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Synthesis and reactivity towards diiodine of palladium(II) and platinum(II) complexes with non-cyclic and cyclic ligands $(C_6H_3\{CH_2NR^1R^2\}_2\text{-}2,6)^-$. End-on diiodine–platinum(II) bonding in macrocyclic $[PtI(C_6H_3\{CH_2NMe(CH_2)_7MeNCH_2\}\text{-}2,6)(\eta^1\text{-}I_2)]$ *

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Abstract

Several new organo-platinum(II) and -palladium(II) complexes $[MX(C_6H_3\{CH_2NR^1R^2\}_2\text{-}2,6)]$ (X = halide, M = Pt, Pd; $R^1 = R^2 = Et$; $R^2 = Me$, $R^1 = {}^tBu$, M = Pt: $R^2 = Me$, $R^1 = Ph$) have been synthesized from $[PtCl_2(SEt_2)_2]$ or $[PdCl_2(COD)]$ (COD = 1, 5-cyclooctadiene) by reaction with $[Li(C_6H_3\{CH_2NR^1R^2\}_2\text{-}2,6]_n$. Two of the intermediate Li complexes, i.e. $[Li((tBu)MeNCN)]_2$ and $[Li((Ph)MeNCN)]_2$ were isolated. In the platinum and palladium complexes the NCN ligands are terdentate bonded through C_{ipso} and two *trans*-positioned amine donor atoms. The complexes $[PtI(C_6H_3\{CH_2NMe(CH_2)_7MeNCH_2\}\text{-}2,6)]$ (**4**), in which the N(Me) atoms of the terdentate ligand are connected by a short $(CH_2)_7$ chain, and $[PtCl(C_6H_3\{CH_2NPh_2\}_2\text{-}2,6)(SEt_2)_2]$, in which the Ph_2NCN ligand is only monodentate bonded via C_{ipso}, were also made. The coordination ability of the NR^1R^2 donor atoms in these compounds was found to decrease in the order $Me_2N - ({}^tBu)MeN > Et_2N > (Ph)MeN > Ph_2N$.

* Dedicated to Prof. F.G.A. Stone on the occasion of his 65th birthday.

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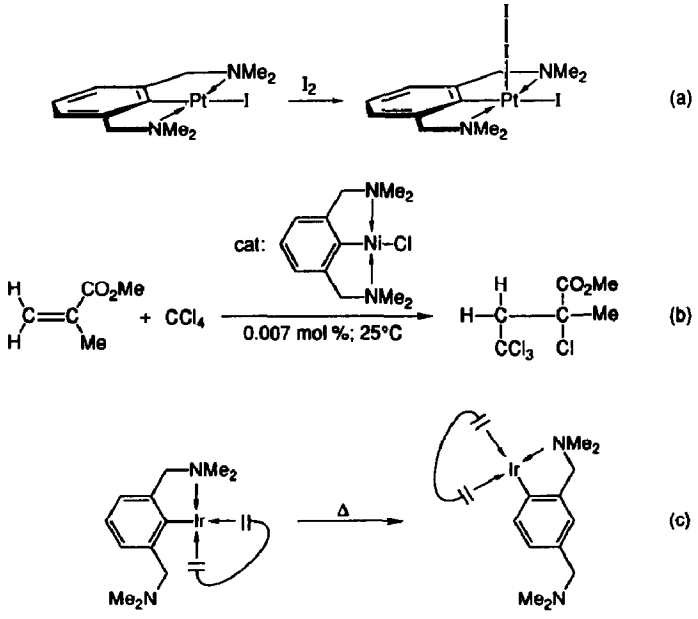
Two new organoplatinum(II) complexes containing an η^1-bonded diiodine molecule have been prepared by the 1/1 molar reactions of **4** and [PtI(C_6H_3-{$CH_2NMe(CH_2)_{10}MeNCH_2$}-2,6)] with diiodine †. The structure of [PtI(C_6H_3-{$CH_2NMe(CH_2)_7MeNCH_2$}-2,6)(η^1-I_2)] was determined by X-ray analysis. A diiodine molecule is bound in an η^1-fashion to platinum(II), with an I–I bond length of 2.814(2) Å and a nearly linear Pt–I–I linkage (bond angle 176.83(5)°).

Introduction

The monoanionic, potentially terdentate, ligand system ($C_6H_3\{CH_2NMe_2\}_2$-2,6)$^-$, (denoted by Me_2NCN) [1], when bonded in the terdentate mode through C_{ipso} and the two N-donor atoms to a d^8 metal centre, enhances the Lewis base character of the metal centre and restricts the coordination of incoming reagents to positions in a plane perpendicular to the plane of the aryl ring [1]. In this way, the number of possible reaction pathways with both organic and inorganic electrophiles is severely restricted [1b,1c]. The characteristic properties of this ligand have been exploited in various contexts, including the isolation of complexes in which a diiodine molecule is η^1-bonded to Pt^{II} [2], catalysis by [NiX(Me_2NCN)] (X = Cl, Br, I) of the Kharasch addition of polyhalogenoalkanes to alkenes [3*], and an unprecedented isomerization reaction of [Ir(Me_2NCN) (COD)] involving a sequence of intramolecular C–H bond activation and C–Ir bond making and breaking steps (see Scheme 1) [4].



Scheme 1. Three examples of the reactivity of metal–Me_2NCN.

† I_2 molecules are referred to as diiodine so following the nomenclature introduced for dihydrogen, H_2.

* Reference number with asterisk indicates a note in the list of references.

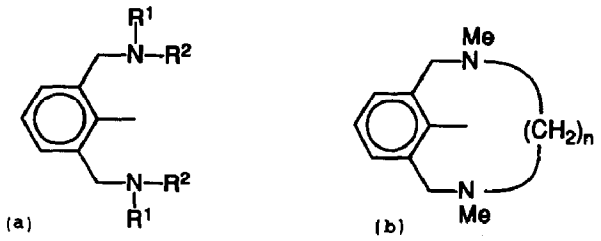


Fig. 1. (a) R^1R^2NCN. (b) $(CH_2)_nMeNCN$.

We are currently investigating ligands of the type $(C_6H_3\{CH_2NR^1R^2\}_2\text{-}2,6)^-$ ($= R^1R^2NCN$, Fig. 1a) having various substituents on the N-atom with the aim of tuning the reactivity of the metal centre and providing an environment around this centre that would leave only one specific channel for substrates to approach the metal. Molecular models show that macrocyclic ligands of the type $(C_6H_3\{CH_2NMe(CH_2)_nMeNCH_2\}\text{-}2,6)^-$ ($= (CH_2)_nMeNCN$, Fig. 1b), in which the two nitrogen atoms are connected by a short chain of methylene units, might effectively screen one side of the metal centre from attack by reagents. A similar effect might also be achieved with non-cyclic ligands having bulky R^1 and/or R^2 substituents.

In this paper, we describe the synthesis and properties of the monoanionic ligands R^1R^2NCN ($R^1 = R^2 = Me$, Et, ^{i}Pr, Ph; $R^2 = Me$, $R^1 = {}^i$Pr, ^{t}Bu, Ph, $(CH_2)_7$ (cf. ref. 5) and some Pt^{II} and Pd^{II} complexes with these ligands. The molecular structure of a new macrocyclic complex in which I_2 is η^1-bonded to Pt^{II} is also reported.

Experimental

General

All syntheses involving organolithium compounds were carried out in a dry nitrogen atmosphere by Schlenk techniques. Other syntheses were carried out without special precautions, unless stated otherwise. Solvents and amines were distilled before use and kept under nitrogen. The compounds $2,6\text{-}(BrCH_2)_2C_6H_3Br$ [6], $[PtCl_2(SEt_2)_2]$ [7] and $[PdCl_2(COD)]$ [8] (COD = 1,5-cyclooctadiene) were synthesized as described in the literature. Although most ligands were prepared in open vessels, they were stored under nitrogen [9*]. ^{1}H NMR spectra were recorded with Bruker AC 100, WM 250 spectrometers and ^{13}C NMR spectra with Bruker WP 80, AC 100 spectrometers. FD- and FI-mass spectra were measured on a Varian MAT 711 double focussed mass spectrometer. Elemental analyses were carried out at the Institute for Applied Chemistry, T.N.O., Zeist, the Netherlands.

Syntheses

Preparation of the aryl bromides [10]*

$2,6\text{-}(Et_2NCH_2)_2C_6H_3Br$. A solution of $2,6\text{-}(BrCH_2)_2C_6H_3Br$ (8.57 g, 25 mmol) in benzene (30 ml) was added dropwise during 1 h to a stirred solution of Et_2NH (14.63 g, 200 mmol) in benzene (30 ml). After 10 min a white precipitate of

$[Et_2NH_2]^+Br^-$ had formed. The mixture was stirred for 18 h and the solid then filtered off and washed once with 10 ml of benzene. The combined benzene solutions were evaporated to dryness to leave a pale red oil, which was purified by distillation (0.5 mmHg, 150 °C). Yield: 6.96 g (85%) of the product as a colourless oil. *m/z* $C_{16}H_{27}N_2Br^+$, 326/328 (1/1)

2,6-($^iPr_2NCH_2$)$_2C_6H_3Br$. A solution of 2,6-$(BrCH_2)_2C_6H_3Br$ (8.57 g, 25 mmol) and $^iPr_2NH$ (20.24 g, 200 mmol) in 50 ml of benzene was boiled under reflux for 48 h. The white salt formed was filtered off and washed with 10 ml of benzene. The combined benzene solutions were evaporated to dryness. Hexane (30 ml) was added to the residual yellow oil to precipitate unchanged 2,6-$(BrCH_2)_2C_6H_3Br$, which was filtered off. After removal of the solvent in vacuo methanol (15 ml) was added to the yellow oily residue and the clear solution was cooled to −20 °C. After 12 h the white solid product, which crystallized out, was filtered off under suction and dried in vacuo. Yield: 5.75 g (60%). Anal. Found: C, 62.58; H, 9.27; N, 7.15; Br, 21.11. $C_{20}H_{35}N_2Br$ calcd.: C, 62.66; H, 9.14; N, 7.31; Br, 20.89%.

2,6-(Ph_2NCH_2)$_2C_6H_3Br$. A solution of 2,6-$(BrCH_2)_2C_6H_3Br$ (8.57 g, 25 mmol) and Ph_2NH (33.85 g, 200 mmol) in 50 ml of benzene was stirred for 16 h (after 1 h the HBr salt of diphenylamine started to form). The white solid was filtered off and washed with 10 ml of benzene. The combined benzene solutions were evaporated to dryness to give a blue solid, which was washed with methanol until it was white. Yield: 5.84 g (45%). *m/z* $C_{32}H_{27}N_2Br^+$, 518/520 (1/1).

2,6-((^iPr)$MeNCH_2$)$_2C_6H_3Br$. A solution of 2,6-$(BrCH_2)_2C_6H_3Br$ (8.57 g, 25 mmol) in benzene (30 ml) was added dropwise to a stirred solution of ^{i}PrMeNH (3.66 g, 50 mmol) and Et_3N (15.72 g, 150 mmol) in benzene (30 ml). After 16 h stirring the white precipitate was filtered off and washed with 10 ml of benzene. The combined benzene solutions were evaporated to dryness and the residual yellow oil purified by vacuum distillation (with Vigreux; 0.5 mmHg, 155 °C). Yield: 3.68 g (45%) of product as a very pale yellow oil. *m/z* $C_{16}H_{27}N_2Br^+$, 326/328 (1/1).

2,6-((^{t}Bu)$MeNCH_2$)$_2C_6H_3Br$. (a) This was synthesized in the way described for 2,6-$((^{i}Pr)$MeNCH_2)_2C_6H_3Br$, but from ^{t}BuMeNH (4.36 g, 50 mmol). Removal of benzene yielded a yellow oil. On addition of hexane to this oil unreacted 2,6-$(BrCH_2)_2C_6H_3Br$ separated and was filtered off. Volatiles were evaporated from the filtrate and 10 mL of methanol were added to the oily residue. This solution was cooled to −20 °C, and after 14 h the white crystals of 2,6-$((^{t}Bu)$MeNCH_2)_2C_6H_3Br$ were isolated. Yield: 3.11 g (35%).

(b) An alternative (and cheaper) synthesis of this compound involved addition of a solution of 2,6-$(BrCH_2)_2C_6H_3Br$ (8.57 g, 25 mmol) in benzene (30 ml) to one of ^{t}BuNH$_2$ (14.63 g, 200 mmol) in benzene (30 ml) in 0.5 h. The mixture was stirred for 14 h and the white precipitate filtered off. The residue was washed with 10 ml of benzene and the combined benzene solutions evaporated to dryness. Hexane was added to the oily solid residue and the resultant suspension was kept at −20 °C for 15 h. The white solid which separated was filtered off and dried in vacuo. This solid, yield 3.67 g, consisted of 2,6-$((^{t}Bu)$HNCH_2)_2C_6H_3Br$ and some unchanged 2,6-$(BrCH_2)_2C_6H_3Br$. This mixture was used in the Eschweiler–Clarke methylation [11], for the conversion of 2,6-$((^{t}Bu)$HNCH_2)_2C_6H_3Br$ into 2,6-$((^{t}Bu)-$MeNCH_2)_2C_6H_3Br$. Crystallization from hexane yielded 3.55 g (40%) of 2,6-$((^{t}Bu)$MeNCH_2)_2C_6H_3Br$. Anal. Found: C, 60.20; H, 8.89; N, 7.67; Br, 22.82. $C_{18}H_{31}N_2Br$ calcd.: C, 60.83; H, 8.79; N, 7.89; Br, 22.49%.

2,6-((Ph)MeNCH$_2$)$_2$C$_6$H$_3$Br. The procedure as described for the synthesis of 2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$Br was followed but with PhMeNH (21.43 g, 200 mmol). After removal of the benzene the green solid residue was washed with methanol until it was white. Yield: 7.41 g (75%). Anal. Found: C, 66.56; H, 5.84; N, 6.91. $C_{22}H_{23}N_2Br$ calcd.: C, 66.84; H, 5.86; N, 7.09%.

3,11-diaza-17-bromo-3,11-dimethylbicyclo[11.3.1]heptadecane-1(17),13,15-triene ((CH$_2$)$_7$MeNCN)Br). The synthesis was carried out in the way described for ((CH$_2$)$_{10}$MeNCN)Br [12]. This involved tosylation of (H$_2$N)$_2$(CH$_2$)$_7$, ring closure of 10 mmol (4.39 g) of the bis-tosylated amine with 10 mmol (3.43 g) of 2,6-(BrCH$_2$)$_2$C$_6$H$_3$Br, detosylation, and finally methylation of the amino groups to obtain the macrocycle. Differences in the procedure from that used for the synthesis of ((CH$_2$)$_{10}$MeNCN)Br were: (a) instead of 3–4 h, the ring closure was carried out during 24 h, followed by additional stirring for 24 h. A mixture of ether/n-hexane (9/1 v/v) was used for the flash column chromatography, to give 2.48 g (40%) of the white product ((CH$_2$)$_7$TsNCN)Br (Ts = Tosyl). Anal. Found: C, 56.48; H, 6.02; N, 4.89; S, 10.59. $C_{29}H_{35}BrN_2O_4S_2$ calcd.: C, 56.21; H, 5.69; N, 4.52; S, 10.35%; (b) yield of detosylation step: 85%, affording 1.06 g of a yellow oil. *m/z* $C_{15}H_{23}N_2Br^+$, 310/312 (1/1); (c) Yield of methylation step: 90%, affording 1.04 g of a pale yellow sticky solid. *m/z* $C_{17}H_{27}N_2Br^+$, 338/340 (1/1). Overall yield of ((CH$_2$)$_7$MeNCN)Br: 31%.

Preparation of the metal complexes

The synthesis of [PtBr(Et$_2$NCN)] (**1a**) is described in detail; the syntheses of the complexes **2–5**, **8** and **9** were carried out analogously, and only differences in experimental details and physical data are given. [PtCl$_2$(SEt$_2$)$_2$] was used as the starting material for **2–5**, whereas [PdCl$_2$(COD)] was the preferred material for the synthesis of **8** and **9**.

[PtBr(C$_6$H$_3${CH$_2$NEt$_2$}$_2$-2,6)] (1a). To a yellow solution of 2,6-(Et$_2$NCH$_2$)$_2$-C$_6$H$_3$Br (0.49 g, 1.5 mmol) in 10 ml of diethyl ether, cooled to −56 °C, was added BuLi (1.2 ml of a 1.25 *M* solution in hexane; 1 equivalent). The dark yellow mixture was allowed to warm to room temperature and then added to a suspension of [PtCl$_2$(SEt$_2$)$_2$] (0.54 g, 1.2 mmol, 0.8 equivalent) in 10 ml of ether. After 18 h stirring, the turbid, yellow mixture was evaporated to dryness. The residue was taken up in acetone and the solution stirred for 3 h with NaBr (2.06 g, 20 mmol). The acetone was removed in vacuo, and H$_2$O added, to give a white precipitate. This was filtered off, washed with H$_2$O (2 × 10 ml) and hexane (2 × 10 ml) and dried in vacuo. Yield: 0.31 g of yellow solid **1a** (50%). Anal. Found: C, 36.46; H, 5.18; N, 5.25; Br, 15.02. $C_{16}H_{27}N_2PtBr$ calcd.: C, 36.78; H, 5.21; N, 5.36; Br, 15.30%.

An alternative route for the synthesis of **1a** involved the addition of the solution of the Li compound to [PtBr$_2$(SEt$_2$)$_2$]. After 18 h stirring the clear yellow solution was evaporated to dryness and the residue was extracted with 20 ml of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was concentrated (5 ml) and hexane added. The resulting precipitate was filtered off, washed with hexane (2 × 10 ml) and dried in vacuo. Yield: 0.39 g (63%) of **1a**.

[PtI(C$_6$H$_3${CH$_2$NEt$_2$}$_2$-2,6)] (1b). As described for **1a**, but with NaI (3.00 g, 20 mmol) instead of NaBr. Yield: 0.34 g (50%) of **1b** as a yellow solid. Anal. Found: C, 34.10; H, 4.87; N, 5.08. $C_{16}H_{27}N_2PtI$ calcd.: C, 33.75; H, 4.78; N, 4.92%. **1b** was

also obtained quantitatively from **1a** by stirring a solution of **1a** in acetone with a 20–30 fold excess of NaI for 3 h, followed by work-up as described for **1a**.

[PtBr($C_6H_3\{CH_2N(^tBu)Me\}_2$-2,6)] (2a). Prepared from 2,6-$((^tBu)MeNCH_2)_2$-C_6H_3Br (0.62 g, 1.74 mmol), 1.20 ml of a 1.45 *M* BuLi/hexane solution and $[PtCl_2(SEt_2)_2]$ (0.62 g, 1.4 mmol) as described for **1a**. Addition of the Li compound to the suspension of $[PtCl_2(SEt_2)_2]$ was carried out at $-56°C$ and the mixture was stirred for 72 h. The precipitate was then filtered off, washed with ether (10 ml), and dissolved in acetone containing NaBr (2.57 g, 25 mmol). After 18 h stirring, work up as described for **1a** yielded 0.56 g (73%) of **2a** as a light yellow solid. Anal. Found: C, 39.51; H, 5.52; N, 5.17; Br, 14.70. $C_{18}H_{31}N_2PtBr$ calcd.: C, 39.27; H, 5.68; N, 5.09; Br, 14.52%.

[PtI($C_6H_3\{CH_2N(^tBu)Me\}_2$-2,6)] (2b). As described for **2a**, with 2,6-$((^tBu)MeNCH_2)_2C_6H_3Br$ (0.40 g, 1.13 mmol), 0.78 ml of a 1.45 *M* BuLi/hexane solution, $[PtCl_2(SEt_2)_2]$ (0.40 g, 0.90 mmol) and NaI (3.75 g, 25 mmol). Yield: 0.38 g (71%) of **2b** as a yellow solid. Anal. Found: C, 36.09; H, 5.21; N, 4.35; I, 21.58. $C_{18}H_{31}N_2PtI$ calcd.: C, 36.18; H, 5.23; N, 4.69; I, 21.24%.

[PtCl($C_6H_4\{CH_2N(Ph)Me\}_2$-2,6)] (3c). Prepared from 2,6-$((Ph)MeNCH_2)_2$-C_6H_3Br (0.70 g, 1.77 mmol), 1.19 ml of a 1.49 *M* BuLi/hexane solution, $[PtCl_2(SEt_2)_2]$ (0.60 g, 1.34 mmol). The aryl bromide was only partially soluble in 10 ml of ether, but after lithiation a clear orange solution was obtained. This solution was added to $[PtCl_2(SEt_2)_2]$ and the mixture was stirred for 18 h and then worked up as described for **2a**, using NaCl (1.75 g, 30 mmol). Yield: 0.41 g (56%) of off-white solid **3c**. Recrystallization from CH_2Cl_2 afforded off-white crystals. Anal. Found: C, 45.39; H, 4.01; N, 4.35. $C_{22}H_{23}N_2PtCl \cdot (0.6CH_2Cl_2)$ calcd.: C, 45.47; H, 4.09; N, 4.69%.

[PtBr($C_6H_3\{CH_2N(Ph)Me\}_2$-2,6)] (3a). Solid AgOTf ($OTf = CF_3SO_3$, triflate; 0.08 g, 0.27 mmol) was added to a stirred suspension of **3c** (0.15 g, 0.27 mmol) in acetone (10 ml) with exclusion of light. After 18 h the precipitate of AgCl was filtered off. The filtrate was evaporated to dryness and H_2O (15 mL) added to the residue. To the resulting solution was added a solution of NaBr (2.57 g, 25 mmol) in 15 ml of H_2O, and the white solid product separated immediately. This was filtered off, washed with H_2O (2×10 ml) and hexane (2×15 ml), and dried in vacuo. Yield: 0.15 g (93%) of white solid **3a**. Anal. Found: C, 44.47; H, 3.99; N, 4.48. $C_{22}H_{23}N_2PtBr$ calcd.: C, 44.75; H, 3.93; N, 4.75%.

[PtI($C_6H_3\{CH_2N(Ph)Me\}_2$-2,6)] (3b). As described for **3a** but with NaI (3.75 g, 25 mmol), yield: 0.16 g (95%) of off-white solid **3b**. Crystallization from CH_2Cl_2 afforded pale grey crystals. Anal. Found: C, 39.44; H, 3.38; N, 3.75. $C_{22}H_{23}N_2PtI \cdot (0.6CH_2Cl_2)$ calcd.: C, 39.43; H, 3.54; N, 4.07%. The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

[PtI($C_6H_3\{CH_2NMe(CH_2)_7MeNCH_2\}$-2,6)] (4). Prepared from 2,6-$\{CH_2NMe(CH_2)_7MeNCH_2\}C_6H_3Br$ (0.37 g, 1.09 mmol), 0.87 ml of a 1.25 *M* BuLi/hexane solution, and $[PtCl_2(SEt_2)_2]$ (0.34 g, 0.76 mmol, 0.7 equivalent). The slightly turbid orange solution of the organolithium complex was added to $[PtCl_2(SEt_2)_2]$ and the mixture stirred for 72 h. The turbid brown solution was then concentrated (5 ml) and the precipitate filtered off and washed with ether (2×10 ml). Treatment of the solid with NaI (3.75 g, 25 mmol) in acetone (15 ml) and work up as described for **1a** yielded a crude product, from which **4** was extracted with benzene (2×10 ml). The combined benzene extracts were concentrated (5 ml) and hexane (40 ml) was added.

The resulting precipitate was filtered off, washed with hexane (2 × 10 ml), and dried in vacuo. Yield: 0.18 g (40%) of pale yellow solid **4**. Anal. Found: C, 35.45; H, 4.67; N, 4.63. $C_{17}H_{27}N_2PtI$ calcd.: C, 35.12; H, 4.68; N, 4.82%.

[PtCl(C_6H_3{CH_2NPh_2}$_2$-2,6)(SEt_2)$_2$] (5). Prepared from 2,6-$(Ph_2NCH_2)_2$-C_6H_3Br (0.78 g, 1.50 mmol), 1.2 ml of a 1.25 *M* BuLi/hexane solution, and $[PtCl_2(SEt_2)_2]$ (0.53 g, 1.2 mmol). The yellow solution of the in-situ-lithiated ligand was turbid. Addition of this solution to $[PtCl_2(SEt_2)_2]$ was carried out at −56 °C. After 18 h stirring the turbid dark brown solution was evaporated to dryness. CH_2Cl_2 (20 ml) was added to the residue and the resulting suspension was filtered through Celite. The brown filtrate was concentrated (5 ml), hexane (15 ml) was added and the solution filtered and then kept at −20 °C for 18 h. This gave brown crystals which were filtered off, washed with hexane (2 × 10 ml), and dried in vacuo. Yield: 0.25 g (24%) of **5**. *m/z* $C_{32}H_{27}N_2PtCl^+$, 670.

[PtI(C_6H_3{$CH_2NMe(CH_2)_7MeNCH_2$}-2,6)(η^1-I_2)] (6). To a yellow solution of **4** (0.05 g, 0.09 mmol) in 5 mL of CH_2Cl_2 was added a solution of I_2 (0.023 g, 0.09 mmol) in 5 mL of CH_2Cl_2. The mixture immediately became dark red/brown. After stirring for 30 min, the solution was concentrated (5 ml), hexane was added (40 ml), and the resulting precipitate filtered off, washed with hexane (2 × 10 ml) and dried in vacuo. Yield: 0.07 g (96%) of red/brown solid **6**. Anal. Found: C, 24.70; H, 3.32. $C_{17}H_{27}N_2PtI_3$ calcd.: C, 24.45; H, 3.26%.

[PtI(C_6H_3{$CH_2NMe(CH_2)_{10}MeNCH_2$}-2,6)($\eta^1$-$I_2$)] (7). As described for **6**, from $[PtI(C_{20}H_{33}N_2)]$ [12] (0.08 g, 0.13 mmol) and I_2 (0.033 g, 0.13 mmol). Yield: 0.10 g (92%).

[PdBr(C_6H_3{CH_2NEt_2}$_2$-2,6)] (8). Prepared from 2,6-$(Et_2NCH_2)_2C_6H_3Br$ (0.4 g, 1.22 mmol), 0.98 ml of a 1.25 *M* BuLi/hexane solution, and $[PdCl_2(COD)]$ (0.28 g, 0.98 mmol). When the lithiated ligand was added to $[PdCl_2(COD)]$ in diethyl ether (15 ml) at 0 °C, the solution immediately turned black. After 18 h stirring at room temperature, the ether was removed in vacuo. CH_2Cl_2 (20 ml) was added to the residue, and the resulting black suspension filtered through Celite. The orange filtrate was evaporated to dryness, the residue taken up in acetone. To this solution was added NaBr (2.57 g, 25 mmol). The mixture was stirred for 18 h and the acetone then removed in vacuo. The orange/brown sticky solid was washed with H_2O (2 × 10 ml). Hexane was added (25 ml) and the resulting yellow precipitate was filtered off, washed with hexane (2 × 10 ml), and dried in vacuo. Yield: 0.31 g (74%) of **8**. Anal. Found: C, 44.20; H, 6.36; N, 6.36. $C_{16}H_{27}N_2PdBr$ calcd.: C, 44.31; H, 6.28; N, 6.46%.

[PdBr(C_6H_3{CH_2(^{t}Bu)Me}$_2$-2,6)] (9). As described for **8**, with 2,6-((^{t}Bu)$MeNCH_2)_2C_6H_3Br$ (0.40 g, 1.13 mmol), 0.90 ml of a 1.25 *M* BuLi/hexane solution, and $[PdCl_2(COD)]$ (0.25 g, 0.86 mmol, 0.76 equivalent). Yield: 0.20 g (50%) of yellow solid **9**. Anal. Found: C, 46.51; H, 6.73; N, 5.99. $C_{18}H_{31}N_2PdBr$ calcd.: C, 46.82; H, 6.77; N, 6.07%.

[Li(C_6H_3{CH_2N(^{t}Bu)Me}$_2$-2,6)]$_2$ (10). To a solution of 2,6-((^{t}Bu)$MeNCH_2)_2$-C_6H_3Br (0.71 g, 2.00 mmol) in 15 ml of diethyl ether, was added 1.6 ml of a 1.25 *M* BuLi/hexane solution at −56 °C. The mixture was stirred for 1 h at room temperature and then evaporated to dryness. The residue was washed with cold hexane (2 × 5 ml; the compound is soluble in hexane at room temperature) and dried in vacuo. Yield: 0.53 g (94%) of white solid **10**.

Table 1

Crystal data and details of the structure determination of [PtI(C_6H_3\{$CH_2NMe(CH_2)_7MeNCH_2$\}-2,6)(η^1-I_2)] (**6**)

Crystal data	
Formula	$C_{17}H_{27}N_2I_3Pt$
Crystal system	monoclinic
Space group	$P2_1$
a, b, c (Å)	13.515(2), 9.638(1), 8.505(1)
β (°)	100.92(1)
V (Å^3)	1087.8(3)
Z	2
D_{calcd} (g/cm^{-3})	2.55
Crystal size (mm)	0.18×0.13×0.13
Data collection	
Radiation	Mo-K_α
μ (cm^{-1})	108.1
T (K)	293
θ_{max} (°)	30
Ref. reflections	011
Total unique reflections	3325
Obsd data ($I > 2.5\sigma(I)$)	2536
Refinement	
No. of refined parameters	208
Weighting scheme	unit weights
Final R and R_w	0.049

Table 2

Positional parameters of the non-hydrogen atoms of **6**

	x	y	z
Pt(1)	−0.25444(4)	−0.00426(10)	−0.20908(6)
I(1)	−0.08026(10)	0.05520(16)	−0.36492(16)
I(2)	−0.30243(9)	−0.24588(13)	−0.37759(14)
I(3)	0.08810(10)	0.11867(18)	−0.50252(15)
N(1)	−0.3495(10)	0.1395(15)	−0.3600(16)
N(2)	−0.1719(11)	−0.0999(15)	0.0033(19)
C(1)	−0.2193(10)	0.1632(17)	−0.0858(17)
C(2)	−0.1645(13)	0.1562(16)	0.0652(20)
C(3)	−0.1452(15)	0.2760(18)	0.1622(22)
C(4)	−0.1810(15)	0.4016(21)	0.0936(26)
C(5)	−0.2293(14)	0.4143(21)	−0.0618(25)
C(6)	−0.2538(12)	0.2923(18)	−0.1586(20)
C(7)	−0.2991(17)	0.2822(19)	−0.3285(24)
C(8)	−0.1221(13)	0.0127(24)	0.1161(20)
C(9)	−0.3708(16)	0.1117(24)	−0.5306(19)
C(10)	−0.0907(15)	−0.1996(22)	−0.0289(27)
C(11)	−0.4486(13)	0.1527(20)	−0.3050(24)
C(12)	−0.5132(12)	0.0238(13)	−0.3174(24)
C(13)	−0.5681(12)	−0.0015(33)	−0.1834(31)
C(14)	−0.4986(23)	−0.0133(36)	−0.0106(41)
C(15)	−0.4209(26)	−0.1199(25)	−0.0001(40)
C(16)	−0.3251(17)	−0.1032(24)	0.1352(27)
C(17)	−0.2410(15)	−0.1831(19)	0.0825(22)

[Li(C_6H_3{$CH_2N(Ph)Me$}$_2$-2,6)]$_2$ (11). As described for **10**, prepared from 2,6-((Ph)MeNCH$_2$)$_2$C$_6$H$_3$Br (0.79 g, 2.00 mmol) and 1.6 ml of a 1.25 *M* BuLi/hexane solution. The reaction was carried out in 15 ml of hexane. The organolithium compound is insoluble in hexane and separates out during the reaction. Yield: 0.62 g (96%) of white solid **11**.

Structure determination of [PtI(C_6H_3{$CH_2NMe(CH_2)_7MeNCH_2$}-2,6)(η^1-I_2)] (6).

Crystal data and other details of the structure determination of [PtI(C$_6$H$_3${CH$_2$ NMe(CH$_2$)$_7$MeNCH$_2$}-2,6)(η^1-I$_2$)] (**6**) are listed in Table 1.

A crystal of dimensions 0.18 × 0.13 × 0.13 mm was used to collect 3325 intensities on a Nonius CAD 4 diffractometer using graphite-monochromated Mo-K_α radiation. Of these, 789 were below the 2.5σ(I) level and were treated as unobserved. The structure was solved by the heavy-atom method. Refinement proceeded through anisotropic block-diagonal least-squares calculations. The H atoms were kept fixed in calculated positions. Unit weights were employed and the anomalous dispersion of Pt and I was taken into account. An extinction correction was included and an empirical absorption correction (DIFABS [13]) was applied. The final R value was 0.049. A similar refinement for the inverted structure resulted in R = 0.038. Therefore, the inverted structure, with atomic coordinates given in Table 2, represents the absolute configuration. The programs used were from XRAY 76 [14].

Results

A. Synthesis and properties of the complexes

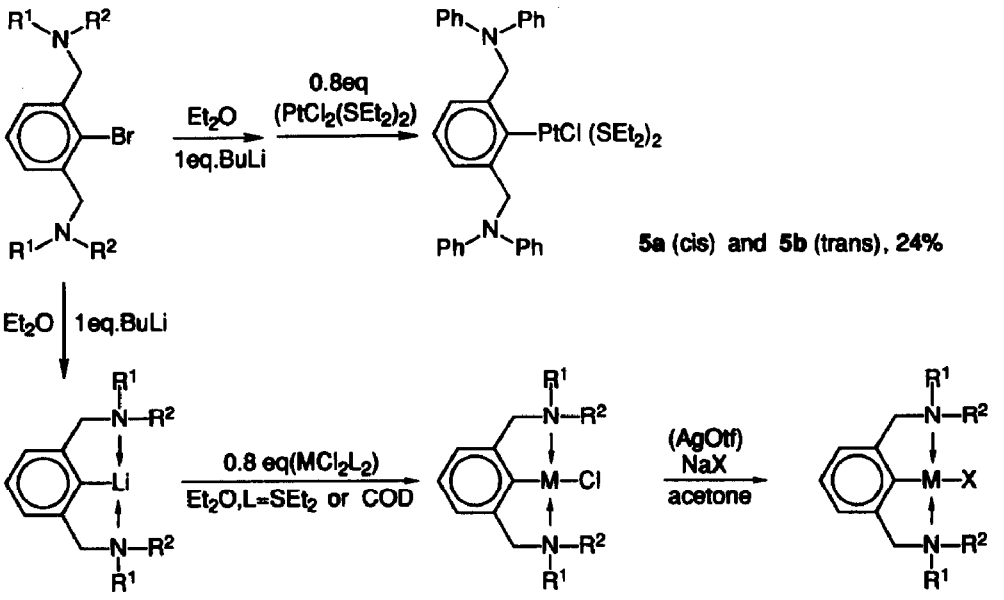
The aryl bromides used in the preparation of the complexes **1**–**5** and **8**, **9** can all be lithiated by their reaction with one equivalent of BuLi. Two of these lithium complexes, [Li((^{t}Bu)MeNCN)]$_2$ (**10**) and [Li((Ph)MeNCN)]$_2$ (**11**), were isolated as white solids in 94 and 96% yield, respectively. The other lithium complexes were not isolated, but prepared in situ. All the aryllithium complexes are soluble in diethyl ether ("Li((CH$_2$)$_7$MeNCN)" only sparingly), and show a high reactivity towards O$_2$ and H$_2$O.

The syntheses of the platinum(II) complexes **1**–**5** and of the palladium(II) complexes **8**, **9** were carried out by addition of the aryllithium compound, prepared in situ, to 0.8 equivalent of [PtCl$_2$(SEt$_2$)$_2$] or [PdCl$_2$(COD)] (COD = 1,5-cyclooctadiene) in diethyl ether.

[PtBr$_2$(SEt$_2$)$_2$] was also used instead of [PtCl$_2$(SEt$_2$)$_2$], to give [PtBr$_2$(Et$_2$NCN)] (**1a**) in a higher yield (63%). In the other syntheses, use of [PtCl$_2$(SEt$_2$)$_2$] afforded higher yields than that of [PtBr$_2$(SEt$_2$)$_2$]. The transmetallation steps proceed only in moderate yields (see Discussion). The difficulty of separating the starting complexes from the products is the reasons why the former were used in a 0.8 equivalent amount relative to the aryl bromide (and the in situ formed lithium complex).

The arylplatinum(II) and -palladium(II) complexes (**1**–**9**) are stable in air. They are all soluble in CH$_2$Cl$_2$, CHCl$_3$, and to a lesser extent in C$_6$H$_6$, but are insoluble in hexane. The solubilities of the various complexes in diethyl ether differ markedly (see Experimental). [PtX((Ph)MeNCN)] (**3**; X = Cl, Br, I) is off-white while [PtCl(Ph$_2$NCN)(SEt$_2$)$_2$] (**5**) is brown. The other square-planar platinum and palladium complexes are yellow.

The two complexes containing the diiodine ligand (**6** and **7**) were readily synthesized in open flasks by adding one equivalent of diiodine to a stirred solution



Scheme 2. Syntheses of the complexes **1–5**, **8** and **9**.

Compound	R^1	R^2	M	X	Yield (%)
1a	Et	Et	Pt	Br	50
1b	Et	Et	Pt	I	50
8	Et	Et	Pd	Br	74
2a	^{t}Bu	Me	Pt	Br	73
2b	^{t}Bu	Me	Pt	I	71
9	^{t}Bu	Me	Pd	Br	50
3a	Ph	Me	Pt	Br	56
3b	Ph	Me	Pt	I	56
3c	Ph	Me	Pt	Cl	56
4	$(CH_2)_7$	Me	Pt	I	40

of either [PtI($(CH_2)_7$MeNCN)] (**4**) or [PtI($(CH_2)_{10}$MeNCN)] in CH_2Cl_2 (see Scheme 1a for a similar reaction of [PtI(Me_2NCN)] with I_2). Like the diiodine complexes we isolated previously [2], **6** and **7** have a very intense colour (red/brown) and are only sparingly soluble in CH_2Cl_2 and $CHCl_3$.

B. Spectroscopic characterization of the ligands and metal complexes

The solid aryl bromides and metal complexes were characterized by elemental analysis and mass spectrometry (see Experimental Section). The solid state structure of [PtI($(CH_2)_7$MeNCN)(η^1-I_2)] (**6**) was determined by an X-ray diffraction study (vide infra). The aryl bromides and complexes were identified by ^{1}H NMR spectroscopy (Table 3); ^{13}C NMR data were also obtained for the organic compounds (Table 4).

General features of the ^{1}H NMR spectra of [PtX(R^1R^2NCN)]

Earlier studies on metal complexes of the monoanionic ligand Me_2NCN have shown that in the solid state square-planar and octahedral complexes possess a

Table 3

^{1}H NMR data [a] of the aryl bromides and of the complexes **1–11**

Compound	N-R^1; N-R^2	CH_2	Aryl
$(Et_2NCN)Br$	2.59(q), 1.04(t)	3.67(s)	7.4(m)
$((^iPr)_2NCN)Br$	3.09(sp), 1.05(d)	3.76(s)	7.5(m)
$(Ph_2NCN)Br$	7.11(m)	5.05(s)	7.11(m)
$((^iPr)MeNCN)Br$	2.90(sp), 1.04(d); 2.12(s)	3.68(s)	7.29(m)
$((^tBu)MeNCN)Br$	1.17(s); 2.18(s)	3.60(s)	7.42(m)
((Ph)MeNCN)Br	6.6–7.5(m); 3.19(s)	4.69(s)	6.6–7.5(m)
$((CH_2)_7MeNCN)Br$	2.30(br, 4H), 1.10(br, 10H); 2.36(s)	4.04, 3.10 [b]	7.23(m)
$[PtBr(Et_2NCN)]$ (**1a**)	3.51(m), 2.88(m) [c,d]; 1.52(t)	4.05(s; 38)	6.94, 6.71
$[PtI(Et_2NCN)]$ (**1b**)	3.66(m), 2.92(m) [c]; 1.50(t)	4.05(s; 36)	6.96; 6.67
$[PtBr((^tBu)MeNCN)]$ (**2a**) [e,f]	3.30(s; 34); 1.32(s) 3.06(s; 39); 1.49(s)	4.29, 3.93 [b,c] 4.36, 3.68 [b,c]	6.72(m)
$[PtI((^tBu)MeNCN)]$ (**2b**) [f]	3.49(s; 35); 1.36(s) 3.31(s; 38); 1.56(s)	4.25, 4.03 [b,c] 4.46, 3.74 [b,c]	6.93, 6.62 [g]
[PtBr((Ph)MeNCN)] (**3a**) [f,h]	3.65(s, br; 38)	4.68, 4.52 [b,c] 4.85 [h]	7.6–6.8(m)
[PtI((Ph)MeNCN)] (**3b**) [f]	3.74(s; 41) 3.76(s; 42)	4.82, 4.38 [b,c] 4.74, 4.51 [b,c]	7.7–6.8(m)
[PtCl((Ph)MeNCN)] (**3c**) [f]	3.58(s; 37) 3.62(s) [c]	4.66, 4.50 [b,c] 4.84, 4.39 [b,c]	7.6–6.8(m)
$[PtI((CH_2)_7MeNCN)]$ (**4**) [i]	2.95(s; 35); 2.35(m, 4H) 2.09(m, 2H); 1.81(m, 2H) 1.39(m, 6H)	3.43(52), 3.23(58) [b]	7.05, 6.60
cis-$[PtCl(Ph_2NCN)(SEt_2)_2]$ (**5a**) [j]	7.0(m)	5.41, 5.20 [b]	7.0(m)
trans-$[PtCl(Ph_2NCN)(SEt_2)_2]$ (**5b**) [k]	6.95(m)	5.30(s; 10 [l])	6.95(m)
$[PtI((CH_2)_7MeNCN)(\eta^1\text{-}I_2)]$ (**6**)	3.42(s; 33); 3.03(m, 2H) 1.90(m, 4H); 1.54(m, 6H) 1.42(m, 2H)	4.32, 4.02 [b,c]	7.07, 6.83
$[PtI((CH_2)_{10}MeNCN)(\eta^1\text{-}I_2)]$ (**7**)	3.35(s; 37); 3.28(m, 2H) 2.89(m, 2H); 2.35(m, 2H) 2.00(m, 2H); 1.55(m, 6H) 1.36(m, 6H)	4.17, [c] 4.13(46) [b]	7.07, 6.82
$[PdBr(Et_2NCN)]$ (**8**)	3.50(m), 2.65(m); 1.61(t)	4.03	6.92, 6.68
$[PdBr((^tBu)MeNCN)]$ (**9**) [f]	2.99(s); 1.51(s) 3.17(s); 1.36(s)	4.33, 3.72 [b] 4.11(s)	6.87(m) 6.63(d)
$[Li((^tBu)MeNCN)]_2$ (**10**)	2.06(s); 1.00(s)	3.78(s)	7.8–6.9(m)
$[Li((Ph)MeNCN)]_2$ (**11**)	2.18(s)	4.23(s)	7.5–6.4(m)

[a] Recorded in $CDCl_3$ unless stated otherwise; δ in ppm (relative to TMS); $^3J(^{195}Pt\text{–}^1H)$ in Hz between parentheses; aromatic protons appear as AB_2 pattern unless stated otherwise; s = singlet, d = double, t = triplet, q = quartet, sp = septet, m = multiplet; br = broad. [b] AB pattern. [c] $^3J(^{195}Pt\text{–}^1H)$ not resolved. [d] $^3J(^1H\text{–}^1H)$ 7 Hz, $^2J(^1H\text{–}^1H)$ 14 Hz. [e] Recorded in CD_2Cl_2. [f] Two isomers (see text for ratios). [g] Only one aromatic pattern observed. [h] Of the second isomer (isomer ratio 5/1) only one part of the AB pattern of the benzylic protons was observed. [i] Recorded in C_6D_6. [j] SEt_2: 2.58(m), 1.18(t). [k] SEt_2: 2.68(m), 1.21(t). [l] $^4J(^{195}Pt\text{–}^1H)$.

two-fold axis type of symmetry while square-pyramidal complexes have a mirror-plane type of symmetry (see Figs. 2a and b, respectively). The symmetry is established by the puckered conformations of the two five membered M–N–C–C–C_{ipso} metallocycles and is reflected in the positions of the N-Me groups. If these distinct molecular symmetries were to be maintained in solution, one would expect

Table 4

^{13}C NMR data [a] of the aryl bromides and lithium complexes **10** and **11** [b]

Compound	N-R^1; N-R^2	$C(H_2)$	Aryl [c]
$(Et_2NCN)Br$	47.10, 11.78	57.72	126.78(C_1), 138.62(C_2) 129.21, 126.42 (C_3, C_4)
$(({}^iPr)_2NCN)Br$	48.62, 20.70	49.47	124.17(C_1), 141.53(C_2) 127.81, 126.18 (C_3, C_4)
$(Ph_2NCN)Br$ [d]	147.46(C–N)	57.24	121.96(C_1), 137.71(C_2) 129.18, 127.21, 126.69 121.44, 120.33
$(({}^iPr)MeNCN)Br$	53.64, 17.87; 36.49	57.75	126.20(C_1), 139.25(C_2) 128.56, 126.37(C_3, C_4)
$(({}^tBu)MeNCN)Br$	54.14, 26.23; 35.45	55.36	125.63(C_1), 140.26(C_2) 128.40, 126.66(C_3, C_4)
((Ph)MeNCN)Br [e]	149.18, 111.85, 129.15, 116.53; [f] 38.55	57.66	137.95(C_2) 126.42, 127.27(C_3, C_4)
$((CH_2)_7MeNCN)Br$	49.11, 25.71, 25.01, 24.27; 41.28	63.77	124.89(C_1), 139.64(C_2) 130.96, 129.59(C_3, C_4)
10, **11**			188 [g]

[a] Recorded in $CDCl_3$, δ in ppm relative to TMS. [b] C_{ipso} only (other resonances not clear because of special conditions to resolve C_{ipso}). [c] C_1 is the carbon atom bonded to Br, C_2 is *ortho* to C_1 etc. [d] C_1, C_2 and C(–N) attributed, other aromatic resonances are listed under aryl. [e] C_1 was not observed. [f] Values in the order C–N, C(*ortho*), C(*meta*), C(*para*). [g] Septet, $^1J(^7Li–^{13}C)$ 20 Hz.

the ^1H NMR spectra of the square-planar complexes, for example, to show two resonances attributable to the differently positioned Me groups (equatorial and axial) and an AB (AX) pattern for the benzylic protons. However, in practice all the square-planar complexes of Me_2NCN at room temperature ($CDCl_3$, 250 MHz) show only one resonance for the methyl protons and a single resonance for the benzylic protons. This behaviour can be attributed to the occurrence of an intramolecular fluxional process which retains the Pt–N coordination and in which a coupled (concerted) ring flip of the two cyclometalated rings, with concomitant

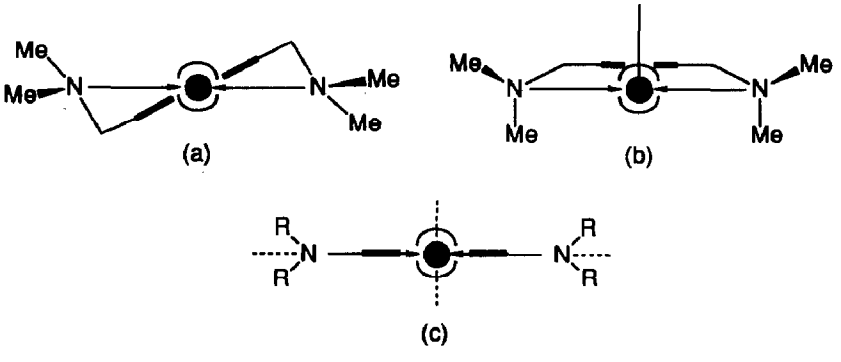


Fig. 2. Projections of a Pt(R^1R^2NCN) grouping as viewed along the Pt(1)–C(4) axis (Pt filled circle, C(1) open circle). (a) Two-fold axis type of symmetry, (b) Mirror-plane type of symmetry, (c) Possible symmetric structure for [PtX(R_2NCN)] (- - - - - - are mirror planes).

wagging around the Pt–C_{ipso} axis, exchanges the environments of the methyl groups and the benzylic protons. This process has a low activation barrier and is fast on the NMR time scale; for [PtX(Me_2NCN)] (X = halide; CD_2Cl_2, 500 MHz) it was still not frozen out at 190 K. A similar situation is found for complexes [MX(R_2NCN)] (M = d^8 metal, X = halide) with R groups other than Me, and only in more rigid systems, e.g. [PtI((CH_2)$_7$MeNCN)] (**4**) (vide infra), and [PtI((CH_2)$_{10}$MeNCN)], is it possible to reach the slow exchange limit for the ring flip process.

At the fast exchange limit, where the coupled ring flips are occurring fast on the NMR time scale, the average situation is one in which molecules [MX(R_2NCN)] acquire an apparent two-fold/mirror-plane type of symmetry as depicted in Fig. 2c. This particular situation (which comprises severe distortion of the cyclometallated rings) can not, a priori, be ruled out as being the real molecular structure but it is energetically highly unlikely.

Complexes of the type [PtX(R^1R^2NCN)] have more complex spectra, since two different substituents on each nitrogen atom combined with stable metal-nitrogen interactions render the N atoms centres of chirality. As a consequence, there are four possible stereoisomers (*RR*, *RS*, *SR* and *SS*), of which the *RS* and *SR* forms are identical, when ring flipping is fast on the NMR time scale, i.e., they represent the meso compound with an apparent internal mirror plane. The *RR* and *SS* complexes are enantiomers and are indistinguishable by ^{1}H NMR. For [PtX(R^1R^2NCN)] complexes one therefore expects two sets of ^{1}H NMR resonances; one attributable to the meso compound and one corresponding to the RR/SS pair. Moreover, the benzylic protons within each methylene group are inequivalent; thus, both sets of benzylic protons are expected to appear as AB (AX) patterns.

^{1}H NMR spectra of the complexes 1–9

The ^{1}H NMR spectrum of [PtBr(Et_2NCN)] (**1a**) shows resonances for the two methylene protons of the N-Et substituents at δ 3.51 and 2.88 ppm, with a geminal coupling of 14 Hz and vicinal couplings (with the Et methyl protons) of 7 Hz, i.e. these protons are diastereotopic. Although the $^3J(^{195}Pt–^1H)$ coupling in these signals was not resolved, the diastereotopicity alone implies that the Pt–N interactions are stable on the NMR time scale [15]. Further evidence for N atom coordination comes from the 38 Hz platinum–proton spin–spin coupling constant $J(^{195}Pt–^1H)$ exhibited by the benzylic protons; this coupling is typical for a three bond rather than a four bond path (vide infra). The chemical shift pattern of **1a** is similar to that of [NiBr(Et_2NCN)] [5], which showed a larger chemical shift difference between the N-Et methylene protons (δ 3.31 and 1.85 ppm). The spectra of ([PtI(Et_2NCN)]) (**1b**) and [PdBr(Et_2NCN)] (**8**) are also similar to that of **1a**.

The ^{1}H NMR spectra of the complexes [PtX((^{t}Bu)MeNCN)] (**2a–b**), [PtX((Ph)MeNCN)] (**3a–c**) and [PdBr((Ph)MeNCN)] (**9**) reflect the features described above for complexes with R^1R^2NCN ligand systems in which R^1 and R^2 are different. The *meso*: *RR/SS* isomeric ratio is found to depend on a combination of factors, the substituents of the NR^1R^2 grouping, the halide and the central metal atoms: **2a, b**, 8/1; **3a**, 5/1; **3b**, 6/5; **3c**, 8/1; **9**, 3/1 (see Discussion). In the spectrum of **9** the singlet pattern for the benzylic protons of the second isomer is noteworthy, and reflects accidental chemical shift coincidence. Moreover, it is surprising that $^3J(^{195}Pt–^1H)$ coupling for the benzylic protons was not resolved in the spectra of [PtX((^{t}Bu)MeNCN))] (**2a–b**) whereas it has a value of 46 Hz in the

spectra of [PtX(Me_2NCN)] [29]. However, three-bond coupling constants are dependent on the angles between the bonds, and in **2** these are probably different from those in [PtX(Me_2NCN].

In the macrocyclic compound [PtI((CH_2)$_7$MeNCN)] (**4**) the two substituents on the nitrogen atoms are also different. However, only the *RS/SR* pair can be formed, since the $(CH_2)_7$ chain is constrained to one side of the platinum coordination plane, and consequently the Me groupings are positioned on the other side. When the ring-flip process is fast, this is the *meso* compound. The benzylic protons are, of course, inequivalent, and are observed in the ^{1}H NMR spectrum (C_6D_6, 250 MHz) as an AB pattern at δ 3.43 and 3.23 ppm with remarkably large $^3J(^{195}Pt-^1H)$ of 52 and 58 Hz, respectively. The Me protons are observed as a singlet at δ 2.95 ppm with a $^3J(^{195}Pt-^1H)$ of 35 Hz. When a solution of **4** in CD_2Cl_2 is cooled to 173 K, the benzylic proton resonances appear as two AB patterns at δ 4.58 and 3.43 ppm ($^2J(^1H-^1H)$ 16 Hz) and at δ 4.12 and 3.78 ppm ($^2J(^1H-^1H)$ 14 Hz); the methyl protons afford two singlets at δ 3.09 and 3.06 ppm. These low temperature ^{1}H NMR data indicate that the slow exchange limit of the ring-flip fluxional process has been reached, with the Me groupings having different positions. The compound now exists as a mixture of *RS* and *SR* enantiomers (indistinguishable by ^{1}H NMR). This situation can be compared with that found for the related compound [PtI((CH_2)$_{10}$MeNCN)] [12].

The ^{1}H NMR spectrum of [PtCl(Ph_2NCN)(SEt_2)$_2$] (**5**) shows that SEt_2 ligands and not the N atoms of the Ph_2NCN ligand are bonded to the platinum centre. The complex is seen to exist as two isomers, those with *cis*- and *trans*- positioned SEt_2 groups. In the *trans* isomer there is a singlet for the benzylic protons at δ 5.30 ppm; the very small platinum coupling of 10 Hz is certainly a $^4J(^{195}Pt-^1H)$ value and indicates that the ligand is bonded in the monodentate mode via C_{ipso}. For the *cis* isomer there is an AB pattern for the benzylic protons at δ 5.41 and 5.20 ppm. The different environments for the benzylic protons result from hindered rotation of the aryl system about the Pt–C axis [16]. The preferred rotamer conformation observed is the one in which the CH_2NPh_2 arms exert the least interference on the *cis* ligands and this corresponds to the situation in which the aryl plane of Ph_2NCN is perpendicular to the Pt coordination plane.

With I_2 bonded η^1 to the platinum centre the macrocyclic complexes **6** and **7** are square-pyramidal (see solid state structures of **6** (vide infra) and [PtI(Me_2NCN)(η^1-I_2)]$_2$). Their ^{1}H NMR spectra are in many ways similar to that of the square-planar [PtI((CH_2)$_7$MeNCN)] (**4**). The $^3J(^{195}Pt-^1H)$ values for the N-Me protons are 33 and 37 Hz for **6** and **7**, respectively, while these are 35 and 37 Hz in the related parent complexes **4** and [PtI((CH_2)$_{10}$MeNCN)] [12]. These values indicate that the Pt centres in **6** and **7** still have a formal oxidation state of II [17*]. In CD_2Cl_2 solution the slow exchange limit for the ring flip process could not be reached with a 250 MHz spectrometer. At 173 K, the ^{1}H NMR spectrum of **6** showed broad signals for the benzylic protons at δ 4.70, 4.44 and 3.98 ppm and a broad singlet without $^3J(^{195}Pt-^1H)$ at δ 3.49 ppm for the Me protons. A similar spectrum was obtained with a solution of **7** in CD_2Cl_2 at 173 K: very broad resonances at δ 4.51 and 4.02 ppm (benzylic protons) and a broad signal at δ 3.36 ppm (Me protons). These low temperature spectra of **6** and **7** correspond to the situation in which ring flipping is at an intermediate exchange rate on the NMR time scale.

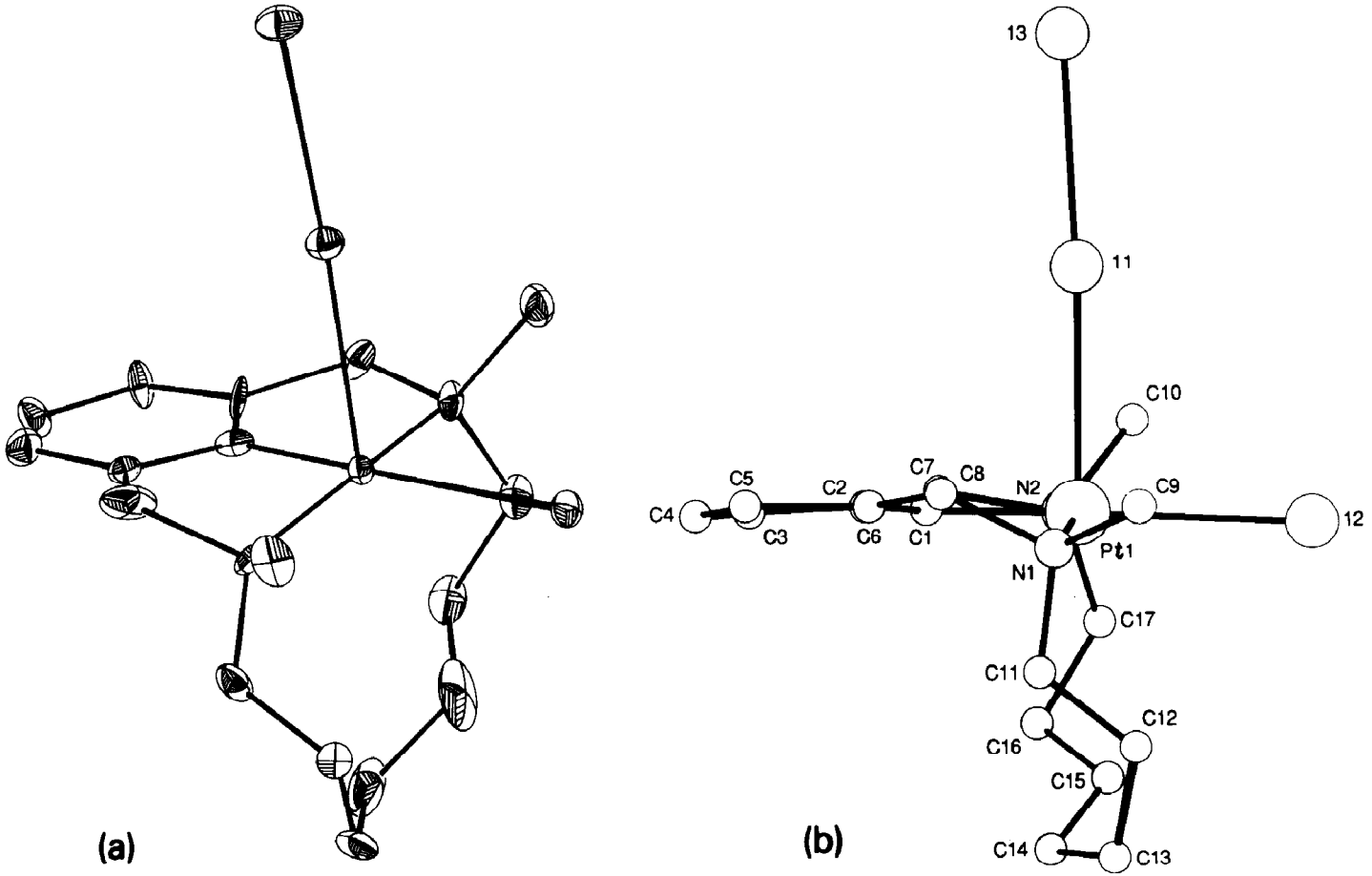


Fig. 3. (a) ORTEP drawing of [PtI(C_6H_3{$CH_2NMe(CH_2)_7MeNCH_2$}-2,6)(η^1-I_2)] (**6**). (b) PLUTO drawing of **6** along with adopted numbering scheme.

Structural characterization of the aryllithium compounds 10 and 11

The spectroscopic data for $[Li((^tBu)MeNCN)]_2$ and $[Li((Ph)MeNCN)]_2$ (**10** and **11**, respectively) are in agreement with those found for the $[Li(Me_2NCN)]_2$, which is dimeric in solution [18]. In the ^1H NMR spectra of **10** and **11** ($CDCl_3$, 250 MHz) at room temperature the benzylic protons appear as singlets, but at 233 K AB patterns are found (**10**: δ 4.48 and 3.09 ppm; **11**: δ 4.90 and 3.45 ppm). Coalescence occurs for **10** at 273 K and for **11** at 255 K. The ^{13}C NMR spectra ($CDCl_3$, 293 K, 20 MHz) show a 7 line pattern for the C_{ipso} resonance in accordance with coupling to two ^7Li nuclei [18]. Consequently **10** and **11** are believed to have dinuclear structures containing three-centre two-electron bonded aryl groups bridging the two Li atoms. Such a dimeric structure exists in the solid state for $[Li(C_6H\{CH_2NMe_2\}_4\text{-}2,3,5,6)]_2$ [19].

Table 5

Bond lengths (Å) and angles (°) of $[PtI(C_6H_3\{CH_2NMe(CH_2)_7MeNCH_2\}\text{-}2,6)(\eta^1\text{-}I_2)]$ (**6**)

Pt(1)–I(1)	2.968(2)	C(1)–C(6)	1.43(2)
Pt(1)–I(2)	2.747(2)	C(2)–C(3)	1.41(2)
Pt(1)–N(1)	2.14(1)	C(2)–C(8)	1.53(3)
Pt(1)–N(2)	2.14(1)	C(3)–C(4)	1.39(3)
Pt(1)–C(1)	1.93(2)	C(4)–C(5)	1.36(3)
I(1)–I(3)	2.816(2)	C(5)–C(6)	1.44(3)
N(1)–C(7)	1.54(2)	C(6)–C(7)	1.46(3)
N(1)–C(9)	1.45(2)	C(11)–C(12)	1.51(2)
N(1)–C(11)	1.51(2)	C(12)–C(13)	1.49(3)
N(2)–C(8)	1.52(2)	C(13)–C(14)	1.59(4)
N(2)–C(10)	1.52(3)	C(14)–C(15)	1.46(4)
N(2)–C(17)	1.49(3)	C(15)–C(16)	1.57(4)
C(1)–C(2)	1.36(2)	C(16)–C(17)	1.51(3)
I(1)–Pt(1)–I(2)	93.42(4)	C(10)–N(2)–C(17)	106(1)
I(1)–Pt(1)–N(1)	92.5(4)	Pt(1)–C(1)–C(2)	120(1)
I(1)–Pt(1)–N(2)	97.4(4)	Pt(1)–C(1)–C(6)	118(1)
I(1)–Pt(1)–C(1)	87.0(5)	C(2)–C(1)–C(6)	122(1)
I(2)–Pt(1)–N(1)	100.4(4)	C(1)–C(2)–C(3)	121(1)
I(2)–Pt(1)–N(2)	96.2(4)	C(1)–C(2)–C(8)	115(1)
I(2)–Pt(1)–C(1)	178.6(4)	C(3)–C(2)–C(8)	124(1)
N(1)–Pt(1)–N(2)	160.1(6)	C(2)–C(3)–C(4)	117(2)
N(1)–Pt(1)–C(1)	81.0(6)	C(3)–C(4)–C(5)	123(2)
N(2)–Pt(1)–C(1)	82.4(6)	C(4)–C(5)–C(6)	120(2)
Pt(1)–I(1)–I(3)	177.72(6)	C(1)–C(6)–C(5)	116(1)
Pt(1)–N(1)–C(7)	106(1)	C(1)–C(6)–C(7)	114(1)
Pt(1)–N(1)–C(9)	118(1)	C(5)–C(6)–C(7)	129(2)
Pt(1)–N(1)–C(11)	110(1)	N(1)–C(7)–C(6)	109(1)
C(7)–N(1)–C(9)	110(1)	N(2)–C(8)–C(2)	112(1)
C(7)–N(1)–C(11)	105(1)	N(1)–C(11)–C(12)	116(2)
C(9)–N(1)–C(11)	108(1)	C(11)–C(12)–C(13)	116(2)
Pt(1)–N(2)–C(8)	109(1)	C(12)–C(13)–C(14)	115(2)
Pt(1)–N(2)–C(10)	113(1)	C(13)–C(14)–C(15)	113(3)
Pt(1)–N(2)–C(17)	110(1)	C(14)–C(15)–C(16)	117(2)
C(8)–N(2)–C(10)	108(1)	C(15)–C(16)–C(17)	107(2)
C(8)–N(2)–C(17)	110(1)	N(2)–C(17)–C(16)	116(2)

C. Description of the molecular structure of 3,11-diaza-17-platinum(iodide)(η^1-diiodine)-3,11-dimethylbicyclo[11.3.1]-heptadecane-1(17),13,15-triene (6)

Figure 3 shows two views of the molecule (ORTEP and PLUTO) along with the adopted numbering scheme. The bond lengths and angles of **6** are listed in Table 5. Table 2 lists the positional parameters (fractional coordinates).

The platinum(II) centre in **6** has a five coordinate square-pyramidal geometry; I(2) of the diiodine molecule is in the apical site while the basal plane is defined by C(1), N(1), N(2), I(1) and Pt. Pt is raised slightly above this plane. Large deviations of these five atoms from their least-squares plane are observed which amount to −0.10, 0.12, 0.12, 0.04 and −0.10 Å, respectively. However, a view from the side of the molecule parallel to the aryl plane (Fig. 3b) reveals that these large deviations in fact are mainly due to the N(1) atom, which is bent out of the plane of the other four atoms. The distances of C(1), N(2), I(1) and Pt from their least-squares plane are only 0.01, 0.00, 0.00 and −0.01 Å, respectively, whereas N(1) lies 0.15 Å from this plane. The Pt–N(1) axis makes an angle of 11.5° with the latter plane. This deformation, which also leads to different Pt–N bond lengths (2.08(1) vs 2.23(1) Å for Pt–N(1) and Pt–N(2), respectively), is probably attributable to the ring strain in the odd-membered-1,7-heptamethylenediyl chain in combination with the mirror type ring puckering of the two fixed five-membered chelate rings.

The structure of **6** has three features in common with those of the only other known organometal diiodine complexes, viz. [PtI(Me_2NCN)(η^1-I_2)] [2] and [PtI_3((^{t}Bu)MeNCN)(η^1-I_2)] [2b]: (i) the Pt–I(2)–I(3) arrangement is almost linear, the angle being 176.83(5)°; (ii) the bond length I(2)–I(3) of 2.814(2) Å is elongated in comparison with the bond length of 2.715(6) Å in free diiodine [20]; (iii) there is a long Pt–I(2) bond length (2.955(1) Å).

The Pt–C(1) bond length of 1.82(2) Å is relatively short compared with the average Pt–C(aryl) bond length of 2 Å [21] and the Pt–C bond length of 1.94(1) Å in the macrocyclic complex [PtI((CH_2)$_{10}$MeNCN)] [12]. In relation to this, the Pt–I(1) bond length of 2.804(1) Å is relatively long, the average value for the Pt–I distance in complexes with trans carbon ligands being 2.70 Å [22]. The Pt–N(2) length of 2.23(1) Å is extremely long in comparison with the Pt–N(1) bond length of 2.08(1) Å and the average value, 2.10 Å, of Pt–N distances in complexes with the Me_2NCN ligand [23]. The small N(1)–Pt–N(2) angle of 162.4 (5)° is a common feature in complexes with R^1R^2NCN ligands [5,23].

The crystal structure shows the presence of helixes formed from molecules of **6** linked to each other by intermolecular I(3) ··· I(1) * contacts of 3.504(3) Å [2,24].

Discussion

Synthesis and properties of the complexes

The aryllithium compounds with R^1R^2NCN ligands ($R^1 = R^2 = Me$; $R^2 = Me$, $R^1 = {}^t$Bu, Ph) are dimeric in solution (see Results B). In both ligands the nitrogen atom of one *ortho* $CH_2NR^1R^2$ arm is coordinated to one Li centre while the nitrogen atom of the other *ortho* group is coordinated to the second Li centre, see Fig. 4, cf. refs. 18 and 25. However, in Li compounds with the cyclic ligands (CH_2)$_n$MeNCN ($n = 7$, 10) such a dinuclear structure is unlikely; molecular models show that the short (CH_2)$_n$ chains limit the required flexibility of the five-membered

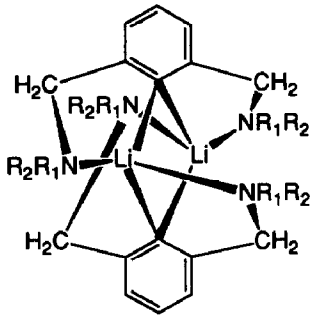


Fig. 4. Schematic structure of $[Li(R^1R^2NCN)]_2$.

chelate rings. These macrocyclic lithium compounds have a lower solubility in diethyl ether than **10** and **11**, and they are likely to have monomeric structures.

As a consequence of the weak donor ability of the (Ph)MeN atoms the basicity of the Pt^{II} centre is not high (vide infra), and therefore halide exchange in complexes [PtX((Ph)MeNCN)] (**3**) must be carried out by use of AgOTf (see Experimental Section).

$[PtCl(Ph_2NCN)(SEt_2)_2]$ was prepared from *cis*-$[PtCl_2(SEt_2)_2]$ and is isolated as a mixture of *cis* (**5a**) and *trans* (**5b**) isomers. The *cis–trans* isomerization that must take place during the synthesis of **5** is comparable to that which occurs in the synthesis of *trans*-$[Pt(Mesityl)(Br)(SEt_2)_2]$ from Li(Mesityl) and *cis*-$[PtCl_2(SEt_2)_2]$; in the latter case the fast *cis–trans* isomerization was said to be accelerated by Li(Mesityl) [26].

The coordination abilities of the amino groups of the R^1R^2NCN ligands

We found previously [5] that the coordination ability of the amino groups in R^1R^2NCN ligands with Ni^{II} decreases in the order: $Me_2N > Et_2N > (^iPr)MeN > (^tBu)MeN > (Ph)MeN$. In the present study an additional criterion for such coordination ability in the $[PtX(R^1R^2NCN)]$ complexes was provided by the $^3J(^{195}Pt-^1H)$ coupling in the ^1H NMR spectra.

The observed trend in the $^3J(^{195}Pt-^1H)$ data for the N-Me protons suggests that the $(^tBu)MeN$ donor has a marginally lower coordination ability towards Pt^{II} than Me_2N. The difference in the donor properties of the $(^tBu)Me$ and Me_2N groups is apparent from the reactions of the $[PtX(R^1R^2NCN)]$ complexes with I_2. Whereas $[PtI(Me_2NCN)]$ reacts with diiodine to give $[PtI(Me_2NCN)(\eta^1\text{-}I_2)]$, exclusively [2], the same reaction with $[PtI((^tBu)MeNCN)]$ yielded $[PtI_3((^tBu)MeNCN)(\eta^1\text{-}I_2)]$ [2b] in which, surprisingly, a second diiodine molecule is coordinated to the iodide ligand to give a triiodide ligand. The formation of this triiodide complex can be rationalized by assuming that the nitrogen atom of the $(^tBu)MeN$ group is a stronger σ-donor than that of the Me_2N group, so making the Pt^{II} centre in **2b** slightly less electrophilic (in the coordination plane) than that in $[PtI(Me_2NCN]$.

It is known that a phenyl-substituted nitrogen atom is not a good Lewis base. The poor donor ability of the (Ph)MeN and Ph_2N groups of the R^1R^2NCN ligands are reflected in halide exchange reactions during the syntheses of $[PtX(R^1R^2NCN)]$ (see Experimental Section). When no sodium salts are added, mixtures of $[PtCl(R^1R^2NCN)]$ and $[PtBr(R^1R^2NCN)]$ are isolated when R^1 and R^2 are alkyl

groups, whereas only [PtCl(R^1R^2NCN)] is isolated when R^2 = Me and R^1 = Ph, and [PtCl(Ph_2NCN)(SEt_2)$_2$] is the product when R^1 and R^2 are both Ph.

In summary, the coordination abilities of the various amino ligands in R^1R^2NCN to Pt^{II} decrease in the order Me_2N ~ (^{t}Bu)MeN > Et_2N > (Ph)MeN > Ph_2N. The reason why this is not the same order as found for the coordination abilities to Ni^{II} [5] is probably that the M–N and M–C distances are shorter in [NiX(R^1R^2NCN)] [5] than in the corresponding platinum complexes. As a consequence the steric interference of the N bonded metal fragment on the other substituents is different in the Pt and the Ni complexes.

Conclusions

The synthesis of a variety of Li, Pd^{II} and Pt^{II} complexes with ligands of the type R^1R^2NCN has provided a better insight into the coordination ability of amine donor ligands in chelating systems. A significant result is that the combination of two alkyl substituents is required to provide a Pt^{II} centre that is nucleophilic enough to coordinate a diiodine molecule end-on. Clearly variation of the N donor substituents is a powerful tool for tuning the reactivity of a metal centre. In particular the use of a loop substituent, which protects one side of the metal coordination sphere from attack of reagents, is an important development for investigating the initial stages of reactions of arylplatinum(II) entities with very reactive reagents.

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