Carbene Adducts of Dimethylcadmium

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Carbene, Cadmium, Ylide, Carbene Complex, Imidazol-2-ylidene

The first examples of carbene-cadmium complexes are reported from the reactions of a variety of imidazol-2-ylidenes or imidazolin-2-ylidenes with dimethylcadmium. Four new carbene complexes are characterized by NMR spectroscopy (¹H, ¹³C and ¹¹³Cd). The cadmium centers are strongly shifted downfield (100 - 150 ppm) by interaction with the carbenes. X-ray structures are reported for three carbene-cadmium 1:1 adducts. The cadmium centers exhibit distorted trigonal-planar geometries in which the carbene ligands have an average 18.2 pm longer bond distance to cadmium compared to the methyl groups. The planes of cadmium coordination are twisted with respect to the plane of the imidazole ring. The more basic imidazolin-2-ylidene is shown to displace imidazol-2-ylidenes from the cadmium center.

Introduction

Since 1991 a number of structurally different types of stable, nucleophilic carbenes have been described, for example several 1,3-disubstituted imidazol-2-ylidenes [1, 2], 1,3,4,5-tetrasubstituted imidazol-2-ylidenes [2-4], 1,3,4-triphenyl-1,2,4triazol-5-ylidene [5], 1,3-disubstituted imidazolin-2-ylidenes [6, 7], N,N,N',N'-tetraisopropylformamidinylidene [8], 3-(2,6-diisopropylphenyl)-4,5dimethylthiazol-2-ylidene [9], air-stable 4,5-dihaloimidazol-2-ylidenes [10], and most recently, aminooxycarbenes [11]. A historical review of the development of these stable nucleophilic carbenes has recently appeared [12] and some of the chemistry of stable heterocyclic carbenes has been reviewed [13]. Stable nucleophilic carbenes possess high Lewis basicity and reveal a strong tendency to react with even mild Lewis acids. As a consequence of this reactivity, their reactions with both metallic and non-metallic Lewis acids furnish many unusual adducts [14].

Donor complexes of nucleophilic carbenes with zinc [14, 15] or mercury [16 - 20] compounds have been previously reported. Carbene-cadmium complexes remain unknown however. With the discoveries that cadmium can substitute for zinc in carbonic anhydrases (retaining some enzymatic activity) [21] and that cadmium can play a role in epoxide/CO₂ copolymerizations [22], the coordination chemistry of cadmium has become more important. Organocadmium compounds, compared to their zinc analogs have a much lower Lewis acidity, and their complex-forming tendencies are considerably decreased. Taking advantage of the high nucleophilicity of imidazol-2-ylidenes and imidazolin-2ylidenes, we now report the first examples of zwitterionic carbene-cadmium complexes.

Results and Discussion

When carbenes **1a-d** were treated with dimethylcadmium at room temperature, a smooth reaction took place in which the cadmium complexes **2ad** were formed in good yields (eqs (1) and (2)). Adducts **2a-d** are colorless, air- and moisture-sensitive solids which are soluble in aromatic hydrocarbons and ethers. Although **2a**, **2c**, and **2d** melt within a rather narrow range of temperatures between 149 °C and 161 °C, a melting range of 280 - 285 °C was observed for **2b**. Such high melting points are often observed for adducts of 1,3-diadamantylimidazol-2-ylidene.

Proton and carbon solution NMR spectra show small chemical shift differences when the adducts

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Property	2b	2c	2d
$r(C^2-Cd)$	240.6 (4)	237.1 (7)	232.7 (2)
$r(Cd-CH_3)$	219.9 (4), 218.5 (4)	218.5 (8), 218.4 (8)	218.5 (4), 218.1 (4)
$r(C^2-N^{1(3)})$	137.2 (5), 136.5 (5)	136.3 (8), 134.1 (8)	133.2 (4), 132.4 (4)
$r(N^{1(3)}-C^{5(4)})$	139.6 (6), 136.8 (6)	137.2 (9), 137.7 (9)	148.7 (4), 147.5 (4)
$r(C^4-C^5)$	136.4 (7)	132.8 (10)	153.0 (5)
θ (CH ₃ -Cd-CH ₃ ')	138.8 (2)	140.0 (3)	136.2 (2)
θ (C ² -Cd-CH ₃)	105.2 (2), 116.0 (2)	111.2 (3), 108.8 (3)	109.9 (2), 114.0 (1)
$\theta(N^1-C^2-N^3)$	104.0 (3)	103.8 (5)	108.6 (3)
$\theta(C^2 - N^{1(3)} - C^{5(4)})$	110.6 (3), 112.1 (4)	110.8 (6), 111.5 (6)	113.0 (3), 113.9 (3)
$\theta(N^{1(3)}-C^{5(4)}-C^{4(5)})$	106.5 (4), 106.8 (4)	107.1 (7), 106.7 (7)	102.2 (3), 102.2 (3)
$\omega(\operatorname{imid}^{(\operatorname{mpl})}-\operatorname{Cd}^{(\operatorname{C}_3-\operatorname{mpl})})$	73.7	69.7	86.8

Table I. Selected bond lengths (pm) and angles ($^{\circ}$) in carbene-cadmium adducts **2b-d**.



2a-d are formed from the corresponding carbenes. There is a 0.2 ppm upfield shift for the imidazole ring protons ($H^{4,5}$) in the dimethylcadmium adducts **2b** and **2c** compared to the respective carbenes. The resonances for the imidazole C² carbons in the cadmium adducts shift upfield by 14 - 18 ppm relative to their positions in the free carbenes. These chemical shift changes are similar to those reported for the diethylzinc adducts of **1a** and **1b** [15].

The most dramatic chemical shift change for adducts **2a-d** is observed for the cadmium nucleus which shifts to lower field by 100 - 155 ppm relative to dimethylcadmium. Nucleophilic interactions with, or additions to, a dialkylcadmium center generally produce a downfield shift in the resonance of the affected cadmium center. Dimethylcadmium has been shown to be subject to rather large solvent shifts (up to 65 ppm downfield) in nucleophilic solvents like thf and diglyme [23]. The tris(trifluoromethyl)cadmate anion resonates 250 ppm downfield of bis(trifluoromethyl)cadmium [24]. The ¹¹³Cd chemical shift changes observed for the formation of 2a-d are intermediate between those of nucleophilic solvent interactions with a cadmium center and cadmate formation. With slightly varied stoichiometries (carbene/CdMe₂ \neq 1), NMR spectra of 2a-d exhibited averaged resonances suggesting that carbene exchanges with the adducts are fast on the NMR time scale. However if different carbenes are available, the dimethylcadmium moiety is transferred to the most nucleophilic carbene center and reverse exchange is no longer evident on the NMR time scale. When a thf- d_8 solution of the diadamantylimidazol-2-ylidene adduct 2b was mixed with the imidazolin-2-ylidene carbene 1d at room temperature, only resonances for 1b and 2d were observed with no evidence of signal averaging.

Crystals of **2b-d** suitable for single crystal X-ray diffraction studies were grown by cooling saturated toluene solutions to -20 °C. The adamantyl substituted adduct **2b** crystallizes in the monoclinic space group Cc (No. 9) with similar dimensions to the corresponding diethylzinc derivative (both structures also include a toluene of crystallization) [15]. However, the two structures are not isomorphic. The mesityl-substituted adducts **2c** and **2d** both crystallize in the monoclinic P2₁/c (No. 14) space group but again the structures are not isomorphic as has been found for other imidazolylidene-imidazolinylidene pairs [2, 7]. Further details on the unit cell parameters and data collection are found in the experimental section.

Selected bond lengths and angles in **2b-d** are presented in Table I and their structures are depicted with the KANVAS [25] drawings in Figs 1 - 3. All three structures show a planar 3-coordinated environment at the cadmium centers although the co-

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Fig. 1. KANVAS drawing of the solid state structure of **2b**.



Fig. 2. KANVAS drawing of the solid state structure of **2c**.

ordination at cadmium is not trigonally symmetric as found for the trimethylcadmate anion [26]. The deviations of the cadmium centers from the plane of their three attached carbon atoms are only 0.6, 3.8 and 0.5 pm respectively for **2b-d**. The valence angles at cadmium show a pattern of one large angle $(136 - 140^\circ)$ between the two methyl groups and two smaller angles $(105 - 116^\circ)$ between the methyl groups and the carbene moiety. The methyl-cadmium distances are all slightly shorter



Fig. 3. KANVAS drawing of the solid state structure of **2d**.

than the average C-Cd distance (224 pm) found in the trimethylcadmate anion [26]. The cadmiumcarbene distances are 240.6, 237.1 and 232.7 pm for **2b-d** and are an average 18.2 pm longer than the cadmium-methyl bonds.

For all three structures the cadmium centers are displaced from the idealized C_2 vectors that pass through the carbene centers. This distortion is greatest for the dimesitylimidazol-2-ylidene adduct 2c in which the cadmium center lies 9.1° off the C_2 vector and rises 33.1 pm out of the plane of the imidazole ring. In the corresponding saturated imidazolin-2ylidene adduct, 2d, the distortion is minimal, and the cadmium resides 9.3 pm out of the imidazole plane and only 3.4° away from the C_2 vector. The adamantyl substituted derivative 2b shows a 8.1° deviation of the cadmium from the idealized imidazole C_2 axis and the cadmium is 33.8 pm out of the imidazole plane. In 2d, the plane of the CdC₃ grouping is twisted 86.8° with respect to the imidazoline plane. For 2b and 2c the inter-plane twists are 73.7° and 69.7°, respectively. The various twists of the cadmium coordination planes with respect to the pendent imidazoles suggest that there are no special $p\pi$ -d π interactions between the imidazole and cadmium centers.

Following the successful coordination of carbenes to dimethylcadmium, dimethylmercury was briefly investigated as a potential Lewis acid partner for carbenes **1a-d**. However, no evidence of adduct formation was detected with this dialkylmercury.

Conclusions

Dialkylcadmium compounds form stable coordination complexes with imidazol-2-ylidenes and imidazolin-2-ylidenes. These cadmium-carbene complexes are novel examples of a hitherto unknown type of cadmium-carbon bond. The dimethylcadmium adducts 2a-d are stable in the solid state and in solution where they show a tendency for carbene ligand exchange in the presence of excess carbene. The geometry at cadmium in these 1:1 adducts is cadmate-like but the trigonal aspect of the coordination is not as fully developed as it is in simple cadmates like $Cd(CH_3)_3^{-1}$ [26]. The carbene-metal bonding appears weaker in 2b and 2c compared to the analogous diethyl zinc derivatives [15]. There is no evidence for $p\pi$ -d π interaction between the cadmium and carbene centers. The cadmium-carbene bond is best described as a simple σ -interaction. There is no evidence of complex formation between dimethylmercury and carbenes 1a-d. Mercuric chloride and mercury(II) ions are however known to form complexes with imidazolederived carbenes [16 - 20].

Experimental

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres dry box or using standard Schlenk techniques. Solvents were dried (using standard procedures) [27], distilled, and deoxygenated prior to use. Glassware was oven-dried at 160 °C overnight. Proton NMR spectra were recorded on a General Electric QE-300 spectrometer. The ¹³C and ¹¹³Cd spectra were recorded on a GE Omega 300WB spectrometer. NMR references are (CH₃)₄Si (¹H, ¹³C), and Cd(CH₃)₂ [via external 0.1 M CdCl₂] (¹¹³Cd). Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY.

1,3,4,5-Tetramethylimidazol-2-ylidene · *dimethylcadmium* (**2a**)

To a solution of 0.124 g (1 mmol) of 1,3,4,5-tetramethylimidazol-2-ylidene (**1a**) in 20 ml of toluene at 23 °C was added a solution of 0.142 g (1 mmol) of dimethylcadmium in 5 ml of toluene. The mixture was stirred for 2 h at 23 °C and subsequently evaporated to give a colorless solid that was recrystallized from toluene at -20 °C. Yield: 0.198 g (74%); m. p. 152 - 154 °C; ¹H NMR (C₆D₆): δ 0.11 (s, 6 H, Cd(CH₃)₂), 1.39 (s, 6 H, CCH₃), 3.44 (s, 6 H, NCH₃); ¹³C NMR (C₆D₆): δ –10.16 (s (br), Cd(CH₃)₂), 8.36 (s, CCH₃), 34.57 (s, NCH₃), 123.54 (s, C^{4,5}), 196.78 (s (br), C²); ¹¹³Cd NMR (C₆D₆): δ 155.0 (s).

Analysis for $C_9H_{18}CdN_2$ (266.7) Calcd C 40.54 H 6.80 N 10.51%, Found C 40.73 H 6.91 N 10.74%.

1,3-Di-1-adamantylimidazol-2-ylidene · dimethyl-cadmium (**2b**)

To a solution of 0.168 g (0.5 mmol) of 1,3-di-1-adamantylimidazol-2-ylidene (**1b**) in a mixture of 10 ml of toluene, and 5 ml of thf at 23 °C was added a solution of 0.071 g (0.5 mmol) of dimethylcadmium in 5 ml of toluene. Immediately a colorless solid precipitated. The mixture was stirred for 16 h at 23 °C and subsequently evaporated to give **2b** as a colorless solid. Recrystallization from toluene at -20 °C furnished colorless crystalls. Yield: 0.192 g (80%); m. p. 280 - 285 °C (dec.); ¹H NMR (C₆D₆): δ -0.02 (s + d, J^2_{CdH} = 46.8 Hz, 6 H, Cd(CH₃)₂), 1.47 (m, 12 H, Ad^{4,6,10}), 1.91 (s, 6 H, Ad^{3,5,7}), 2.12 (s, 12 H, Ad^{2.8,9}), 6.72 (s, 2 H, H^{4,5}); ¹³C NMR (C₆D₆): δ -6.03 (s, Cd(CH₃)₂), 29.89 (s, Ad^{3,5,7}), 35.99 (s, Ad^{4,6,10}), 44.46 (s, Ad^{2.8,9}), 57.01 (s, Ad¹), 114.92 (s, C^{4,5}), 201.78 (s, C²); ¹¹³Cd NMR (C₆D₆): δ 102.6 (s).

X-ray structure determination of 2b

Crystals of 2b were grown from a solution in toluene at -20 °C. Crystal data for 2b at -114 °C with MoK a radiation: a = 1593.7(1), b = 1387.6(1), c = 1291.0(1) pm, $\beta =$ $102.61(1)^{\circ}$, monoclinic, Cc, Z = 4, μ (Mo) = 8.01 cm⁻¹. The data were collected using a Rigaku RU300 R-AXIS image plate area detector. Filament size 10.0×0.5 mm, anode power 55 Kv \times 200 ma, crystal to plate distance 8.5 mm, 105 μ pixel raster, 45 frames, oscillation range 4.0°/frame, exposure 17 min/frame, box sum integration, 7221 data collected 7.4° = 2θ = 48.2°, maximum h, k, l 18 15 14, no absorption correction. 2390 duplicates, 1.3% R-merge, 2026 unique reflections with I > 3.0 σ (I). The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on F. Carbon, nitrogen, and cadmium were refined with anisotropic thermal parameters. Because the refinement gave large thermal parameters for some of the hydrogens, all hydrogens were idealized close to their previously refined positions. The largest residual electron density in the final difference Fourier map was $0.37 e^{3}$. The data/parameter ratio was 6.42. The final R factors were R = 0.027 and $R_w = 0.035$. Crystallographic data for the structure of 2b have been deposited with the Cambridge Crystallographic Data Centre (ref. Nr. 127341). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

1,3-Dimesitylimidazol-2-ylidene · dimethylcadmium (2c)

A solution of 0.071 g (0.5 mmol) of dimethylcadmium in 5 ml of toluene was added to a solution of 0.152 g (0.5 mmol) of 1,3-dimesitylimidazol-2-ylidene (**1c**) in a mixture of 10 ml of toluene and 5 ml of thf at 23 °C. The mixture was stirred for 16 h at 23 °C, and subsequently evaporated to give **2c** as a colorless solid. Recrystallization from toluene at -20 °C afforded colorless crystals suitable for X-ray diffraction. Yield: 0.170 g (76%); m. p. 149 - 151 °C; ¹H NMR (C₆D₆): δ –0.41 (s, 6 H, Cd(CH₃)₂), 2.08 (s, 18 H, *o*-CH₃ + *p*-CH₃), 6.23 (s, 2 H, H^{4,5}), 6.74 (s, 4 H, *m*-CH); ¹³C NMR (C₆D₆): δ –7.7 (s (br), 6 H, Cd(CH₃)₂), 17.61 (s, *o*-CH₃), 20.98 (s, *p*-CH₃), 121.36 (s, C^{4,5}), 129.32 (s, *m*-C), 135.12 (s, *o*-C), 136.45 (s, ipso-C), 138.64 (s, *p*-C), 202.82 (s (br), C²); ¹¹³Cd NMR (C₆D₆): δ 152.6 (s).

Analysis for C₂₃H₃₀CdN₂ (446.9) Calcd C 61.81 H 6.77 N 6.27%,

Found C 60.62 H 6.94 N 6.29%.

X-ray Structure Determination of (2c)

Crystals of **2c** were grown from a solution in toluene at -20 °C. Crystal data for 2c at -115 °C with Mo K α radiation: $a = 825.9(1), b = 1580.7(1), c = 1714.6(1) \text{ pm}, \beta =$ 92.26 (1)°, monoclinic, P2₁/n, Z = 4, μ (Mo) = 9.79 cm⁻¹. The data were collected using a Rigaku RU300 R-AXIS image plate area detector. Filament size 10.0×0.5 mm, anode power 55 Kv \times 200 ma, crystal to plate distance 8.5 mm, 105 μ pixel raster, 45 frames, oscillation range 4.0°/frame, exposure 15 min/frame, box sum integration, 9961 data collected $3.5^\circ = 2\theta = 48.2^\circ$, maximum h, k, l 9 18 19, no absorption correction. 2889 duplicates, 2.6% R-merge, 1907 unique reflections with I > 3.0 σ (I). The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on F. Carbon, nitrogen, and cadmium were refined with anisotropic thermal parameters. Because the refinement gave large thermal parameters for some of the methyl hydrogens, all hydrogens except H^{4,5} were idealized close to their previously refined positions. The largest residual electron density in the final difference Fourier map was $0.46 \text{ e/}^{\circ 3}$ near C1. The data/parameter ratio was 7.83. The final R factors were R = 0.052 and $R_w = 0.056$. Crystallographic data for the structure of 2c have been deposited with the Cambridge Crystallographic Data Centre (ref. Nr. 127342). Copies of the data can be obtained free of charge from the address listed under **2b**.

1,3-Dimesitylimidazolin-2-ylidene · dimethylcadmium (**2d**)

A solution of 0.142 g (1 mmol) of dimethylcadmium in 5 ml of toluene was added to a solution of 0.153 g (0.5 mmol) of 1,3-dimesitylimidazolin-2-ylidene (**1d**) in 20 ml of hexane at 23 °C. Immediately a colorless solid precipitated. The mixture was stirred for 1 h at 23 °C, and subsequently evaporated to give **2d** as a colorless solid. Recrystallization from toluene at -20 °C furnished colorless crystals suitable for X-ray diffraction. Yield: 0.176 g (78%); m. p. 161 - 164 °C; ¹H NMR (C₆D₆): δ -0.43 (s (br), 6 H, Cd(CH₃)₂), 2.03 (s, 6 H, *p*-CH₃), 2.24 (s, 12 H, *o*-CH₃), 3.08 (s, 4 H, H^{4,5}), 6.72 (s, 2 H, *m*-CH); ¹³C NMR (C₆D₆): δ -7.67 (s (br), Cd(CH₃)₂), 17.86 (s, *o*-CH₃), 20.96 (s, *p*-CH₃), 50.78 (s, *C*^{4,5}), 129.68 (s, *m*-*C*), 136.09 (s, *o*-*C*), 136.12 (s, ipso-*C*), 137.99 (s, *p*-*C*), 226.09 (s, *C*²); ¹¹³Cd NMR (C₆D₆): δ 142.0 (s).

Analysis for $C_{23}H_{32}CdN_2 \cdot ({}^{1}/_{2} C_{7}H_8)$ (483.0) Calcd C 63.41 H 7.51 N 5.80%,

Found C 63.51 H 7.68 N 5.71%.

X-ray structure determination of 2d

Crystals of 2d were grown from a saturated solution in toluene at -20 °C. Crystal data for 2d at -114 °C with MoK α radiation: a = 1795.2(2), b = 907.6(1), c = $1708.7(2) \text{ pm}, \beta = 112.83(1)^{\circ}, \text{ monoclinic}, P2_1/c, Z = 4,$ $\mu(Mo) = 8.60 \text{ cm}^{-1}$. The data were collected using a Rigaku RU300 R-AXIS image plate area detector. Filament size 10.0 \times 0.5 mm, anode power 55 Kv \times 180 ma, crystal to plate distance 8.5 mm, 105 μ pixel raster, 45 frames, oscillation range 4.0 °/frame, exposure 17 min/frame, box sum integration, 11647 data collected $4.8^\circ = 2\theta = 48.2^\circ$, maximum h, k, l 20 9 19, no absorption correction. 3341 duplicates, 1.7% R-merge, 3037 unique reflections with I > 3.0 σ (I). The structure was solved by automated Patterson analysis (PHASE) and refined by full-matrix least-squares on F. Carbon, nitrogen, and cadmium were refined with anisotropic thermal parameters. Because the refinement gave large thermal parameters for some of the methyl hydrogens, all hydrogens were idealized close to their previously refined positions. The largest residual electron density in the final difference Fourier map was 0.45 e/°3. The data/parameter ratio was 10.82. The final R factors were R = 0.039 and $R_w = 0.046$. Crystallographic data for the structure of 2c have been deposited with the Cambridge Crystallographic Data Centre (ref. Nr. 127343). Copies of the data can be obtained free of charge from the address listed under 2b.

Reaction of 2b with 1d

To a solution of 0.048 g (0.1 mmol) of **2b** in 5 ml of thf- d_8 were added at 23 °C 0.031 g (0.1 mmol) of **1d**. The mixture was stirred at 23 °C for 1 h, and investigated by ¹H NMR which indicated that **1d** had completely replaced the di-1-ada-matylimidazol-2-ylidene in **2b**, giving a solution of **2d** and **1b**.

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