^3J(H,H) = 4 Hz, 2H, CH); 7.45 (d, ^3J(H,H) = 4 Hz, 2H, CH); 6.7 (dd, ^2J(H,H) = −16 Hz, 2H, NCH_2N); 1.1 (s, Me). ^{13}C NMR: 169.4 (MC); 123.1 (CH); 122.4 (CH); 62.6 (NCH_2N); 36.9 (Me). IR: 3422s [ν(OH)]; 3142w, 3103m, 3070m [ν(CH)]; 1562m [ν(N=C=N)]; 1465s; 1414s; 1361s; 1250s; 1224s; 1181s; 1070vs, br; 806m; 762m; 744s.

3.2. *Bis(1,1′-methylene-3,3′-diethyldiimidazolin-2,2′-diylidene)palladium tetrafluoroborate (2)*

Compound **2** was prepared in the same way as **1** from 0.72 g (1.50 mmol) of PdI_2 and 1.35 g (3.50 mmol) of 1,1′-methylene-3,3′-diethyldiimidazolium tetrafluoroborate to give 0.138 g (0.21 mmol, 14%) of a white solid, m.p. 235°C (decomp.). Anal. Found: C, 36.71; H, 5.13; N, 15.52. Calc. for $C_{22}H_{32}B_2F_8N_8Pd + 2\ H_2O$ (724.6): C, 36.46; H, 4.97; N, 15.46%. Mass spectrum (*m/z*): 514 (4%, $[PdL_2]^+$); 310 (17%, $[PdL]^+$); 281 (12%, $[PdL - Et]^+$); 175 (base, $[L - Et]^+$). ^{1}H NMR (DMSO-d_6): 7.9 (d, ^3J(H,H) = 4 Hz, 2H, CH); 7.8 (d, ^3J(H,H) = 4 Hz, 2H, CH); 6.55 (dd, ^2J(H,H) = −14 Hz, 2H, NCH_2N); 3.8 (dt, ^2J(H,H) = −16 Hz, ^3J(H,H) = 8 Hz, 2H, NCH_2Me); 3.4 (dq, ^2J(H,H) = −16 Hz, ^3J(H,H) = 8 Hz, 2H, NCH_2Me); 1.1 (t, ^3J(H,H) = 8 Hz, 6H, Me). ^{13}C NMR: 168.8 (MC); 122.7 (CH); 121.5 (CH); 63.0 (NCH_2N); 45.1 (CH_2Me); 16.1 (Me). IR: 3451s [ν(OH)]; 3131m, 3098m, 2985m [ν(CH)]; 1560m [ν(N=C=N)]; 1474s; 1427s; 1266s; 1213s; 1177s; 1063vs, br; 747s; 692s.

3.3. *Crystal structure determination*

Crystals of **1** were obtained from methanol/water.

3.3.1. *Crystal data*

$C_{18}H_{28}I_2N_8O_2Pd$, $M = 748.64$, triclinic, $a = 8.813(1)$, $b = 8.866(2)$, $c = 10.290(2)$ Å; $\alpha = 65.01(1)$, $\beta = 72.37(2)$, $\gamma = 75.94(2)°$; $U = 688.5$ Å^3, $\lambda = 0.71069$ Å, space group $P\bar{1}$, $Z = 2$, $d_c = 1.811$ g cm^{-3}. Colourless prisms, crystal dimensions 0.18 × 0.28 × 0.55 mm μ(Mo Kα) = 59.05 cm^{-1}. $F(000) = 150$.

3.3.2. *Data collection*

A Nonius CAD 4 diffractometer (scan mode $\omega - 2\theta$, scan width $4° \leqslant 2\theta \leqslant 60°$, graphite-monochromated Mo Kα radiation) was used; 3725 unique reflections were measured, of which 3197 were of $I \geqslant 4\sigma(F_o)$.

3.3.3. *Structure analysis and refinement*

The position of the Pd atom was taken from a Patterson map. Non-hydrogen atoms were located using successive Fourier syntheses and refined with anisotropic thermal parameters by least-squares methods. A correction for anomalous dispersion and isotropic extinction [20] was carried out in the final cycles of refinement. The applied weighting scheme was $w = 1/\sigma^2\ (F)$. Final R and R_w values are 0.033 and 0.037 and the final residual electronic density is < 1.078 e Å^{-3}. Atomic scattering factors for neutral atoms and anomalous dispersion coefficients were taken from the International Tables for X-Ray Crystallography [21]. The programs SHELXS-86 [22], XTAL 3.0 [23] and DIFABS [24] were used for processing and refinement and ORTEP [25] for drawings.

Further details of the crystal structure are available in the supplementary material deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany) (CSD 58256). Any request should be accompanied by the full literature citation for this paper.

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