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1,3-Bis(α -aminoisopropyl)benzene, *meta*-C₆H₄(CMe₂NH₂)₂: An *N*,*N*-bridging and *N*,*C*,*N*-cyclometalating ligand

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Abstract

Saponification of the bis(carbamic acid ester) 1,3-C₆H₄(CMe₂NHCO₂Me)₂ (1), made by the addition of methanol to commercial 1,3-C₆H₄(CMe₂NCO)₂, yielded the *meta*-phenylene-based bis(tertiary carbinamine) 1,3-C₆H₄(CMe₂NH₂)₂ (2). Dinuclear [{(η^4 -1,5-C₈H₁₂)RhCl}₂{µ-1,3-C₆H₄(CMe₂NH₂)₂] (3) resulted from the action of 2 on [{(η^4 -1,5-C₈H₁₂)Rh(µ-Cl)}₂] in toluene. Combination of 2 with PdCl₂ or K₂[PdCl₄] gave the dipalladium macrocycle *trans*,*trans*-[{µ-1,3-C₆H₄(CMe₂NH₂)₂] (4) along with cyclometalated [{2,6-C₆H₃(CMe₂NH₂)₂- $\kappa N, \kappa C^1, \kappa N'$ }PdCl] (5). Substitution of PEt₃ for the labile chlorido ligand of 5 afforded [{2,6-C₆H₃(CMe₂NH₂)₂- $\kappa N, \kappa C^1, \kappa N'$ }Pd(PEt₃)]Cl (6). The crystal structures of the following compounds were determined: bis(carbamic acid ester) 1, ligand 2 as its bis(trifluoroacetate) salt [1,3-C₆H₄(CMe₂NH₃)₂](O₂CCF₃)₂, 2 · (HAc_f)₂, complexes 3 and 6, as well as 1,3-C₆H₄(CMe₂OH)₂ (the diol analogue of 2).

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Keywords: 1,3-Bis(a-aminoisopropyl)benzene; Rhodium complex; Palladium complexes; X-ray structure analysis

1. Introduction

It is well known that coordinatively unsaturated amido derivatives of the platinum metals can make good catalysts for the heterolytic activation of the dihydrogen molecule but tend to decompose through β -hydride elimination to generate imine products [1–4]. However, they can be isolated when there are no hydrogen atoms adjacent to the amide function, such as in the 16*e* ruthenium and iridium complexes [RuH(PPh₃)₂(HNCMe₂CMe₂NH₂)] [2] and [(η^4 -1,5-C₈H₁₂)Ir(HNCMe₂CH₂PPh₂)] [4] described by Morris et al. and ourselves.

With the aim of expanding the family of eliminationresistant α -peralkylated nitrogen donors we recently designed the novel $N \cap N \cap N$ tridentate ligand 2,6-bis-(α -aminoisopropyl)pyridine, 2,6-C₅H₃N(CMe₂NH₂)₂ [5]. In this paper, we report on its $N \cap C(H) \cap N$ analogue 1,3-bis(α -aminoisopropyl)benzene, 1,3-C₆H₄(CMe₂NH₂)₂, where the *meta*-phenylene backbone was introduced to promote cyclometalation producing metal complexes similar to the wide range of organometallic products derived from van Koten's "pincer" ligand 1,3-C₆H₄(CH₂NMe₂)₂ [6]. Prior to this contribution, 2-phenyl-6-(α -aminoisopropyl)pyridine, 2-C₆H₅C₅H₃NCMe₂NH₂-6, which coordinates through its two nitrogen donors and one deprotonated *ortho* carbon atom of the phenyl ring, was introduced into organometallic chemistry by Song and Morris as the only other example of a cyclometalating tridentate amine ligand having no hydrogen atoms on the α carbon atom of the NH₂ group [7].

2. Experimental

2.1. General remarks

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. – IR: Mattson

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Infinity 60 AR. - NMR: Bruker DPX 300 (300.1 MHz for ¹H, 75.5 MHz for ¹³C, and 121.5 MHz for ³¹P) with SiMe₄ as internal or H₃PO₄ as external standards (downfield positive; "m": deceptively simple multiplet) at ambient temperature, unless stated otherwise. - Mass spectra: Micromass ZabSpec $(FAB^+ mode with 3-nitrobenzylalcohol as$ matrix). - Dimethyl isophthalate, 1,3-bis(1-isocyanato-1methylethyl)benzene, and triethylphosphine were used as purchased from Aldrich. The diol 1,3-C₆H₄(CMe₂OH)₂ (which is also commercially available), resulted from treatment of $1.3-C_6H_4(CO_2Me)_2$ with slightly more than 4 equiv. of MeMgI in diethyl ether. The platinum metal compounds RhCl₃ · xH₂O ($x \cong 3$), PdCl₂ and K₂[PdCl₄] were products of Pressure Chemical Co. (Pittsburgh) and Strem Chemicals, Inc. (Bischheim); $[{(\eta^4-1,5-C_8H_{12})Rh(\mu-1,5-C_8$ Cl)₂[8,9] was prepared as reported in the literature.

2.2. 1,3-Bis(α-aminoisopropyl)benzene

2.2.1. $1,3-C_6H_4(CMe_2NHCO_2Me)$] (1)

A solution of 10 mL (~43 mmol) of 1,3-bis(1-isocyanato-1-methylethyl)benzene in 30 mL of methanol was stirred for 3 days at ambient conditions. Concentration of the mixture under vacuum resulted in the deposition of the product as a colorless precipitate which was filtered off, washed with pentane, and dried under vacuum; yield 12.44 g (93%). ¹H NMR (CDCl₃): $\delta = 1.59$ (s, 12H, CCH₃), 3.51 (s, 6H, OCH₃), 5.0 (br, 2H, NH), 7.22 (m, 3H, H-4,5,6), 7.36 (s, 1H, H-2). ¹³C{¹H} NMR (CDCl₃): $\delta = 29.67$ (CCH₃), 51.99 (C_{tert}), 55.74 (OCH₃), 121.64 (C-4,6), 123.62 (C-5), 128.74 (C-2), 147.48 (C-1,3), 155.58 (C=O). *Anal.* Calc. for C₁₆H₂₄N₂O₄ (308.37): C, 62.30; H, 7.85; N, 9.09. Found: C, 62.88; H, 7.86; N, 8.92%.

2.2.2. $1,3-C_6H_4(CMe_2NH_2)_2$ (2)

A solution of 10.79 g (35.0 mmol) of **1** in 100 mL of *n*butanol containing 12.0 g of added potassium hydroxide was heated under reflux for 24 h. Vacuum evaporation of the solvent left an oily residue which was dissolved in 50 mL of water. Extraction into THF (3×50 mL), followed by drying over Na₂SO₄ and removal of all volatile material afforded 5.80 g (86%) of the product as a colorless to bright yellow oil. IR (KBr): 3353, 3277, 3099, 3062, 3020, 2964, 2928, 2868, 1601, 799 cm⁻¹. ¹H NMR (CDCl₃): $\delta = 1.41$ (s, 12H, CH₃), 1.63 (br, 4H, NH₂), 7.22, 7.35, 7.72 (all m, 4 phenylene H). ¹³C{¹H} NMR (CDCl₃): $\delta = 31.83$ (CH₃), 51.45 (C_{tert}), 119.74 (C-4,6), 121.49 (C-5), 126.83 (C-2), 149.06 (C-1,3).

2.3. Metal complexes

2.3.1. $[\{(\eta^4-1,5-C_8H_{12})RhCl\}_2\{\mu-1,3-C_6H_4(CMe_2NH_2)_2\}](3)$

A quantity of 120 mg (0.62 mmol) of ligand **2** dissolved in 1 mL of toluene was added dropwise to a stirred solution of 149 mg (0.28 mmol) of $[{(\eta^4-1,5-C_8H_{12})Rh(\mu-Cl)}_2]$ in 10 mL of the same solvent to precipitate 160 mg (83%) of the product as bright yellow microcrystals which were collected by filtration, washed with *n*-pentane, and dried in the vacuum of an oil pump. – ¹H NMR (CDCl₃, –50 °C): $\delta = 1.51$, 1.63 (both m, 4H each, CH₂), 1.76 (s, 12H, CH₃), 2.12, 2.24 (both m, 4H each, CH₂), 3.40, 3.54, 4.42 (all "s" (br), 4H each, diene CH and NH₂), 7.41 ("s", 3H, H-4,5,6), 7.91 (s, 1H, H-2). *Anal.* Calc. for C₂₈H₄₄Cl₂N₂Rh₂ (685.37): C, 49.07; H, 6.47; N, 4.09. Found: C, 49.14; H, 6.48; N, 4.31%.

2.3.2. trans, trans-[$\{\mu$ -1,3-C₆H₄(CMe₂NH₂)₂ $\}_2(PdCl_2)_2$] (4) and [$\{2,6-C_6H_3(CMe_2NH_2)_2-\kappa N, \kappa C^l, \kappa N'\}PdCl$] (5)

Equimolar mixtures of 2 (510 mg, 2.65 mmol) with PdCl₂ (469 mg, 2.65 mmol) and K₂[PdCl₄] (864 mg, 2.65 mmol), respectively, were heated in acetonitrile (50 mL) at reflux temperature for 16 h. Complex 4 separated from solution as a sparingly soluble pale yellow precipitate which was filtered off, washed with $3 \times 5 \text{ mL}$ of acetonitrile and dried under vacuum; yield 705 mg (72%). - ¹H NMR (DMSO d_6): $\delta = 1.79$ (s, 24H, CH₃), 3.99 (br, 8H, NH₂), 7.30 (m, 6H, H-4,5,6), 7.72 (s, 2H, H-2). ¹³C{¹H} NMR (DMSO d_6): $\delta = 31.26$ (CH₃), 57.31 (C_{tert}), 123.42 (C-5), 123.72 (C-4,6), 128.33 (C-2), 147.10 (C-1,3). IR (CsCl): $v(Pd^{-35,37}Cl) = 318$, 313(sh) cm⁻¹. FAB-MS: $m/z = \{703\}$ (100%), 705 (99%), 702 (79%), 701 (76%)} $[M - Cl]^+$, $\{631 (100\%), 633 (84\%), 629 (82\%), 630 (78\%)\}$ [M - Cl - 2 HCl]⁺. Anal. Calc. for C₂₄H₄₀Cl₄N₄Pd₂ (739.25): C, 38.99; H, 5.45; N, 7.58. Found: C, 39.40; H, 5.59; N, 7.51%.

Evaporation of the mother liquor followed by re-dissolution of the residue in methanol, filtration and renewed removal of the volatiles furnished 245 mg (27%) of the cyclometalated product **5** as orange yellow microcrystals which pertinaciously retained residual solvent and, hence, did not give satisfactory analyses. – ¹H NMR (DMSO d_6): $\delta = 1.37$ (s, 12H, CH₃), 4.71 (br, 4H, NH₂), 6.46 (d, ³*J*(H,H) = 7.53 Hz, 2H, H-3,5), 6.75 (t, 1H, H-4). ¹³C{¹H} NMR (DMSO- d_6): $\delta = 29.49$ (CH₃), 65.63 (C_{tert}), 116.90, 118.76, 121.82, 155.13 (C-1). *Anal.* Calc. for C₁₂H₁₉ClN₂Pd (333.17): C, 43.26; H, 5.75; N, 8.41. Found: C, 40.24; H, 5.41; N, 7.46%.

2.3.3. $[\{2, 6-C_6H_3(CMe_2NH_2)_2 - \kappa N, \kappa C^1, \kappa N'\}Pd(PEt_3)]Cl$ (6)

A solution of 60 mg (0.18 mmol) of cyclometalated complex **5** in 4 mL of MeOH/THF (1:1) was treated with 0.25 mL (20 mg, 0.17 mmol) of PEt₃, which caused the mixture to change color from orange to bright yellow. After stirring for 30 min at room temperature all volatile material was evaporated in vacuo to leave a pale yellow solid shown by ³¹P{¹H} NMR to be a 3:1 mixture of **6** (see below) and *trans*-[PdCl₂(PEt₃)₂]: δ (CDCl₃) = 19.05; Ref. [10]: δ (CH₂Cl₂) = 17.8. Recrystallization from dichloromethane afforded almost colorless single crystals of the cyclometalated complex as an addition compound containing two molecules of lattice solvent per formula unit, **6** · 2CH₂Cl₂. – ¹H NMR (CDCl₃): δ = 1.12 (dt, ³*J*(H,H) = 7.95, ³*J*(P,H) = 15.90 Hz, 9H, phosphine CH₃), 1.63 (s, 12H, amine CH₃), 1.86 (dq, ²*J*(P,H) = 15.45 Hz, 6H, PCH₂), 4.42 (br, 4H,

NH₂), 6.61 (dd, ${}^{3}J(H,H) = 7.53$ Hz, ${}^{6}J(P,H) = 2.64$ Hz, 1H, H-4), 6.96 (t, 2H, H-3,5). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): $\delta = 8.67$ (s).

2.4. X-ray structure determinations

Single crystals of $1,3-C_6H_4(CMe_2OH)_2$ and bis(carbamic acid methyl ester) 1 were grown from THF/n-pentane. Ligand 2 was structurally characterized as its bis(trifluoroacetate) $[1,3-C_6H_4(CMe_2NH_3)_2](O_2CCF_3)_2, 2 \cdot (HAc_f)_2,$ crystals of which were obtained from ethanol/trifluoroacetic acid. Compounds 3 and $6 \cdot 2CH_2Cl_2$ were crystallized from dichloromethane. Diffraction measurements were made at +20(2) (1, $2 \cdot (HAc_f)_2$, 3) and $-90(2) \circ C$ [1,3-C₆H₄(CMe₂OH)₂] on an Enraf-Nonius CAD-4 MACH 3 diffractometer and, for $6 \cdot 2CH_2Cl_2$, at -173(2) °C on a Bruker-Nonius Kappa CCD instrument using Mo Ka radiation ($\lambda = 0.71073$ Å); data either uncorrected for absorption $[1,3-C_6H_4(CMe_2OH)_2, 1, 2 \cdot (HAc_f)_2]$ or corrected for absorption using appropriate semi-empirical [11] ($\mathbf{6} \cdot 2CH_2Cl_2$: $T_{\min} = 0.749$, $T_{\max} = 0.820$) or refined [12] (3: $T_{\min} = 0.522$, $T_{\max} = 0.850$) methods. The structures were solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing both the SHELXTL NT 6.12 [13] and the WINGX [14a] packages with some of the relevant programs (SIR-97 [15], SHELXL-97 [16], ORTEP-3 [14b]) implemented therein. $-1,3-C_6H_4(CMe_2OH)_2$ (0.45 × 0.20 × 0.13 mm): $C_{12}H_{18}O_2$ (194.26); monoclinic, P_{21}/c , a =5.7178(9), b = 20.907(2), c = 9.030(1) Å, $\beta = 93.23(1)^{\circ}$, $V = 1077.7(2) \text{ Å}^3$, Z = 4, $D_{\text{calc}} = 1.197 \text{ g cm}^{-3}$, μ (Mo $K\alpha$ = 0.080 mm⁻¹; 1.95° $\leq \Theta \leq 25.27^{\circ}$, 2151 reflections collected $(0 \le h \le +6, 0 \le k \le +25, -10 \le l \le +10)$, 1951 unique ($R_{int} = 0.0377$); $wR_2 = 0.1739$ for all data and 127 parameters, $R_1 = 0.0626$ for 1098 intensities $I > 2\sigma(I)$. – 1 $(0.40 \times 0.32 \times 0.27 \text{ mm})$: C₁₆H₂₄N₂O₄ (308.37); monoclinic, $P2_1/n$, a = 10.204(1), b = 12.196(2), c = 13.934(3) Å, $\beta = 100.40(1)^{\circ}, V = 1705.6(5) \text{ Å}^3, Z = 4, D_{\text{calc}} = 1.201$ g cm⁻³, μ (Mo K α) = 0.086 mm⁻¹; 2.24° $\leq \Theta \leq 30.36^{\circ}$, 5341 reflections collected $(-14 \le h \le +14, 0 \le k \le +17,$ $0 \le l \le +19$), 5153 unique ($R_{int} = 0.0185$); $wR_2 = 0.1512$ for all data and 202 parameters, $R_1 = 0.0517$ for 3396 intensities $I \ge 2\sigma(I)$. – **2** · (**HAc**_f)₂ (0.35 × 0.25 × 0.23 mm): $C_{12}H_{22}N_2$, 2(C₂F₃O₂) (420.36); monoclinic, $P2_1/c$, a =10.363(2), b = 17.0298(9), c = 11.538(2) Å, $\beta = 102.93(1)^{\circ}$, $V = 1984.6(5) \text{ Å}^3$, Z = 4, $D_{\text{calc}} = 1.407 \text{ g cm}^{-3}$, μ (Mo K α) = 0.136 mm⁻¹; 2.02° $\leq \Theta \leq 25.37^\circ$, 3832 reflections collected $(-12 \leq h \leq +12, 0 \leq k \leq +20, 0 \leq l \leq +13),$ 3641 unique ($R_{int} = 0.0275$); $wR_2 = 0.1308$ for all data and 335 parameters, $R_1 = 0.0503$ for 2036 intensities $I > 2\sigma(I)$; CF₃CO₂⁻ anions with two- and, respectively, threefold rotational disorder of the CF_3 groups. - 3 $(0.35 \times 0.08 \times 0.06 \text{ mm})$: C₂₈H₄₄Cl₂N₂Rh₂ (685.37); monoclinic, $P2_1/n$, a = 11.594(3), b = 10.978(4), c = 22.521(4)Å, $\beta = 90.96(2)^{\circ}$, V = 2866(1) Å³, Z = 4, $D_{calc} = 1.588$ $g \text{ cm}^{-3}$, μ (Mo K α) = 1.357 mm⁻¹; 1.81° $\leq \Theta \leq 24.18^{\circ}$,

4854 reflections collected $(0 \le h \le +13, 0 \le k \le +12,$ $-25 \leq l \leq +25$, 4604 unique ($R_{int} = 0.0371$); $wR_2 =$ 0.0942 for all data and 307 parameters, $R_1 = 0.0499$ for 2967 intensities $I \ge 2\sigma(I)$. – $6 \cdot 2CH_2Cl_2$ (0.22×0.21× 0.17 mm): C₁₈H₃₄N₂PPd, Cl, 2(CH₂Cl₂) (621.14): mono- $P2_1$, a = 13.3080(14), b = 13.0846(7), clinic, c =17.1308(11) Å, $\beta = 108.616(7)^{\circ}$, V = 2826.9(6) Å³, Z = 4, $D_{\text{calc}} = 1.459 \text{ g cm}^{-3}, \ \mu \ (\text{Mo} \ \text{K}\alpha) = 1.196 \text{ mm}^{-1}; \ 2.95^{\circ} \leqslant$ $\Theta \leq 28.70^{\circ}$, 56486 reflections collected ($-17 \leq h \leq +17$, $-17 \le k \le +17$, $-23 \le l \le +23$), 14384 unique ($R_{int} =$ 0.0334); $wR_2 = 0.0515$ for all data and 524 parameters, $R_1 = 0.0236$ for 12971 intensities $I > 2\sigma(I)$; the specimen investigated showed twinning by inversion with a ratio of the twin domains close to unity: absolute structural parameter x = 0.51(2) [17].

3. Results and discussion

3.1. Ditertiary carbinamine ligand 2

Traditionally, tertiary carbinamines (compounds in which the amino group is bonded to a tertiary carbon atom) have been prepared by the Ritter reaction of tertiary alcohols. The method employs the alcohol together with a cyanide salt or an organic nitrile, typically MeCN, under strongly acidic conditions to form - by addition of the initially generated carbenium ions R_3C^+ to the nitrile function – aminium intermediates $[R_3CNCR']^+$ (R' = H, Me). These are subsequently reacted with aqueous alkali to give acid amides $R_3CNHC(O)R'$, from which the "Ritter amines" R₃CNH₂ are set free by alkaline hydrolysis [18,19]. However, this protocol failed with 1,3-C₆H₄(CMe₂OH)₂ which is commericially available as a cheap industrial by-product formed in one of the technical resorcinol processes. Attempted conversion of this diol to $1,3-C_6H_4(CMe_2NH_2)_2$ with NaN₃ in acidic solution and reduction of the resulting diazide to the diamine as described for the preparation of cumylamine from α -cumyl alcohol [20] likewise remained unsuccessful.

In the literature, the synthesis of tertiary carbinamines has also been achieved by the Ciganek reaction of nitriles, which involves the double addition to the $RC \equiv N$ triple bond of organocerium reagents, generated in situ from anhydrous cerium trichloride and alkyllithium reagents [21–23]. In fact, the *para* and *meta* isomers of dicyanobenzene were briefly reported to produce $1,4-C_6H_4(CMe_2NH_2)_2$ and $1,3-C_6H_4(CMe_2NH_2)_2$, i.e., compound 2, if reacted with the CeCl₃/MeLi reagent [22]. As previously communicated, we ourselves used the Ciganek protocol as a method of synthesis for the pyridine-based $N \cap N \cap N$ ligand 2,6- $C_5H_3N(CMe_2NH_2)_2$ from 2,6-pyridinedicarbonitrile but observed that its successful preparation critically depended on the strict keeping to very narrow reaction parameters [5]. In view of these limitations a more straightforward (and less cost-intensive) method of synthesis was sought for 1,3-C₆H₄(CMe₂NH₂)₂ (2). 1,3-Bis(1-isocyanato-1-methylethyl)benzene – a low-cost technical intermediate made by



Scheme 1.

the addition of isocyanic acid to 1,3-diisopropenylbenzene – turned out to be particularly suitable for this purpose: stirring with methanol at ambient conditions cleanly afforded the bis(carbamic acid ester) $1,3-C_6H_4(CMe_2NHCO_2Me)_2$ (1) which then was saponified in strongly alkaline medium (KOH/refluxing *n*-butanol) to produce high yields (>85%) of **2** (Scheme 1).

Compound 2 was fully characterized by an X-ray structure analysis of the bis(trifluoroacetate) salt $[1,3-C_6H_4(CMe_2NH_3)_2](O_2CCF_3)_2$, 2 · (HAc_f)₂. For the sake of comparison, crystal structure determinations were also carried out for its direct precursor 1 and the diol 1,3- $C_6H_4(CMe_2OH)_2$ representing the amide and OH analogues of 2. In the solid state, molecules of 1,3- $C_6H_4(CMe_2OH)_2$ exhibit approximate C_2 symmetry with the hydroxyl groups on opposite sides of the aromatic systems and only slightly different dihedral angles between the ring *l.s.q.* plane and the two planes defined by the *meta*- and α -carbon as well as the oxygen atoms (Fig. 1). Molecules of bis(carbamic acid ester) 1 deviate more severely from axial symmetry as shown by the disparity of the two dihedral angles given in the legend to Fig. 2. Diammonium dication 2^{++} has its NH₃⁺



Fig. 1. Perspective view of $1,3-C_6H_4(CMe_2OH)_2$; selected bond lengths (Å) and angles (°): O1–C7, 1.445(4); O2–C10, 1.442(3); C2–C7, 1.535(4), C6–C10, 1.530(4). O1–C7–C2, 107.9(2); O2–C10–C6, 108.4(2). Hydrogen bonds (Å and °): O1(H)···O2#1, 2.892(3) and 164.0(3); O2(H)···O1#2, 2.892(3) and 166.3(2) (symmetry transformations used to generate equivalent atoms: #1 x + 1, -y + 1/2, z + 1/2; #2 x - 1, -y + 1/2, z - 1/2). Dihedral angles (°): *l.s.q.* plane C1–C6 vs. plane O1···C7···C2, 36.9; *l.s.q.* plane C1–C6 vs. plane O2···C10···C6, 36.4.



Fig. 2. Perspective view of $1,3-C_6H_4(CMe_2NHCO_2Me)_2$ (1); selected bond lengths (Å) and angles (°): N1–C7, 1.477(2); N2–C12, 1.485(2); C1–C7, 1.542(2), C3–C12, 1.534(2). N1–C7–C1, 111.6(1); N2–C12–C3, 110.4(1). Hydrogen bonds (Å and °): N1(H)···O3#1, 3.076(2) and 171.7(2); N2(H)···O1#2, 3.059(2) and 121.4(2) (symmetry transformations used to generate equivalent atoms: #1 – x + 1, –y, –z; #2 –x + 1/2, y – 1/2, –z + 1/2). Dihedral angles [°]: *l.s.g.* plane C1–C6 vs. plane N1···C7···C1, 17.5; *l.s.g.* plane C1–C6 vs. plane N2···C12···C3, 39.4.

groups oriented to the same side of the phenylene backbone as a result of hydrogen-bonding to the two $F_3CCO_2^-$ counterions (Fig. 3). The OH functions of $1,3-C_6H_4(CMe_2OH)_2$ likewise participate in multiple intermolecular hydrogen bonds as do the NHCO₂Me residues of **1**. Bond lengths and angles within the α -CMe₂X groups of the three compounds do not warrant further discussion since they are close to those measured for some related molecules, such as diol $1,4-C_6H_4(CMe_2OH)_2$ [24], the triol $1,3,5-C_6H_3(CMe_2OH)_3$ [25], the 1,1,3,3-tetramethylisoindolinium cation $1,2-C_6H_4(CMe_2)_2NH_2^+$ [26], and the amido derivative $C_6H_5CMe_2NHC(O)CH(Br)Bu-t$ [27].



Fig. 3. Perspective view of $[1,3-C_6H_4(CMe_2NH_3)_2](O_2CCF_3)_2$, **2** · (HAc_f)₂, with rotationally disordered CF₃ groups in the anions; selected bond lengths (Å) and angles (°): N1–C7, 1.515(3); N2–C10, 1.520(3); C1–C7, 1.537(4); C3–C10, 1.529(4). N1–C7–C1, 108.6(2); N2–C10–C3, 108.3(2). Hydrogen bonds (Å and °): N1(H)···O1, 2.856(3) and 174.9(2); N2(H)···O3, 2.815(3) and 164.3(2); N1(H)···O2#1, 2.862(3) and 168.7(3); N1(H)···O4#2, 2.839(3) and 174.4(2); N2(H)···O1#3, 2.892(3) and 156.9(3); N2(H)···O3#3, 2.836(3) and 168.2(2) (symmetry transformations used to generate equivalent atoms: #1 x, -y + 1/2, z - 1/2; #2 x + 1, y, z; #3 -x, -y, -z + 1). Dihedral angles (°): *l.s.q.* plane C1–C6 vs. plane N1···C7···C1, 45.6; *l.s.q.* plane C1–C6 vs. plane N2···C10···C3, 68.6.

3.2. Metal complexes

1.3-Disubstituted aromatic hydrocarbons with two meta-positioned alkylated or arylated nitrogen, phosphorus, sulfur, or selenium donors CH₂D ($D = NR_2$ [6], PR₂ [28], SR [29], or SeR [30]) are well known for their propensity to form "pincer" complexes $[{C_6H_3(CH_2D)_2}$ o,o' ML_n by chelation-assisted orthometalation at C-2 if treated with suitable precursors of the platinum metals. Thus, the cyclometalation through activation of aryl-C-H bonds adjacent to tertiary benzylamine (or 2-pyridyl) functionalities has been established as one of the most simple and widely applicable methods for the construction of metalacycles - in particular, palladacycles [31]. However, this orthometalation (specifically, orthopalladation) reaction will normally not occur with primary benzylamines except that the amine, the metal precursor and the reaction conditions (solvent and temperature) meet very narrow requirements [31–33].

When $1,3-C_6H_4(CMe_2NH_2)_2$ (2) was reacted with $RhCl_3 \cdot xH_2O$ in ethanol under the conditions described for the preparation of $[RhCl_2{C_6H_3(CH_2NMe_2)_2-o,o'}]$ -(OH₂)][34], a red-brown precipitate was formed that contained non-metalated 2 (¹H NMR) but could not be worked up to give any unequivocally identifiable product. We assume that this material is similar to the one postulated to be composed of the initial coordination complexes between 1.3-C₆H₄(CH₂NMe₂)₂ and hydrated RhCl₃, *i.e.*, has an $N \cap C(H) \cap N$ ligand bonded in a bidentate fashion to a single metal center and/or bears one rhodium atom on each nitrogen donor of a bridging diamine [34]. With Rh^{I} as the central metal, such a 1,3-bis(α -aminoisopropyl)benzene-linked dinuclear complex, $[{(\eta^4-1,5-C_8H_{12})}-$ RhCl $_2$ { μ -1,3-C₆H₄(CMe₂NH₂)₂] (**3**), was isolated from the reaction of **2** with $[\{(\eta^4-1, 5-C_8H_{12})Rh(\mu-Cl)\}_2]$ in toluene (Scheme 2). As far as we are aware, there are only two well-defined previous examples possessing a non-cyclometalated $1,3-C_6H_4(CR_2D)_2$ linkage with two terminally "dangling" complex fragments, viz. [(MeReO₃)₂{µ-1,3- $C_{6}H_{4}(CH_{2}NMe_{2})_{2}$][35] and [{[2,6- $C_{5}H_{3}N(CH_{2}NMe_{2})_{2}]R$ $uCl_{2}_{2}[\mu-1,3-C_{6}H_{4}(CH_{2}PPh_{2})_{2}]$ [36].

In the crystal structure of **3**, the CMe₂NH₂ donors are positioned on opposite sides of the aromatic ring in such a way that the molecule displays approximate C_2 symmetry along the C13...C19 axis (Fig. 4). Not unexpectedly, the bonds between nitrogen and rhodium are much longer than





Fig. 4. Perspective view of the complex molecule $[\{(\eta^{4}-1,5-C_{8}H_{12})RhCl\}_{2}\{\mu-1,3-C_{6}H_{4}(CMe_{2}NH_{2})_{2}\}]$, 3 (hydrogen atoms are omitted for clarity); selected bond lengths (Å) and angles (°): Rh1–N1, 2.186(5); Rh1–Cl1, 2.386(2); Rh2–N2, 2.165(6); Rh2–Cl2, 2.382(2). N1–Rh1–Cl1, 84.1(1); N2–Rh2–Cl2, 83.8(1); Rh1–N1–C9, 126.4(4); Rh2–N2–C15, 129.9(4).

those previously measured for the Rh^{III} complex *mer*-[RhCl₃{2,6-C₅H₃N(CMe₂NH₂)₂}] bearing a 2,6-bis(α aminoisopropyl)pyridine chelate ligand: 2.165 and 2.185 Å versus 1.948 and 2.075 Å [5]. The near axial-symmetric geometry of the molecule observed in the solid state is stabilized by intermolecular NH···Cl hydrogen bonds: d(NH···Cl), 3.446(6) Å; N–H···Cl, 158.4(2)°.

The ¹H NMR spectra of **3** are significantly temperaturedependent: at -50 °C in CDCl₃, the NH₂ and =CH signals appear as slightly broadened singlets at $\delta = 3.40, 3.54$, and 4.42 with relative intensities corresponding to 4H each; the 16 methylene protons give rise to four unresolved multiplets of equal intensity located at $\delta = 1.51, 1.63, 2.12, \text{ and } 2.24$ and the four CH_3 groups show equivalence of their ¹H nuclei causing a singlet resonance at $\delta = 1.76$. At 25 °C, the signals of the amine and olefinic protons merge into a very broad resonance centered at $\delta = 4.25$, the methyl and methylene protons appearing as two broadened peaks at $\delta = 1.66$ and 2.35. The low-temperature spectrum is consistent with the presence in solution of **3** as N,N-bridged molecules with conformations resembling the one found in the solid state. The broad overlapping resonances observed at higher temperature point to exchange processes between differently coordinated " $(\eta^4-1,5-C_8H_{12})Rh$ " forms present in temperature-dependent equilibria which, however, could not be resolved. Such species could include $[(\eta^4-1,5 C_8H_{12}$ (N \cap N)]⁺ and [{(η^4 -1,5- C_8H_{12})RhCl₂]⁻ ions as were previously proposed in order to account for the solution behavior of several related [{(η^4 -1,5-C₈H₁₂)-RhCl}₂(μ -N \cap N)] complexes bridged by aliphatic diamines [37], κ^2 -bonded tris- and bis(pyrazolyl)amines [38], or α -diimines [39,40].

Heating equimolar mixtures of **2** with PdCl₂ or K₂[PdCl₄] in acetonitrile gave the sparingly soluble bis(diamine)-bridged dipalladium complex *trans,trans*-[{ μ -1,3-C₆H₄(CMe₂NH₂)₂}₂(PdCl₂)₂] (**4**), precipitating directly from solution, together with cyclometalated [{2,6-C₆H₃(CMe₂NH₂)₂- $\kappa N, \kappa C^{1}, \kappa N'$ }PdCl] (**5**), which was isolated from the mother liquor (Scheme 3).



The bimetallic structure of 4 containing a 16-membered macrocycle with two trans-PdCl₂ building blocks was inferred from the results of FAB mass spectrometry and far-infrared spectroscopy: The mass spectrum showed the dipalladium cations $[C_{24}H_{40}Cl_3Pd_2]^+$ and $[C_{24}H_{38}ClPd_2]^+$ with correct isotopic distributions of their traces as the most abundant fragments in the m/z range covering the molecular ion and dimetallic fragments derived therefrom, and in the infrared the complex displayed but one Pd-Cl stretching at 318 cm^{-1} [v(Pd- 35 Cl)] with a shoulder at 313 cm^{-1} $[v(Pd-^{37}Cl)]$, as expected for the two *trans*-Pd(NH₂R)₂Cl₂ building blocks [41]. Although band-broadening due to the presence of six stable palladium isotopes (102, 104, 105, 106, 108, and 110) could blur the $v(Pd-^{35}Cl)/$ $v(Pd-^{37}Cl)$ splitting of the M-Cl vibration of the compound, conditions are favorable for observing (and assigning) the isotopically split Pd–Cl stretching vibration of 4 because of the lessened influence of the high atomic weight of the metal on the reduced mass of the system [42]. Dipalladium complexes having crystallographically established macrocyclic *trans,trans*- $[(\mu - N \cap N)_2(PdCl_2)_2]$ structure motifs similar to the one derived for 4 from spectroscopic data were recently obtained by combining [PdCl₂(NCPh)₂] with meta-phenylene-based N,N'-bis(pyridin-3-yl)-1,3-benzenedicarboxamide ligands such as 1,3-C₆H₄(CON- $HC_5H_4N-3)_2$ and the like [43].

The presence of a direct metal-to-aryl linkage in [{2,6-C₆H₃(CMe₂NH₂)₂- $\kappa N, \kappa C^1, \kappa N'$ }PdCl] (**5**) was evidenced from both the ¹H and ¹³C{¹H} NMR spectra, where the remaining three *meta* and *para* phenylene protons H-3,5 and H-4 appear as separate doublet and triplet signals ($\delta = 6.46$ and 6.75) and the ¹³C resonance of the metalbound *ipso* atom C-1 displays the significant downfield shift ($\delta = 155.13$ versus $\delta = 126.83$ for the free ligand) known to be diagnostic of carbon coordination to a transition metal [44]. The chlorido ligand opposite to the Pd–C bond is substitutionally labile as shown by the reaction between **5** and triethylphosphine, which produces [{2,6- $C_6H_3(CMe_2NH_2)_2-\kappa N,\kappa C^1,\kappa N'$ }Pd(PEt_3)]Cl (**6**) together with some $N \cap C \cap N$ -free *trans*-[PdCl₂(PEt_3)₂] within 30 min at room temperature (Scheme 3). Prior to this work, [{2,6- $C_6H_3(CH_2NMe_2)_2-\kappa N,\kappa C^1,\kappa N'$ }Pd(PPh_3)]BF₄, obtained by substituting PPh₃ for the weakly bound BF₄⁻ ligand of [{2,6- $C_6H_3(CH_2NMe_2)_2-\kappa N,\kappa C^1,\kappa N'$ }Pd(FBF_3)], was briefly described as the only other example of an $N \cap C \cap N$ pincer complex of Pd(II) containing an additional phosphine ligand [45a]. Closely related compounds that have been studied in some more detail, include the $P \cap C \cap P$ -coordinated cation [{2,6- $C_6H_3(CH_2PPh_2)_2-\kappa P,\kappa C^1,\kappa P'$ }Pd(PEt_3)]⁺ [46] as well as the Pt(II)-centered $N \cap C \cap N$ chelates [{2,6- $C_6H_3(CH_2NMe_2)_2-\kappa N,\kappa C^1,\kappa N'$ }Pt(PR_3)]⁺, where PR_3 = PPh_3 [45a-c] or PHPh_2 [45d].

Pincer complex **6** was characterized both spectroscopically and by an X-ray structure analysis of its solvate **6** · 2CH₂Cl₂. The cation exhibits a ³¹P{¹H} singlet resonance at $\delta = 8.67$ (downfield of free PEt₃ at $\delta \cong -29$). An unusual ¹H NMR feature worth mentioning is the observation of long-range spin–spin coupling over six bonds between the phosphorus nucleus and the *para* proton of the aromatic ring, which appears as a doublet of doublets with ³J(H,H) = 7.53 and ⁶J(P,H) = 2.64 Hz [47]. The asymmetric unit of the triclinic unit cell of the dichloromethane-solvated complex contains two crystallographi-



Fig. 5. Perspective view of the two crystallographically independent $[\{2, 6-C_6H_3(CMe_2NH_2)_2-\kappa N, \kappa C^1, \kappa N'\}$ hydrogen-bonded ion-pairs Pd(PEt₃)]Cl of 6 · 2CH₂Cl₂ (carbon-bonded hydrogen atoms omitted for clarity); selected bond lengths (Å) and angles (°): Pd1-P1, 2.3591(7); Pd1-N1, 2.080(2); Pd1-N2, 2.085(2); Pd1-C6, 1.956(2); Pd2-P2, 2.3652(6); Pd2-N3, 2.094(2); Pd2-N4, 2.090(2); Pd2-C24, 1.955(2). P1-Pd1-N1, 98.48(6); P1-Pd1-N2, 101.55(6); P1-Pd1-C6, 177.02(7); N1-Pd1-N2, 159.74(8); N1-Pd1-C6, 79.82(9); N2-Pd1-C6, 80.29(9); P2-Pd2-N3, 101.45(6); P2-Pd2-N4, 99.52(6); P2-Pd2-C24, 176.35(7); N3-Pd2-N4, 159.01(8); N3-Pd2-C24, 79.53(9); N4-Pd2-C24, 79.48(9). Hydrogen bonds (Å and °): N1(H)···Cl1, 3.272(2) and 152.72(1); N2(H)···Cl2, 3.690(2) and 146.78(1); N3(H)···Cl2, 3.510(2) and 148.26(1); N2(H)···Cl1#1, 3.414(2) and 159.18(1); N3(H)···Cl2#2, 3.389(2) and 170.92(1); N4(H)···Cl2#3, 3.341(2) and 151.71(1) (symmetry transformations used to generate equivalent atoms: #1 - x, y + 1/2, -z + 1; #2 - x, y - 1/2, -z + 1; #3 x, y, z + 1).

cally independent ion-pairs linked by multiple hydrogenbonding (Fig. 5). The structures of the cations are based on four-coordinate Pd(II) centers in slightly distorted square-planar environments where the palladium and phosphorus atoms deviate from the planes defined by the donor atoms of the terdentate $N \cap C \cap N$ ligand by 0.01 and 0.28 in molecule 1 as well as by 0.06 and 0.17 Å in molecule 2. The Pd-NH₂ bond lengths fall in the range 2.080(2)-2.094(2) Å and thus are only marginally shorter than the Pd-NMe₂ distances of 2.108(2) and 2.109(9) Å previously measured for the cation of $[\{2,6-C_6H_3 (CH_2NMe_2)_2 - \kappa N, \kappa C^1, \kappa N' Pd(OH_2)]BF_4$ [45e]. In the latter complex the length of the Pd-Cipso bond trans to Pd-OH2 amounts to 1.909(2) Å. Because of the substantially higher trans-bond weakening influence of a phosphine than that of an aqua ligand the corresponding Pd-aryl bonds in cations 6^+ are elongated to 1.955(2) and 1.956(2) (Å). The Pd-PEt₃ distances of 2.3591(7) and 2.3652(6) Å compare favorably with that of 2.358(2) Å found for the two crystallographically identical Pd–P bonds of $[{2,6-C_6H_3-}]$ $(CH_2PPh_2)_2 - \kappa P, \kappa C^1, \kappa P' Pd(PEt_3)]BF_4$ [46].

4. Concluding remarks

The ditertiary carbinamine 1,3-C₆H₄(CMe₂NH₂)₂ has been prepared by a straightforward two-step synthesis based on commercial 1,3-C₆H₄(CMe₂NCO)₂ as an inexpensive starting material. A first study of its coordination behavior towards platinum metal ions has shown that the diamine can form bimetallic complexes such as $[{(n^4-1,5 C_8H_{12}$ RhCl}₂{ μ -1,3- C_6H_4 (CMe₂NH₂)₂} and trans, trans- $[\{\mu-1, 3-C_6H_4(CMe_2NH_2)_2\}_2(PdCl_2)_2]$ with one or two N,N-bridges but can also produce $N \cap C \cap N$ -chelated metalaheterocycles as examplified by $[{2,6-C_6H_3(CMe_2 NH_{2}_{2}-\kappa N,\kappa C^{1},\kappa N'$ PdCl] and [{2,6-C₆H₃(CMe₂NH₂)₂- $\kappa N, \kappa C^1, \kappa N'$ Pd(PEt₃)]Cl. Further work aiming at the extension of the cyclometalation chemistry displayed by the $1,3-C_6H_4(CMe_2NH_2)_2$ ligand and the synthesis of stable amido derivatives with $H_2N \cap C^- \cap NH^-$ "pincer" motifs, which are stable against β -hydride elimination, is under way.

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Appendix A. Supplementary material

CCDC 653196, 653297, 653198, 653199 and 653200 contain the supplementary crystallographic data for 1,3- $C_6H_4(CMe_2OH)_2$, **3**, **1**, **2** · (**HAc**_f)_2 and **6** · 2CH_2Cl_2. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit @ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.08.027.

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