New Ruthenium(II) Complexes of Functionalized Monoanionic Aryldiamine *N,C,N'*-Terdentate Ligands: Syntheses of $[Ru^{II}\{2,6\text{-}(Me_2NCH_2)_2\text{-}4\text{-}R\text{-}C_6H_2\}(terpy)]^+Cl^-$; X-ray Structure of a Dimeric Organolithium Compound, $[Li\{2,6\text{-}(Me_2NCH_2)_2\text{-}4\text{-}Ph\text{-}C_6H_2\}]_2$

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Abstract: The new anionic functionalized aryldiamine ligands $[2,6\text{-}(Me_2NCH_2)_2\text{-}4\text{-}R\text{-}C_6H_2]^-$ (R = $Me_3SiC{\equiv}C$, C_6H_5, Me_3Si), formally derived from $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$, have been prepared as their lithium compounds. The compound $[Li\{2,6\text{-}(Me_2NCH_2)_2\text{-}4\text{-}Ph\text{-}C_6H_2\}]_2$ crystallizes in the monoclinic space group *C*2/c (no. 15) with $a = 13.1225(5)$, $b = 13.5844(7)$, $c = 18.9859(12)$ Å, $\beta = 105.329(5)°$, $V = 3264.0(3)$ Å^3, $Z = 4$. The structure refinement converged to $R_1 = 0.0374$ for 2037 observed reflections $[F_o > 4\sigma(F_o)]$ and $wR_2 = 0.0922$ for 2560 unique data. The organolithium compounds have been used in transmetalation reactions to give the corresponding functionalized organoruthenium(II) complexes $[Ru^{II}\{2,6\text{-}(Me_2NCH_2)_2\text{-}4\text{-}R\text{-}C_6H_2\}(terpy)]^+Cl^-$ (terpy = 2,2';6',2''-terpyridine). The Ru^{II} species with R = $HC{\equiv}C$ has also been synthesized.

Keywords
aryldiamines · chelate ligands · organometallic compounds · ruthenium complexes · structure elucidation

Introduction

Organometallic complexes of the potentially *N,C,N'*-terdentate ligand $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ (NCN) have been prepared in our group to study intermediates in organometallic transformations as well as in catalytic processes, for example, oxidative addition of dihalogens,[1] nickel(II)-catalyzed Kharasch addition of polyhalogenated alkanes to olefins,[2] and ruthenium(II)-catalyzed hydrogen transfer and direct hydrogenation reactions.[3] Functionalization of the NCN ligand, mostly starting from ring-substituted *m*-xylenes,[4] has provided insight into the mechanism of these catalytic reactions (Fig. 1 a and b). Some functionalized *N,C,N'*-terdentate ligands can also be used to synthesize multimetallic systems (Fig. 1 c,[5] d,[6] and e[7]) or to immobilize the organometallic moiety in materials such as polymers[8] and dendrimers.[9]

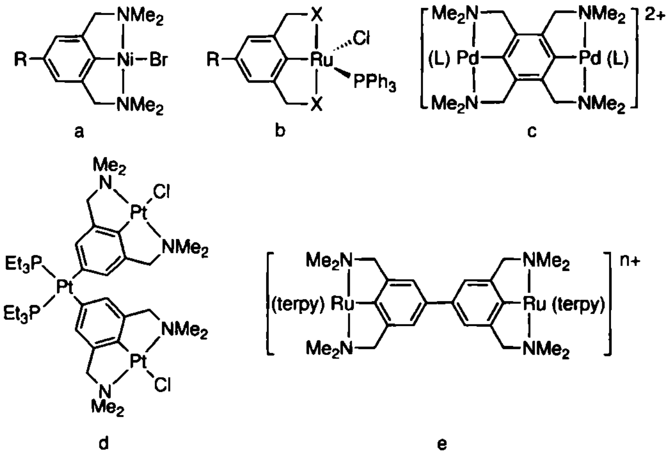

Fig. 1. Examples of organometallic and multimetallic complexes containing *para*-functionalized *N,C,N'*-terdentate ligands: a) R = H, NO_2, NH_2, MeC(O)N(H), Cl, PhCH=N, MeO, MeC(O); b) X = NMe_2, PPh_2 and R = H, Ph; c) L = MeCN; e) *n* = 2, 3, 4; terpy = 2,2';6',2''-terpyridine.

Recently, we reported on a new series of organoruthenium(II) complexes of the unsubstituted ligand $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$.[10] Ruthenium complexes containing derivatives of this ligand are also interesting, because of their catalytic applications, as well as their electronic and optical properties. We have already reported an example of electronic communication between two ruthenium centers separated by 10.829(2) Å by a bisterdentate ligand (Fig. 1 e) containing a bridging biphenylene dianion.[7] To develop systems that place the metal centers at even larger separations, we have been investigating the functionalization of NCN to enable construction of multimetallic systems. To this end we have now studied the synthesis of potential-

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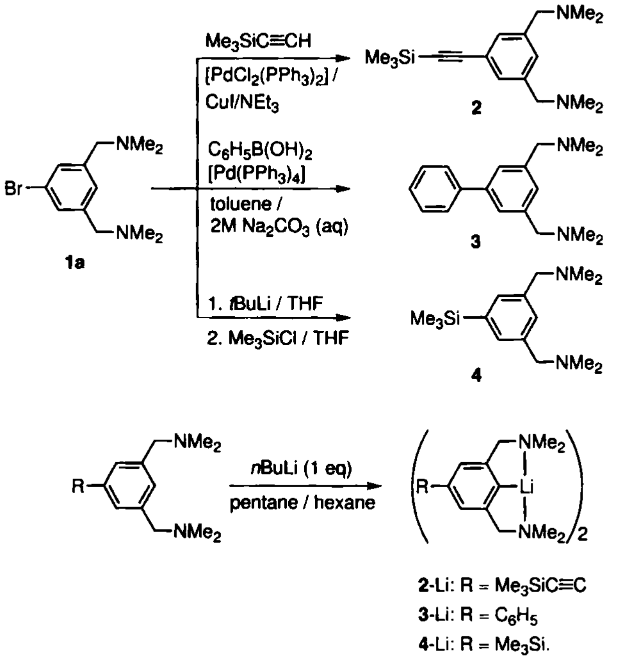
ly *N,C,N′*-terdentate ligands $[2,6\text{-}(Me_2NCH_2)_2\text{-}4\text{-}R\text{-}C_6H_2]^-$ with alkynyl, aryl, and trimethylsilyl *para* substituents. These new ligands have been used to prepare functionalized analogues of $[Ru\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(terpy)]Cl$.[10] Multimetallic systems derived from these complexes as well as aspects of metal–metal communication are currently being developed.

Results and Discussion

Synthesis of organic starting materials: We prepared the 5-bromo-substituted aryldiamine **1a**, which is a colorless oil, as a precursor to a range of 1,3-aryldiamines functionalized in the 5-position (see Scheme 1). Benzylic bromination of 5-bromo-*m*-xylene,[11] followed by a nucleophilic amination with dimethylamine afforded **1a** in 45–55% overall yield.



Scheme 1. Preparation of compounds **2**, **3**, and **4**, and their corresponding organolithium compounds **2**-Li, **3**-Li, and **4**-Li.

A Pd/Cu-catalyzed coupling[12] of **1a** with trimethylsilylacetylene gave the trimethylsilyl-protected acetylene-substituted compound **2** in moderate yield (66%). An impurity caused by homocoupling of the copper acetylide intermediate, bis(trimethylsilyl)butadiyne, could be removed by heating the crude product in vacuo at 120 °C. The phenyl-substituted aryldiamine compound **3** was obtained in 83% yield by a palladium-catalyzed Suzuki coupling[13] of **1a** and phenylboronic acid in a two-phase system of toluene and alkaline water.

A potentially important reaction of the bromo-substituted compound **1a** is the generation of the 1-lithiated compound **1b** for transmetalation reactions.[6] Direct lithiation of **1a** with one equivalent of *n*-butyllithium in hexane gave a mixture of at least two products formed by lithium–halogen exchange and aromatic deprotonation, respectively. However, the use of two equivalents of *tert*-butyllithium in THF at −100 °C allowed quantitative formation of 3,5-bis[(dimethylamino)methyl]phenyllithium (**1b**). Quenching experiments with D_2O and H_2O established the fact that lithiation takes place exclusively at the 1-position. Quenching of **1b** with Me_3SiCl gave the 1-trimethylsilyl-substituted compound **4** quantitatively, as determined by ^1H NMR spectroscopy. Compounds **2**–**4** were purified by flash distillation to give colorless oils.

Synthesis and characterization of aryldiaminelithium reagents: To be able to selectively introduce metals in the position between the two CH_2NMe_2 substituents of **2**–**4**, the corresponding organolithium compounds **2**-, **3**-, and **4**-Li were prepared. The previously used route for the preparation of $[Li\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}]_2$ was based on a lithium–halogen exchange reaction of the bromo compound $2,6\text{-}(Me_2NCH_2)_2C_6H_3Br$.[14] We have now investigated a new general procedure for the synthesis of the desired organolithium derivatives, based on a directed aromatic lithiation of compounds **2**–**4** (which do not contain bromine), and a simple protocol has been developed: A solution of **2**–**4** in pentane or hexane is cooled to −78 °C and treated with one equivalent of *n*-butyllithium. The reaction mixture is allowed to warm up to room temperature, and after 16 h the desired air-sensitive organolithium compounds **2**-, **3**-, and **4**-Li (off-white solids, soluble in alkane solvents) can be isolated simply by removing the solvent in vacuo. The solvent used in this protocol is crucial. In alkane solvents the lithiation is selectively directed to the 1-position through coordination of both of the CH_2NMe_2 substituents to the butyllithium aggregate prior to metalation. However, the use of a more polar and coordinating solvent (e.g., diethyl ether) seems to partially prevent one of the CH_2NMe_2 N-donor substituents from coordination to lithium prior to metalation, and this results in both 1-lithiation (83%) and 3-lithiation (17%).[15]

When an unstirred reaction mixture of **3** with *n*-butyllithium in hexane was allowed to slowly warm to room temperature, crystals of **3**-Li formed, which were suitable for an X-ray analysis. The molecular geometry of **3**-Li is depicted in Figure 2. In the solid state **3**-Li has a dimeric structure, consisting of two lithium atoms Li(1) and Li(2) and two monoanionic aryldiamine ligands. The coordination geometry of the lithium atoms in **3**-Li is distorted tetrahedral; each lithium atom is coordinated by two nitrogen donors of two different ligands and two bridging aryl C_{ipso} atoms. The dimer is C_2-symmetrical (C_2 axis through the lithium atoms), and the two C_{ipso} atoms and the two lithium atoms afford a dihedral angle C(1)-Li(2)-C(1A)-Li(1) of 0.0(8)° with C(1)–Li(1) and C(1)–Li(2) distances of 2.200(3) and 2.188(3) Å, respectively. The C_{ipso} atom of each ligand is bonded to both lithium atoms with a characteristically acute Li(1)-C(1)-Li(2) angle of 66.80(13)°, indicative for a 2-electron–3-center bridging aryl anion. The structure of **3**-Li shows distortions in the lithium-bonded aryl ring. For example, the C-C_{ipso}-C angle of 114.24(13)° is less than 120° and similar to that found in $[LiPh(Me_2NCH_2CH_2NMe_2)]_2$.[16] These distortions are also

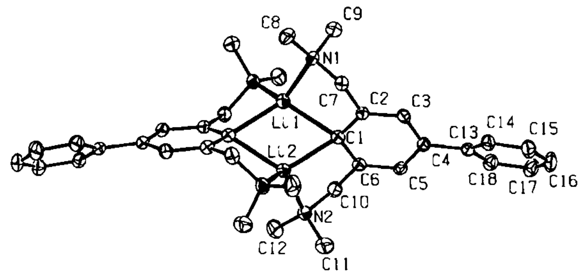


Fig. 2. ORTEP diagram [26] of **3**-Li (ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity).

seen in a lengthening of the C–C bonds involving C_{ipso}; C(1)–C(2) and C(1)–C(6) bonds have an average bond length of 1.407 Å, whereas the average length of the other four C–C bonds of the lithium-bonded aryl ring is 1.394 Å. Such distortions are also seen in the solid-state structure of $[Li\{2\text{-}(Me_2NCH_2CH_2N(Me)NCH_2)C_6H_4\}]_2$.[17] In the two five-membered rings, C(1)-Li(1)-N(1)-C(7)-C(2) and C(1)-Li(2)-N(2)-C(10)-C(6), which are formed by coordination of the N-donor substituents, the bite angles C(1)-Li(1)-N(1) and C(1)-Li(2)-N(2) are 86.22(5) and 86.87(5)°, respectively. These values are comparable with those of C-Li-N angles in the related dimeric compounds $[Li\{2\text{-}(Me_2NCH_2CH_2N(Me)NCH_2)\text{-}C_6H_4\}]_2$ and $[Li\{2,3,5,6\text{-}(Me_2NCH_2)_4C_6H\}]_2$.[18a] The two aromatic rings of each aryldiamine ligand of dimeric **3**-Li are rotated out of plane giving a C(3)-C(4)-C(13)-C(14) dihedral angle of 31.8(2)°, which is normal for (substituted) organic biphenyl systems in the solid state.[18b, c]

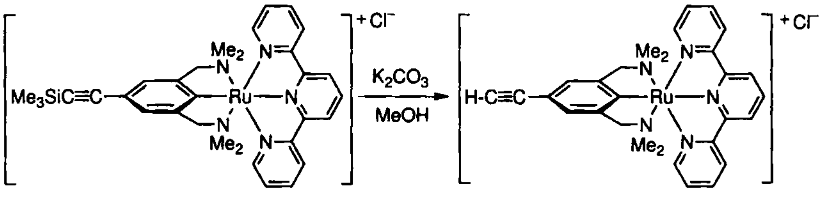
Organolithium compound **3**-Li is most probably also dimeric in benzene and toluene solution. In its low-temperature (260 K) ^1H NMR spectrum ($[D_8]$toluene), the benzylic protons give rise to an AX pattern ($\delta = 4.11$ and 2.94; $^2J_{HH} = 11.2$ Hz), and the protons of the dimethylamino unit (NMe_2) afford two singlets ($\delta = 1.96$ and 1.78), which is in accord with the expected C_2 symmetry of dimeric **3**-Li. At ambient temperature (298 K) all the CH_2NMe_2 resonances are broad. At elevated temperature (345 K) one singlet is observed for both sets of benzylic protons ($\delta = 3.59$) and the NMe_2 protons ($\delta = 2.02$). The dimeric structure of $[Li\{2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2$ in benzene solution could be unambiguously assigned from the multiplicity of the ^{13}C NMR C_{ipso} atom resonance, observed as a heptet with 1:2:3:4:3:2:1 intensity ($^1J(^{13}C,^7Li)$), indicating a coupling with two equivalently bonded lithium atoms.[14b, 18a, 19a] The multiplicity of C_{ipso} ($\delta = 188.0$) of **3**-Li, however, was not resolved even at low temperature ($[D_8]$toluene, 253 K, 50 MHz).

Synthesis and characterization of arylruthenium(II) complexes: The organolithium compounds **2**-, **3**- and **4**-Li could be successfully employed in transmetalation reactions to afford the corresponding five-coordinate organometallic ruthenium(II) complexes **5**, **6**, and **7** (Scheme 2), respectively. The use of $[RuCl_2(PPh_3)_4]$ instead of its well-known tristriphenylphosphine analogue appeared to be essential for acceptable yields of the new complexes **5**–**7**.[10]

Reaction of **3**-Li with $[RuCl_2(PPh_3)_4]$ in tetrahydrofuran yielded the blue air-sensitive 16-electron complex **6**, which is highly soluble in dichloromethane, moderately soluble in benzene, and insoluble in alkanes and diethyl ether. These solubility properties make it possible to isolate and purify the complex from free triphenylphosphine. The ^1H NMR spectrum of **6** shows an AB pattern for the benzylic protons and two singlets for the NMe_2 units. This indicates that the structure of **6** is similar to the square-pyramidal structure (with an apically positioned PPh_3 ligand) of its unsubstituted NCN analogue (R = H).[10] Subsequent reaction of **6** with 2,2′;6′,2″-terpyridine (terpy) in methanol gave a blue, air-stable ionic complex **9**, which, like its unsubstituted NCN analogue,[10] is crystalline and soluble in methanol and water.

Transmetalation of both **2**-Li and **4**-Li with $[RuCl_2(PPh_3)_4]$ in tetrahydrofuran yielded the expected blue 16-electron organoruthenium(II) complexes **5** and **7**, respectively, but their high solubility in pentane (as a result of the hydrophobic Me_3Si groups) hindered the isolation of pure **5** and **7**, free from triphenylphosphine and ruthenium phosphine complexes. However, the impure products reacted in situ with terpy in methanol to afford the expected blue, 18-electron, 6-coordinate, ionic complexes **8** and **10** (Scheme 2) in 42% and 19% yield (based on **2**- and **4**-Li), respectively, after an aqueous workup. Despite the fact that both **8** and **10** contain a hydrophobic Me_3Si group, these ruthenium(II) complexes are crystalline and water-soluble like their NCN congener $[Ru\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(terpy)]$-Cl.

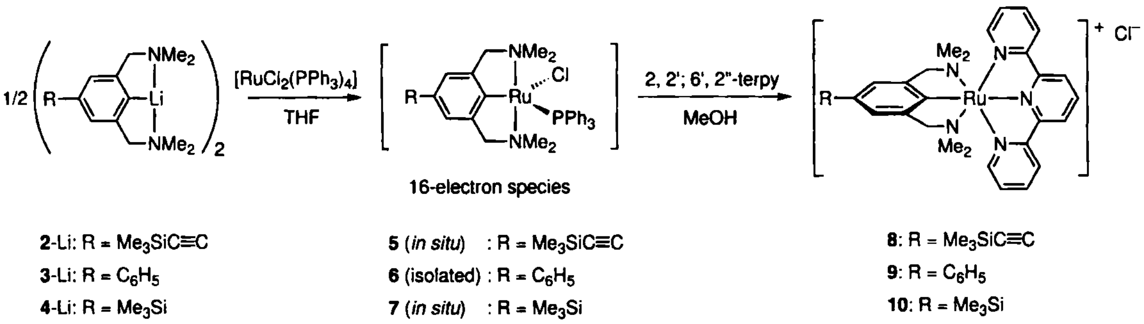
The trimethylsilyl group of **8** was readily removed with a catalytic amount of K_2CO_3 in methanol as solvent to give the blue terminal acetylene species **11** quantitatively (Scheme 3). This ionic organoruthenium(II) species is an interesting, readily accessible derivative for the potential synthesis of multimetallic systems through functionalization of the acetylenic group.



8 **11**

Scheme 3. Deprotection of the acetylenic group in **8**.

All NMR spectroscopic and analytical data for the new ionic 18-electron organoruthenium(II) compounds **8**–**11** were as expected for their proposed six-coordinate structures and similar to those of the analogous complexes containing unsubstituted NCN. Infrared spectra of **8** ($\tilde{\nu}_{C\equiv C} = 2143\ cm^{-1}$) and **11** ($\tilde{\nu}_{C\equiv C} = 2095\ cm^{-1}$; $\tilde{\nu}_{C\equiv C-H} = 3304\ cm^{-1}$) show the expected bands for nonterminal and terminal alkyne groups, respectively. The UV/Vis spectra of **8**–**11** are compared to that of $[Ru\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(terpy)]Cl$[10] in Table 1. The absorptions in



Scheme 2. Synthesis of organoruthenium(II) complexes **5**–**10**.

Table 1. UV/Vis data of the complexes [Ru{2,6-$(Me_2NCH_2)_2$-4-R-C_6H_2}(terpy)]Cl [a].

R	No.	λ_{max} (nm) [ε (10^4 $M^{-1}cm^{-1}$)]						
$Me_3SiC{\equiv}C$	**8**	627	586	519	368	324	280	240
		[0.67]	[0.73]	[0.79]	[1.66]	[3.26]	[2.46]	[3.37]
C_6H_5	**9**	638	594	525	367	326	281	239
		[0.75]	[0.76]	[0.84]	[1.61]	[4.07]	[2.61]	[3.69]
H [b]		641	597	527	396	325	282	238
		[0.71]	[0.67]	[0.69]	[0.79]	[3.65]	[2.81]	[2.81]
Me_3Si	**10**	641	596	527	392	325	282	238
		[0.64]	[0.63]	[0.67]	[0.73]	[3.45]	[2.61]	[2.72]
$HC{\equiv}C$	**11**	638	590	525	386	325	281	236
		[0.59]	[0.68]	[0.75]	[0.95]	[3.21]	[2.49]	[2.96]

[a] Solution in CH_2Cl_2 (≈10^{-4} M). [b] Previously reported in CH_3CN.

the UV part of the spectra (200–400 nm) are not significantly influenced by the different *para* substituents, except for the absorption at 396 nm (R = H: $\varepsilon = 0.79 \times 10^4 M^{-1}cm^{-1}$), which shows a substantial hypsochromic shift for the *para*-substituted NCN complexes to 368 nm (**8**, R = $Me_3SiC{\equiv}C$: $\varepsilon = 1.66 \times 10^4 M^{-1}cm^{-1}$), 367 nm (**9**, R = Ph: $\varepsilon = 1.61 \times 10^4 M^{-1}cm^{-1}$), and 386 nm (**11**, R = $HC{\equiv}C$: $\varepsilon = 1.66 \times 10^4 M^{-1}cm^{-1}$). The increased intensity of these absorptions of the substituted complexes can be explained in terms of increased conjugation, and the absorptions can therefore be attributed to an MLCT from the ruthenium center to the aryldiamine ligand. In the visible region (400–800 nm) of the UV/Vis spectra, the most substantial hypsochromic shift, relative to the unsubstituted NCN analogue, is found for **8** (8, 11, and 14 nm for the three absorptions). The hypsochromic shifts for complexes **9** and **11** relative to the unsubstituted NCN analogue are significantly smaller (2–7 nm). Complex **10** affords a UV/Vis spectrum similar to that of its unsubstituted NCN analogue.

These hypsochromic shifts in the MLCT region for this series of Ru^{II} complexes contrast with the results from Ni^{II} complexes of NCN and some *para*-substituted derivatives. In the latter case there is no significant shift found upon substitution of the NCN ligand.[4] Also, oxidation of organonickel(II) complexes of NCN leads exclusively to one-electron transfer oxidation of the Ni^{II} center to the corresponding Ni^{III} complex. In contrast, the cationic Ru^{II}(terpy) complex of (unsubstituted) NCN forms a dinuclear [Ru^{III}–Ru^{III}] complex on oxidation (see Fig. 1e) through selective activation of the *para* C–H bond and selective C–C bond formation, that is, in Ru^{II} complexes of NCN a mixing between filled metal and empty arene orbitals seems to be feasible.

Conclusion

The aryldiamine system $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ lends itself readily to functionalization in the position *meta* to the CH_2NMe_2 groups through a procedure employing the key precursor 3,5-$(Me_2NCH_2)_2C_6H_3Br$. From the functionalized compounds 1,3-$(Me_2NCH_2)_2$-5-R-C_6H_3 directed lithiation affords the corresponding organolithium compounds, which can be used successfully to generate ruthenium(II) complexes functionalized at the *para*-position relative to the metal center. A route towards multimetallic systems and organometallic polymers as well as towards immobilized organometallic species should now be possible through chemical derivatization of the *para* substituent.

Experimental Section

General: All experiments were conducted in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over appropriate materials and distilled prior to use. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany); ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 298 K on a Bruker AC 200 or AC 300 spectrometer. UV/Vis spectra were recorded on a Varian Cary 1. $[RuCl_2(PPh_3)_4]$ [20] and phenylboronic acid [21] were prepared according to literature procedures; $RuCl_3 \cdot 3H_2O$ was obtained from Degussa.

Synthesis of 3,5-$(BrCH_2)_2C_6H_3Br$: 3,5-$(CH_3)_2C_6H_3Br$ (100 g, 0.54 mol), *N*-bromosuccinimide (195 g, 1.1 mol), and azobisisobutyronitrile (0.5 g) were heated to reflux in methyl formate (600 mL) under illumination (200 W incandescent bulb) for 16 h. The reaction mixture was evaporated in vacuo, and the residue extracted with boiling hexane (5 × 150 mL). Upon chilling (− 25 °C) a solid precipitated from the combined extracts. The solid was recrystallized from diethyl ether or hexane to give white crystals of 3,5-$(BrCH_2)_2C_6H_3Br$ (91 g, 51 %). ^1H NMR (C_6D_6, 200 MHz): δ = 6.94 (s, 2H, ArH), 6.62 (s, 1H, ArH), 3.57 (s, 4H, CH_2Br); ^{13}C NMR (C_6D_6, 50 MHz): δ = 140.5, 131.6, 128.1, 122.6, 31.3.

Synthesis of 3,5-$(Me_2NCH_2)_2C_6H_3Br$ (1a): A solution of 3,5-$(BrCH_2)_2C_6H_3Br$ (34.0 g, 99 mmol) in benzene (200 mL) was added to a solution of dimethylamine (50 g, 1.1 mol) in benzene at 5 °C over 1 h. The reaction was stirred at this temperature for a further 2 h. The mixture was filtered and the volatiles removed in vacuo from the filtrate. The residue was flash-distilled to give **1a** (22 g, 74%) as a yellow oil at room temperature, which crystallized at −20 °C. ^1H NMR (C_6D_6, 200 MHz): δ = 7.47 (s, 2H, ArH), 7.26 (s, 1H, ArH), 3.09 (s, 4H, CH_2N), 2.00 (s, 12H, NMe_2); ^{13}C NMR (C_6D_6, 50 MHz): δ = 142.3, 130.6, 128.0, 122.7, 63.7, 45.3. Anal. calcd. for $C_{12}H_{19}BrN_2$: C, 53.14; H, 7.06; N, 10.33. Found: C, 53.28; H, 7.16; N, 10.26.

Synthesis of 1-$(Me_3SiC{\equiv}C)$-3,5-$(Me_2NCH_2)_2C_6H_3$ (2): A solution of **1a** (10 g, 36.9 mmol), trimethylsilylacetylene (5.06 g, 52 mmol), $[PdCl_2(PPh_3)_2]$ (2.55 g, 3.6 mmol), and CuI (685 mg, 3.6 mmol) in triethylamine (130 mL) was heated at reflux for 14 h. The volatiles were removed, diethyl ether (200 mL) was added and the mixture filtered through a pad of neutral alumina. The filtrate was evaporated down to a brown oil (9 g) on a rotary evaporator. ^1H NMR spectroscopy showed the presence of 80% **2** and 20% **1a**. The above reaction was repeated on this mixture: trimethylsilylacetylene (1.27 g, 13 mmol), $[PdCl_2(PPh_3)_2]$ (630 mg, 0.9 mmol), CuI (171 mg, 0.9 mmol), and triethylamine (100 mL) were added, and the mixture heated to reflux for 17 h. Workup as above gave a brown oil containing only **2** and some by-product identified as bis(trimethylsilyl)butadiyne. This was removed by heating at 120 °C in vacuo for 6 h, to give **2** (7.0 g, 66%), sufficiently pure for the synthesis of **8**. ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.32 (s, 2H, ArH), 7.20 (s, 1H, ArH), 3.53 (s, 4H, CH_2N), 2.21 (s, 12H, NMe_2), 0.20 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 139.2, 131.5, 130.0, 122.7, 105.2, 93.7, 63.9, 45.4, −0.16; IR (CH_2Cl_2): $\tilde{\nu}(C{\equiv}C)$ = 2148 cm^{-1}.

Synthesis of [Ru{2,6-$(Me_2NCH_2)_2$-4-$(Me_3SiC{\equiv}C)C_6H_2$}(terpy)]Cl (8): *n*BuLi (434 µL, 1.6 M solution in hexane, 0.694 mmol) was added to a solution of **2** (200 mg, 0.694 mmol) in hexane (5 mL) over 2 min. The solution was stirred for 4 h, and the volatiles removed to leave an orange solid. This was dissolved in THF (5 mL) and added dropwise to a solution of $[RuCl_2(PPh_3)_4]$ (846 mg, 0.694 mmol) in THF (10 mL) over 2 min. After 1 h of stirring, the volatiles were removed and a solution of 2,2′;6′,2″-terpyridine (162 mg, 0.694 mmol) in MeOH (15 mL) was added. The resulting solution was heated to reflux for 3 h, after which the volatiles were removed. The residue was washed with pentane (2 × 50 mL), extracted with H_2O (30 mL), and the resulting solution filtered. The filtrate was extracted repeatedly with CH_2Cl_2 (30 mL portions) until the water layer was no longer blue, and the combined extracts evaporated to dryness to give **8** as a blue solid (200 mg, 42%). Analytically pure samples could be obtained by slow concentration of a CH_2Cl_2/toluene/hexane solution. ^1H NMR (CD_3CN, 200 MHz): δ = 8.66 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 8.51 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 8.17 (d, 2H, $^3J_{HH}$ = 5.0 Hz, ArH), 8.01 (t, 1H, $^3J_{HH}$ = 8.0 Hz, ArH), 7.92 (t, 2H, $^3J_{HH}$ = 5.0 Hz, ArH), 7.41 (t, 2H, $^3J_{HH}$ = 6.0 Hz, ArH), 7.27 (s, 2H, ArH), 3.61 (s, 4H, CH_2N), 1.19 (s, 12H, NMe_2), 0.26 (s, 9H, $SiMe_3$); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 208.5, 162.1, 156.1, 154.3, 144.4, 137.0, 131.8, 128.6, 125.7, 125.2, 124.2, 109.9, 92.6, 76.3, 53.6, 1.8; IR (CH_2Cl_2): $\tilde{\nu}(C{\equiv}C)$ = 2143 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$10^4 M^{-1}cm^{-1}$]) = 627 (0.67), 586 (0.73), 519 (0.79), 368 (1.66), 324 (3.26), 280 (2.46), 240 (3.37). Anal. calcd. for $[C_{32}H_{38}ClN_5Ru + 0.5CH_2Cl_2]$: C, 55.40; H, 5.67; N, 10.09. Found C, 55.13; H, 5.84; N, 9.65.

Synthesis of [Ru{2,6-$(Me_2NCH_2)_2$-4-$(HC{\equiv}C)C_6H_2$}(terpy)]Cl (11): Compound **8** (160 mg, 0.244 mmol) and K_2CO_3 (24 mg, 0.171 mmol) were stirred together in MeOH (15 mL) for 3 h. The solution was then filtered, and the filtrate evaporated to dryness to leave **11** as a blue solid (131 mg, 91%). Analytically pure samples were obtained by slow evaporation of a CH_2Cl_2/toluene/hexane solution. ^1H NMR (CD_3CN, 200 MHz): δ = 8.66 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 8.50 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 8.17 (d, 2H, $^3J_{HH}$ = 5 Hz, ArH), 8.01 (t, 1H, $^3J_{HH}$ = 8.0 Hz, ArH), 7.93 (t, 2H, $^3J_{HH}$ = 7.0 Hz, ArH), 7.42 (t, 2H, $^3J_{HH}$ = 7.0 Hz, ArH), 7.33 (s, 2H, ArH), 3.61 (s, 4H, CH_2N), 3.31 (s, 1H, CCH), 1.19 (s, 12H, NMe_2); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 206.8, 160.7, 154.7, 152.8, 143.1, 135.6,

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130.4, 127.2, 124.4, 124.0, 122.9, 113.5, 86.6, 74.9, 74.7, 52.2; IR (CH_2Cl_2): $\tilde{\nu}(C{\equiv}C) = 2095\ cm^{-1}$, $\tilde{\nu}(C{\equiv}C\text{-}H) = 3304\ cm^{-1}$; UV/Vis ($CH_2Cl_2$): λ_{max} [nm] ($\varepsilon[10^4\ M^{-1}cm^{-1}]$) = 638 (0.59), 590 (0.68), 525 (0.75), 386 (0.95), 325 (3.21), 281 (2.49), 236 (2.96). Anal. calcd. for $[C_{29}H_{30}ClN_5Ru + CH_2Cl_2]$: C, 53.77; H, 4.81; N, 10.45. Found C, 54.00; H, 5.02; N, 9.95.

Synthesis of 1-(C_6H_5)-3,5-($Me_2NCH_2)_2C_6H_3$ (3): This compound was prepared by a modification of a literature procedure for aryl coupling [13]. A solution of phenylboronic acid (4.64 g, 45 mmol) in MeOH (20 mL) was added dropwise to a vigorously stirred mixture of 2 M aqueous Na_2CO_3 (35 mL) and toluene (70 mL), containing **1a** (9.0 g, 33 mmol) and $[Pd(PPh_3)_4]$ (2.1 g, 1.85 mmol) at room temperature. The reaction mixture was stirred vigorously for 18 h at 80 °C. This was followed by partitioning between CH_2Cl_2 (300 mL) and aqueous 2 M Na_2CO_3 (200 mL) containing concentrated ammonia (25 mL). The separated organic layer was washed with saturated aqueous NaCl (35 mL), dried over $MgSO_4$, and the volatiles removed in vacuo. The crude product was purified by flash distillation to yield pure **3** (7.83 g, 83%) as a colorless oil. ^1H NMR (C_6D_6, 300 MHz): δ = 7.62–7.56 (m, 4H, ArH), 7.50 (s, 1H, ArH), 7.22–7.15 (m, 3H, ArH), 3.36 (s, 4H, CH_2), 2.14 (s, 12H, NMe_2); ^{13}C NMR (C_6D_6, 75 MHz): δ = 141.83, 141.65, 140.48, 128.99, 128.74, 127.59, 127.35, 126.74, 64.56, 45.44. Anal. calcd. for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44. Found: C, 80.69; H, 9.12; N, 10.32.

Synthesis and isolation of [Li{2,6-($Me_2NCH_2)_2$-4-($C_6H_5)C_6H_2$}]$_2$ (3-Li): A solution of *n*BuLi (4.7 mL, 1.6 M in hexanes) was added to a solution of **3** (2.01 g, 7.5 mmol) in hexane (60 mL) at −78 °C. The undisturbed reaction mixture was allowed to warm to room temperature over 2 h and left at this temperature for 16 h. Off-white crystals of **3-Li** were collected by centrifugation, washed with pentane (2 × 20 mL), and dried in vacuo. Yield: 1.77 g (86%). ^1H NMR ([D_8]toluene, 300 MHz, 260 K): δ = 7.72 (d, 2H, $^3J_{HH}$ = 7.8 Hz, ArH), 7.32 (s, 2H, ArH), 7.28 (t, 2H, $^3J_{HH}$ = 7.8 Hz, ArH), 7.14 (t, 1H, $^3J_{HH}$ = 7.8 Hz, ArH), 4.11 and 2.94 (AB pattern, 4H, $^2J_{HH}$ = 11.2 Hz, CH_2), 1.96 and 1.78 (2s, 12H, NMe_2); ^1H NMR spectra were also recorded at 298 and 345 K (see text); ^{13}C NMR (C_6D_6, 75 MHz): δ = 188.0 (br m), 152.8, 144.0, 137.6, 128.9, 127.4, 126.3, 122.3, 72.8, 45.5 (br s). Anal. calcd. for $[C_{18}H_{23}LiN_2]_2$: C, 78.81; H, 8.45; N, 10.21. Found: C, 78.68; H, 8.53; N, 10.16.

X-ray structure determination of 3-Li: A colorless transparent crystal (0.40 × 0.50 × 0.50 mm) was mounted on a Lindemann glass capillary, and transferred into the cold nitrogen stream on a Enraf-Nonius CAD4-T diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined from the setting angles of 25 reflections (SET4 [22]) in a range $9.8 < \theta < 13.9°$. Reduced-cell calculations did not indicate higher lattice symmetry [23]. Crystal data and details on data collection and refinement are shown in Table 2. Data were corrected for Lp effects. The structure was solved by automated direct methods (SHELXS-86 [24]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93 [25]); no observance criterion was applied during refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter of 1.5 or 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms, for the methyl hydrogen atoms and all other hydrogen atoms, respectively. Weights were optimized in the final refinement cycles. The structure of **3-Li** contains one independent small spherical void of 22 Å^3 at 0.25, 0.25, 0.5. However, no significant residual density was found in that area (PLATON/SQUEEZE [27]). Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography [28]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-30. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

Table 2. Crystallographic data for **3-Li**.

formula	$C_{36}H_{46}Li_2N_4$
molecular weight	548.67
crystal system	monoclinic
space group	*C*2/c (no. 15)
a/Å	13.1225(5)
b/Å	13.5844(7)
c/Å	18.9859(12)
β/°	105.329(5)
V/Å^3	3264.0(3)
ρ_{calcd}/g cm^{-3}	1.117
Z	4
F(000)/e	1184
μ/cm^{-1}	0.6
crystal size/mm	0.40 × 0.50 × 0.50
T/K	150
θ_{min}, θ_{max}/°	2.2, 24.0
wavelength ($Mo_{K\alpha}$)/Å	0.71073 (graphite monochrom.)
scan type	$\omega/2\theta$
$\Delta\omega$/°	$0.51 + 0.35\tan\theta$
horz., vert. aperture/mm	3.00, 4.00
X-ray exposure time/h	11.7
linear decay/%	1
reference reflections	4 0 4, −4 0 4, 2 4 2
data set	−14:9, −15:15, 0:21
total data	5167
total unique data	2561
no. of refined param.	195
final $R1$ [a]	0.0374 [2037 $F_o > 4\sigma(F_o)$]
final $wR2$ [b]	0.0922 [2560 data]
goodness of fit	1.02
w^{-1} [c]	$\sigma^2(F^2) + (0.0453P)^2 + 1.1160P$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.001
min, max resid. density/e Å^{-3}	−0.18, 0.15

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; [c] $P = (\max(F_o^2,0) + 2F_c^2)/3$.

Synthesis of [RuCl{2,6-($Me_2NCH_2)_2$-4-($C_6H_5)C_6H_2$}(PPh_3)] (6): The preparation followed that reported for [RuCl{2,6-($Me_2NCH_2)_2C_6H_3$}(PPh_3)] [10] with **3-Li** (1.08 g, 4.0 mmol) as the organolithium reagent. The product was purified by dissolving the evaporated crude reaction mixture in CH_2Cl_2 (5 mL) and layering it with hexane (20 mL) to yield a blue powder, 2.21 g (83%), sufficiently pure for the synthesis of **9**. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.66–7.61 (m, 8H, ArH), 7.43 (t, 2H, $^3J_{HH}$ = 7.3 Hz, ArH), 7.31–7.17 (m, 10H, ArH), 7.08 (s, 2H, ArH), 2.98 and 2.71 (AB pattern, 4H, $^2J_{HH}$ = 13.8 Hz, CH_2N), 2.37 and 2.15 (2s, 12H, NMe_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 186.6 (d, $^2J_{PC}$ = 16 Hz), 149.2, 142.8, 136.7 (d, $^1J_{PC}$ = 47 Hz), 134.5 (d, $^3J_{PC}$ = 10 Hz), 133.4, 128.9 (d, $^4J_{PC}$ = 2 Hz), 128.7, 127.3 (d, $^2J_{PC}$ = 10 Hz), 126.4, 125.9, 118.8, 74.4, 52.4, 48.7; ^{31}P NMR ($CDCl_3$, 81 MHz, reference: H_3PO_4): δ = 90.4 (s, PPh_3).

Synthesis of [Ru{2,6-($Me_2NCH_2)_2$-4-($C_6H_5)C_6H_2$}(terpy)]Cl (9): The preparation followed that reported for [Ru{2,6-($Me_2NCH_2)_2C_6H_3$}(terpy)]Cl [10] with **6** (0.22 g, 0.33 mmol) and 2,2′;6′,2″-terpyridine (80 mg, 0.34 mmol). Yield: (0.19 g, 92%), blue needles. ^1H NMR ($CDCl_3$, 300 MHz, 325 K): δ = 9.08 (d, 2H, $^3J_{HH}$ = 7.9 Hz, ArH), 8.92 (d, 2H, $^3J_{HH}$ = 7.8 Hz, ArH), 8.23 (d, 2H, $^3J_{HH}$ = 5.0 Hz, ArH), 8.14 (t, 1H, $^3J_{HH}$ = 7.9 Hz, ArH), 7.99 (t, 2H, $^3J_{HH}$ = 7.3 Hz, ArH), 7.74 (d, 2H, $^3J_{HH}$ = 7.4 Hz, ArH), 7.55 (s, 2H, ArH), 7.46 (t, 2H, $^3J_{HH}$ = 7.5 Hz, ArH), 7.39 (t, 2H, $^3J_{HH}$ = 6.4 Hz, ArH), 7.29 (t, 1H, $^3J_{HH}$ = 7.1 Hz, ArH), 3.73 (s, 4H, CH_2N), 1.27 (s, 12H, NMe_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 200.3, 160.8, 154.5, 152.3, 142.9, 142.6, 135.2, 130.3, 128.9, 128.7, 126.5 (2s), 126.0, 124.5, 123.2, 119.2, 75.2, 52.0; UV/Vis (CH_2Cl_2): λ_{max} [nm] ($\varepsilon[10^4\ M^{-1}cm^{-1}]$) = 638 (0.75), 594 (0.76), 525 (0.84), 367 (1.61), 326 (4.07), 281 (2.61), 239 (3.69). Anal. calcd. for $[C_{33}H_{34}ClN_5Ru + CH_2Cl_2]$: C, 56.55; H, 5.02; N, 9.70. Found: C, 56.14; H, 5.55; N, 9.68.

Synthesis of 1-(Me_3Si)-3,5-($Me_2NCH_2)_2C_6H_3$ (4): *t*BuLi (2.35 mL, 1.7 M solution in pentane, 4.0 mmol) was added to a solution of **1a** (0.49 g, 1.8 mmol) in THF (25 mL) at −100 °C over 2 min; the solution turned deep green immediately. After 15 min of stirring at −100 °C, the reaction mixture was quenched with Me_3SiCl (0.44 g, 4 mmol) and allowed to warm to room temperature. The volatiles were evaporated in vacuo. ^1H NMR spectroscopy at this point showed exclusively **4**. The mixture was dissolved in diethyl ether (20 mL), water (10 mL) was added and the mixture stirred vigorously. The separated organic layer was dried on $MgSO_4$ and evaporated in vacuo, yielding a slightly yellow oil (0.24 g, 50%). ^1H NMR (C_6D_6, 200 MHz): δ = 7.59 (s, 2H, ArH), 7.54 (s, 1H, ArH), 3.37 (s, 4H, CH_2N), 2.13 (s, 12H, NMe_2), 0.27 (s, 9H, $SiMe_3$); ^{13}C NMR (C_6D_6, 50 MHz): δ = 140.1, 139.2, 132.9, 130.6, 64.8, 45.5, −0.9. Anal. calcd. for $C_{15}H_{28}N_2Si$: C, 68.12; H, 10.67; N, 10.59. Found: C, 68.09; H, 10.63; N, 10.64.

Synthesis of [Ru{2,6-($Me_2NCH_2)_2$-4-($Me_3Si)C_6H_2$}(terpy)]Cl (10): The preparation followed that described for **8**, with **4** in place of **2**. Analytically pure crystals were obtained by slow concentration of a CH_2Cl_2/toluene solution. Yield: 0.11 g (19%) dark blue microcrystalline material. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 8.80 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 8.63 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 8.21 (d, 2H, $^3J_{HH}$ = 5.3 Hz, ArH), 8.06 (t, 1H, $^3J_{HH}$ = 8.0 Hz, ArH), 7.93 (dt, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, ArH), 7.40 (m, 4H, ArH), 3.63 (s, 4H, CH_2), 1.22 (s, 12H, NMe_2), 0.37 (s, 9H, $SiMe_3$); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 204.8, 162.3, 156.4, 154.5, 144.0, 136.5, 131.0, 130.1, 128.6, 127.0, 125.5, 124.1, 76.9, 53.7, 1.2; UV/Vis (CH_2Cl_2): λ_{max} [nm] ($\varepsilon[10^4\ M^{-1}cm^{-1}]$) = 641 (0.64), 596 (0.63), 527 (0.67), 392 (0.73), 325 (3.45), 282 (2.61), 238 (2.72). Anal. calcd. for $[C_{30}H_{34}ClN_5RuSi]$: C, 56.78; H, 6.25; N, 10.04. Found: C, 56.90; H, 6.05; N, 11.06.

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