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Versatile *N,C,N* Coordination Behavior of a Monoanionic Aryldiamine Ligand in Ruthenium(II) Complexes: Syntheses and Crystal Structures of $[Ru^{II}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}X(L)]$ (L = Norbornadiene, X = Cl, SO_3CF_3; L = PPh_3, X = I) and $[Ru^{II}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(2,2'{:}6',2''\text{-terpyridine})]Cl$

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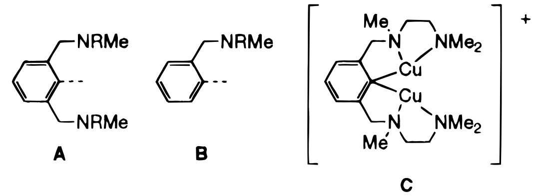
The monoanionic ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, a potentially terdentate *N,C,N* bonding system, has been employed to synthesize a series of new ruthenium(II) complexes $[Ru\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}X(L)]$ (L = PPh_3, X = Cl (**2a**), I (**2b**); L = norbornadiene (nbd), X = Cl (**4**), η^1-OSO_2CF_3 (**5**)) and $[Ru\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(2,2'{:}6',2''\text{-terpyridine})]Cl$ (**3**). X-ray crystal structures of **2b** and **3**−**5** have been determined, in which the *N,C,N* coordination geometry with respect to the metal center is found to differ considerably. In each complex the aryldiamine ligand is terdentate, η^3-*N,C,N*-bonded as a six electron donor system. However, depending on the other ligands in the Ru(II) coordination sphere, this ligand demonstrates considerable flexibility in adopting coordination geometries which range from *meridional* in **3** through *pseudomeridional* in **2b** to *pseudofacial* in **4** and **5**. In the structures of **4** and **5** significant distortions of the aryl ring, involving bending of the six-membered ring into a boatlike conformation, are found. The different combinations of the *N,C,N* ligand with sets of other ligands lead to a range of metal geometries, *i.e.* square pyramidal in **2b**, octahedral in **3**, and bicapped tetrahedral in **4** and **5**.

Introduction

Recently we formulated the concept of organometallic cavities, *i.e.* cavities in which anionic polydentate ligands have at least one anionic C-donor atom binding to the metal center to form a M−C σ-bond.[1] Such a M−C bond can only be disrupted by metathesis with a strong nucleophile or by reactions based on heterolytic or homolytic bond cleavage. Consequently, a metal is more tightly contained in an organometallic cavity than in a ligand cavity system that only employs neutral two electron donor atoms. Of course, in an organometallic cavity the other binding components will often be neutral donor atom to metal interactions and for an organometallic cavity one can therefore envisage the use of polydentate ligands that are either symmetrical, type **A**, or unsymmetrical, type **B** (Scheme 1).[1,2] More elaborate examples include the potentially pentadentate *N′,N,C,N,N′*-bonding, monoanionic ligand in cation **C**[3] and monoanionic oxygen donor systems of the type $\{C_6H_3O(CH_2CH_2O)_n\text{-}3\}^-$ (n = 3, 4) employed by Bickelhaupt *et al.*[4]

Scheme 1. Ligands for Organometallic Cavities



R = Me, $(CH_2)_2NMe_2$, etc.

We are currently examining the various factors which determine the flexibility of the coordination geometry exhibited by the monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, which is formally a 6-electron donor when it is terdentate *N,C,N′*-bonded to a metal center. In this way, we aim to obtain a better understanding of the steric and geometric properties and coordination potential of this and related ligands in complexes that exhibit homogeneous catalytic activity; for example, $[Ni\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}X]$ catalyzes the Kharasch addition reaction of halocarbons to alkenes

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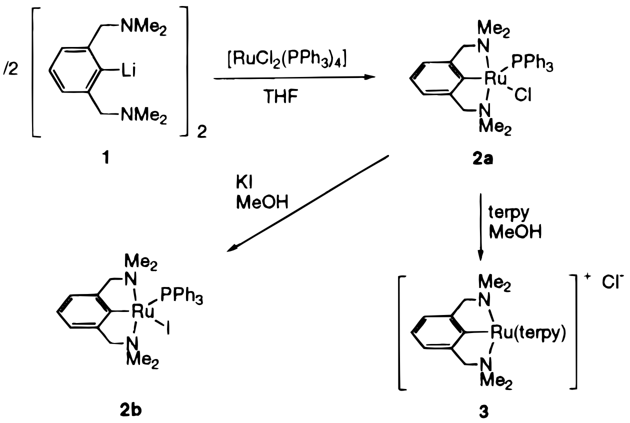
Scheme 2. Preparation of 2a,b, and 3



with high selectivity.[5a−d] The utility of this type of ligand system has been further demonstrated by using the *para* position of the aryl ring to anchor catalytically active centers to silica supports,[5b] to organized macromolecules such as dendrimers,[5c] and to polymers,[5d] with retention of catalytic activity. For the Kharasch addition reaction we have discovered that the catalytic cycle involves a Ni^{II}/Ni^{III} couple in which, remarkably, the $Ni-C_{ipso}$ bond is not disrupted. The adaptability of this ligand during the catalytic cycle is illustrated by model nickel complexes in which the N−Ni−N angle needs only to vary a little from 166.59(6)° in a square-planar Ni(II) species[6] to 152.0(2)° in a square-pyramidal complex with a Ni(III) center.[7] The present paper describes the syntheses of some new ruthenium complexes with the $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand and gives crystallographic data for four of these complexes in which acute N−Ru−N angles demonstrate the flexible coordination geometry of this aryldiamine ligand system. The properties of this 6-electron donor ligand are compared and contrasted with those of classical $C_5H_5^-$ and $C_5Me_5^-$ anions, and its coordination behavior is found to show parallels to that of $C_5Me_5^-$.

Results

Synthesis of Ruthenium Complexes of [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$. The dimeric organolithium complex [Li{$C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$, **1**,[8] proves to be an excellent reagent for the synthesis of a number of stable Ru(II) species containing the $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand. The reaction of **1** with [$RuCl_2(PPh_3)_4$] in THF affords a new complex identified by elemental microanalysis and NMR data as the ruthenium(II) species [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(PPh_3)], **2a**, in 60% yield (Scheme 2). The same product is also obtained when **1** is reacted with [$RuCl_2(PPh_3)_3$], but the yield is substantially lower. The iodide analogue [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}(I)(PPh_3)], **2b**, can be obtained from **2a** by a halide metathesis reaction with KI in MeOH (Scheme 2). Complexes **2a**,**b** are obtained, after crystallization from CH_2Cl_2/hexane solutions, as blue, crystalline, air-sensitive solids which are soluble in solvents such as dichloromethane and benzene. Characteristic solution spectroscopic data for **2a** include a singlet ^{31}P NMR resonance at 79.0 ppm ($CDCl_3$) and in the ^1H NMR spectrum ($CDCl_3$) two singlets for the NMe_2 groups and an AB pattern for the methylene protons; i.e., the methyl groups and methylene protons are diastereotopic. Similar spectra were obtained for the iodide complex **2b**. In order to establish the nuclearity of this type of complex and the stereochemistry of the ligand array around ruthenium, an X-ray structure determination of complex **2b** was carried out. Suitable crystals of **2b** were grown from a benzene solution layered with pentane. An ORTEP drawing of the determined molecular structure (Figure 1) shows **2b** to be a mononuclear, pentacoordinate ruthenium(II) species. The metal coordination geometry is best described as square-pyramidal with the aryldiamine ligand functioning as a *N,C,N* terdentate system (N(1), C(1), and N(2)) that occupies three positions in the basal plane of the pyramid; the N−Ru−N angle is 147.59(7)°. The iodine atom occupies the other basal position (∠C(1)−Ru−I = 160.44(6)°) and the PPh_3 is coordinated apically (∠C(1)−Ru−P = 92.19(6)°). The nature of the ligands in **2b** make this a 16-electron species, and the square-pyramidal geometry found in the solid state is consistent with the solution NMR data.

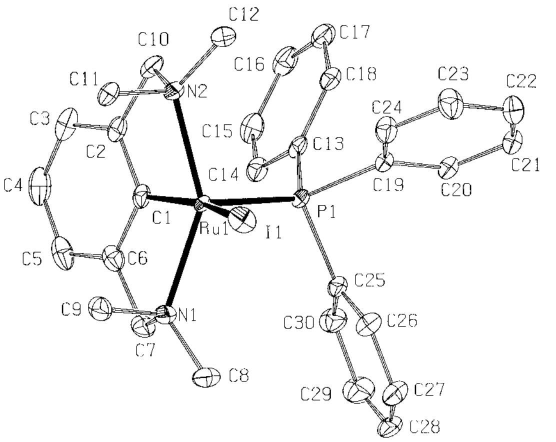


Figure 1. Thermal motion ellipsoid plot (50% probability level) of **2b**. H atoms were omitted for clarity.

The potential of complexes of type [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}X(PPh_3)], **2**, to provide routes to other organometallic species of $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ has been investigated by reaction with 2,2′:6′,2″-terpyridine (terpy). The reaction of terpy with **2a** in MeOH affords by a ligand substitution reaction a new ionic organoruthenium complex which was isolated and characterized by elemental microanalysis and NMR data as [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}(terpy)]Cl, **3**, which contains no PPh_3 (Scheme 2). Complex **3** is a blue air-stable solid which, in accord with its ionic nature, is soluble in water and alcohols. The NMR data for **3** reveal a high degree of symmetry within the complex cation; for example, in its ^1H NMR spectrum ($CDCl_3$) the [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$ ligand system affords a singlet resonance for the

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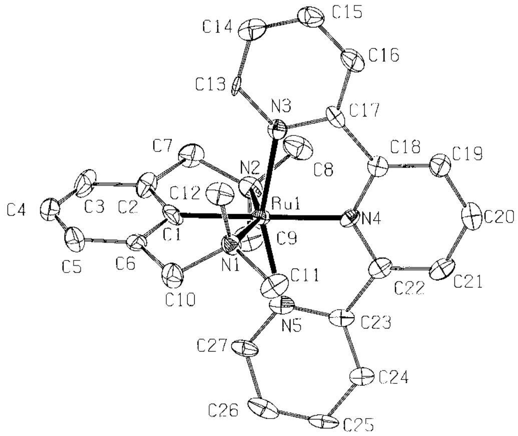


Figure 2. Thermal motion ellipsoid plot (50% probability level) of **3**. H atoms were omitted for clarity.

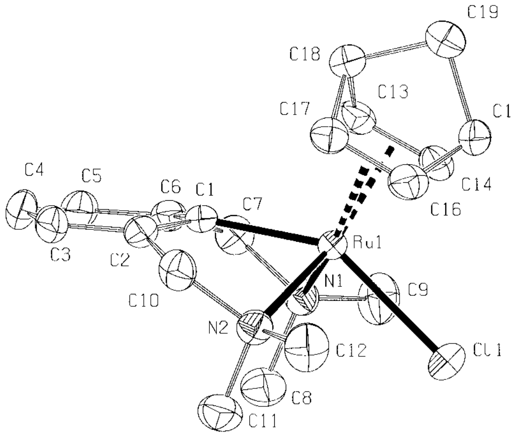
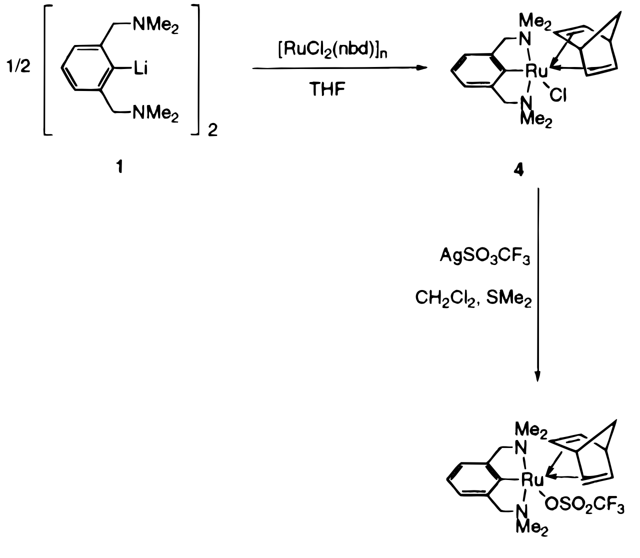


Figure 3. Thermal motion ellipsoid plot (50% probability level) of **4**. H atoms were omitted for clarity.

Scheme 3. Preparation of 4 and 5



1 **4** **5**

four methylene protons, and a singlet resonance for the methyl groups of the two NMe_2 units. These data suggest a simple octahedral geometry at the metal, with both the *N,C,N* and terpyridine ligands coordinating *meridionally*, making **3** an 18-electron complex. In order to establish more precisely the ligand arrangement in this complex, an X-ray structure determination was carried out. Suitable crystals of **3** were grown by slow evaporation of a CH_2Cl_2/toluene solution. An ORTEP drawing of the determined molecular structure of the cation of **3** is shown in Figure 2. The structure determination confirms the *meridional* bonding of the aryldiamine ligand ($\angle$N$-$Ru$-$N = 156.2(2)°) and the overall C_2 symmetry inferred from the solution NMR spectra. The proximity of the NMe_2 groups to the shielding π-systems of the terpy group accounts for the high-field chemical shift of these protons in the ^{1}H NMR spectra of 1.25 ppm ($CDCl_3$). We have briefly reported this compound and its reaction with excess $CuCl_2$ to give a dimeric product elsewhere.[9]

To further develop non-phosphine$-$ruthenium chemistry, 1 equiv of polymeric $[RuCl_2(nbd)]_n$, (nbd = norbornadiene)] was reacted with 0.5 equiv of dimer $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$, **1**, to afford a new complex **4**, whose elemental microanalysis and NMR data are consistent with the formulation $[Ru\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}Cl(nbd)]$, in 20$-$30% isolated yield; see Scheme 3. Complex **4** is a yellow, air-stable, solid which is readily soluble in CH_2Cl_2 and slightly soluble in THF. The ^{1}H and ^{13}C NMR spectral data of **4** ($CDCl_3$) are consistent with the presence of a single mirror-type symmetry plane that is perpendicular to the aryl ring and so positioned that the metal center, the CH_2 bridge of the norbornadiene ligand, and the *ipso* and *para* carbons of the aryl ring are also in this plane. As was also found for **2**, the methylene protons and methyl groups of each CH_2NMe_2 group are diastereotopic. A single-crystal X-ray structural analysis of **4**, carried out to investigate the geometry of the ligand array, shows this complex to be a mononuclear species $[Ru\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}Cl(nbd)]$ with a hexacoordinate ruthenium(II) center (see Figure 3). The ligand array of halide, η^4-bonded (bidentate) norbornadiene, and *N,C,N*-bonded $C_6H_3(CH_2NMe_2)_2\text{-}2,6^-$ makes this an 18-electron species in which the overall positioning of the ligands in the solid state aggrees with the observed solution NMR data. A most interesting and very evident aspect of the structure is that the aryldiamine ligand has adopted a *pseudofacial N,C,N* coordination mode, with a N$-$Ru$-$N angle that is only 110.09(7)°. The chloride is positioned approximately *trans* to C_{ipso} (C(1)). The metal coordination geometry in this complex is best described as a bicapped tetrahedron[10] in which the centroids of the two coordinated alkenes together with C_{ipso} and Cl form a *pseudo*tetrahedron, with the N-donor atoms of the aryldiamine

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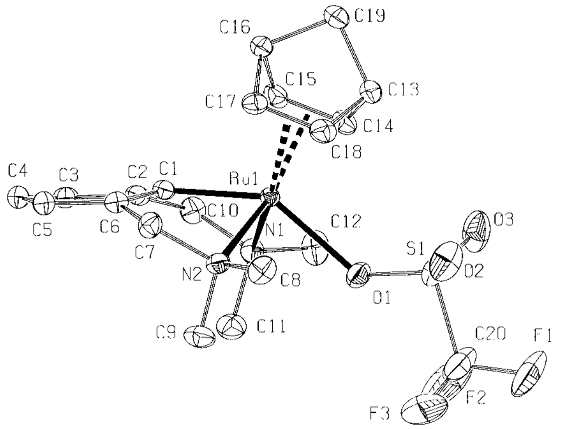


Figure 4. Thermal motion ellipsoid plot (50% probability level) of **5**. H atoms were omitted for clarity.

capping two of its faces. A detailed comparative discussion of this metal coordination geometry, which is accompanied by aryl ring distortions, is presented below. The bond lengths between ruthenium and the olefinic carbons atoms are in the normal range for hexacoordinate ruthenium norbornadiene complexes.

Substitution of the Cl atom in [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(nbd)], **4**, for the weakly nucleophilic trifluoromethanesulfonate anion ($OSO_2CF_3^-$, triflate) was investigated with the intention of generating a five-coordinate complex cation [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}(nbd)]$^+$ whose chemical reactivity would be different from that of neutral **4**. The reaction of **4** with [$AgSO_3CF_3$] in the presence of excess SMe_2 leads to quantitative formation of AgCl and formation of a new air-stable species **5**, which could be isolated as yellow crystals in good yield. Elemental microanalysis data were consistent with the composition Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}(nbd)(SO_3CF_3) (Scheme 3). However, since the ^1H and ^{13}C NMR data for **5** (C_6D_6) are very similar to those of neutral **4** and not consistent with an ionic composition, a single-crystal X-ray structure determination of **5** was undertaken. This study shows **5** to be the neutral mononuclear complex [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6})(η^1-OSO_2CF_3)(nbd)] that is likewise a hexacoordinate, 18-electron, ruthenium(II) species (Figure 4). The overall bicapped tetrahedral structure is very similar to that of **4**, and as well as the bidentate bonding of norbornadiene to the metal center there is again terdentate *N,C,N* bonding of the $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand in a *pseudofacial* coordination mode; the N–Ru–N′ angle of 109.35(6)° is slightly more acute than in **4**. Interesting is the fact that the sixth coordination site in **5**, *pseudo-trans* to C_{ipso}, is occupied by an η^1-OSO_2CF_3 anion with a Ru–O(1) distance of 2.2327(16) Å. Only a limited number of ruthenium complexes with an η^1-OSO_2CF_3 ligand are known.[11]

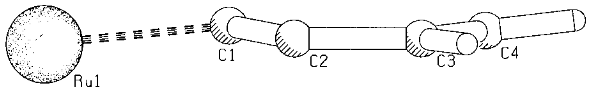
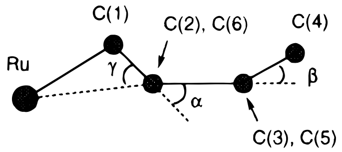


Figure 5. Edge-on view of the distorted aryl–ruthenium interaction in **5**.

Scheme 4. Exaggerated Schematic View of the Aryl–Ruthenium Interaction and Distorted Aromatic Ring in 2b, 4, and 5, with Tabulation of Relevant Angles



	2b	3	4	5
α =	1.3(2)°	0.7(10)°	10.3(3)°	12.5(2)°
β =	0.8(3)°	0.7(10)°	5.1(3)°	6.3(2)°
γ =	6.9(2)°	1.2(11)°	12.8(3)°	12.9(2)°

Aryl–Ruthenium Interaction in 2b and 3–5. The most straightforward of the structures determined is that of the octahedral terpyridine complex **3**. The $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand is *meridionally* bonded (as is the terpy ligand) giving rise to an unstrained aryl ring which is not significantly distorted from planarity and a ruthenium center which lies within the mean plane defined by the aryl ring. However, examination of the structure of the 16-electron complex **2b** shows that in this complex the coordination of the *N,C,N* ligand is no longer perfectly *meridional*, with the angle C(1)–Ru–I = 160.44(6)°. In the norbornadiene complexes **4** and **5** this perturbation of the aryl–ruthenium geometry is even more evident. In these species not only does the metal atom lie significantly out of the C_{ipso} sp^2 hybridization plane but there are also appreciable distortions from nonplanarity within the aromatic ring itself. The aryl ring is bent into a shallow boat conformation, as illustrated in Figure 5, with C_{ipso} and the C atom *para* to the metal center (C(1) and C(4), respectively) lying above the mean plane defined by the four other aryl carbon atoms (C(2)C(3)C(5)C(6)). Scheme 4 tabulates the principle aryl distortions in **2b** and **3–5** in terms of the planes defined by C(2)C(3)C(5)C(6), C(1)C(2)C(6), and C(3)C(4)C(5), together with a schematic view of the aryl–ruthenium moiety perpendicular to the Ru–C(1) bond. In all these complexes the C–C bond lengths are within their normal ranges. Predictably, the strongest puckering of the aryl ring is found for **5**, where the N–Ru–N′ angle is the smallest. The origin of these ring distortions is readily found in the *pseudofacial* coordination of $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ to ruthenium whereby the donor NMe_2 units have to come far out of the aryl plane and the C(methylene)–C(aryl) bonds are put under tension. Consequently these bonds are pulled out of the aryl plane and the geometric distortion this causes at the sp^2 aryl atom to which CH_2NMe_2 arms are attached then perturbs the rest of the aryl framework.

Discussion

N,C,N Flexibility. In previous studies we have usually found that square-planar and octahedral metal complexes containing the terdentate bonded $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand have the metal and the *N,C,N′*-ligating atoms in one plane;[12] the N-donor atoms are then *pseudo trans*-positioned, and for Pt^{II}, Pd^{II}, Pt^{IV}, Ni^{II}, and Ni^{III} N–M–N angles of ±160–165° are normal.[1] In these systems the metal coordination geometry is not optimal, but the formation of two five-membered chelate

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rings clearly compensates for the N−M−N angle of less than 180°. Examples of nonplanar M(*N,C,N*) arrangements are rare but include square-pyramidal paramagnetic Ni^{III} [6,7] and Fe^{III} [13] species,[7,13] where the N−M−N angles are somewhat less at 152.0(6) and 142.98(6)°, respectively. This situation is still not ideal but the N−M−N angle is now fairly close to that found in pyramidal complexes of Ni(II) and Fe(II) containing monodentate ligands. What is evident from the present study is that the $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand can achieve much smaller N−M−N angles of ±110° (norbornadiene complexes **4** and **5**). This corroborates our previous observation of an N−M−N angle of 118.63(14)° in the tantalum alkylidene complex $[Ta(Cl)_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(CH^tBu)]$.[14] This flexibility of the *N,C,N* terdentate coordination mode is far higher than we originally anticipated. The *pseudofacial* coordination of $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ in these complexes is accompanied by a bicapped tetrahedral geometry at the metal center. A bicapped tetrahedron is not a common arrangement for a hexacoordinate metal complex, and it is therefore significant that we have recently also identified this arrangement in some Ta,[14] Ti,[15a] and Lu[15b] complexes of this aryldiamine.

Ruthenium Coordination Geometry: Electronic and Steric Factors. As shown above, *pseudofacial* coordination of this ligand leads to distortions of the aryl ring whose magnitude is directly related to the N−Ru−N angle, and this is naturally a consequence of the overall coordination geometry of the metal center. The structures of **2b** (*pseudomeridional* coordination), **3** (*meridional* coordination), and **4** and **5** (*pseudofacial* coordination) show for the first time in a series of *homo*metallic complexes how the $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand accommodates its coordination geometry in concert with the steric and electronic requirements of other ligands. In the bicapped tetrahedral coordination geometry of complexes **4** and **5** (Figures 3 and 4), for example, the geometry seems to be strongly influenced by steric factors and the resulting structure is one in which crowding between the aryldiamine ligand, in particular the NMe_2 groups, and the other ligands in the ruthenium coordination sphere are minimized. On this basis one could say that it is the demanding and inflexible bidentate bonding of norbornadiene that forces the aryldiamine ligand to adopt its *pseudofacial* coordination geometry. However, the situation is complicated further not only by chelate ring strain and the related energetics of aryl ring distortions but also by electronic factors which tend to impose their preferred geometry at the metal center. To try to evaluate which of these factors dominate in producing particular $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ geometries, and in particular the occurrence of a bicapped tetrahedral geometry for certain metal centers, we are now embarking on a series of theoretical and modelling studies.

However, even at this stage we can identify one aspect of the aryldiamine ligand that is likely to be important and which is not encountered with many other ligand systems, namely its variation in steric bulk as a function of coordination mode. For example, in square-pyramidal **2b**, shown in Figure 1, it is evident that the aryldiamine ligand occupies a large volume about the metal center and the five-membered chelate rings are puckered in such a way as to bring the methyl groups away from the bulky apical PPh_3 ligand. The result of this arrangement is that the potential sixth coordination site becomes sterically crowded by the NMe_2 groups; *i.e.* the terdentate ligand is acting as a very bulky ligand. In contrast, in **4** and **5** (with *pseudofacia*l coordination) the aryldiamine acts as a much smaller ligand that allows all three remaining sites on ruthenium to be occupied. Thus it appears that the *N,C,N* ligand markedly adjusts its effective steric bulk in accordance with the demands of the other ligands present. This suggests that it may be possible to tune its bulk by judicious choice of ancilliary ligands. The flexibility shown by this ligand in adopting several coordination geometries, as well as its ability in adapting to the demands of the metal center, make it ideal for the stabilization of transient intermediates in organometallic transformations. The reaction of **2a** with 2,2′:6′,2″-terpyridine (Scheme 2) to give **3**, during which the aryldiamine coordination geometry switches to a *meridional* one in order to allow *meridional* η^3-*N,N′,N″* coordination of the incoming terpy illustrates the ready interconversion of these two coordination modes.

Comparison of $\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}^-$ with the Cyclopentadienyl and Pentamethylcyclopentadienyl Ligands. The cyclopentadienyl ligand ($C_5H_5^-$, Cp) and its permethylated derivative ($C_5Me_5^-$, Cp*) are usually encountered in transition metal complexes as monoanionic 6-electron donors, occupying three *facial* coordination sites at a metal center. Despite obvious differences in symmetry, there exists in this sense a formal relationship between these ligands and $C_6H_3(CH_2NMe_2)_2$-2,6$^-$, also a monoanionic 6-electron donor, when it is *N,C,N pseudofacially* coordinated, as in the norbornadiene complexes **4** and **5**. This relationship expresses itself practically in the existence of Cp and Cp* complexes, namely [Ru(Cp)(cod)Cl][16] and [Ru(Cp*)(diene)Cl] (diene = norbornadiene, *cis,cis*-1,5-cyclooctadiene, etc.),[17,18] which are stoichiometrically analogous to **4** and **5**. In ruthenium(II) complexes where phosphines exist in conjunction with the Cp* ligand, one or two phosphines may coordinate to ruthenium, depending on the steric demands of the phosphine. Thus bulky ligands like triisopropylphosphine and tricyclohexylphosphine afford the mono(phosphine) 16-electron complexes $[Ru(Cp^*)(PR_3)Cl]$ (R = ^{i}Pr, Cy), which are deep blue in color.[19] These species are directly related to our new mono(triphenylphosphine) complex **2**, which is also deep blue. The color arises in each case from a single absorption at 576 nm (ϵ = 1692 M^{-1} cm^{-1}; $[Ru(Cp^*)(P^iPr_3)Cl]$), 580 nm (ϵ = 1742 M^{-1} cm^{-1}; $[Ru(Cp^*)(PCy_3)Cl]$), and 557 nm (ϵ = 1287 M^{-1} cm^{-1}; **2a**). Unfortunately, the UV/vis spectra cannot be fully compared since for **2a** the UV region is dominated by strong absorptions between 230 and 340 nm, due to triphenylphosphine and the aromatic aryldiamine ligand. Perhaps significantly, an attempt to prepare the bis(triphenylphosphine) complex $[Ru(Cp^*)(PPh_3)_2Cl]$ failed.[20] Coordination of a second triphenylphosphine to **2a** does not occur either (there is excess phosphine present

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Table 1. Crystallographic Data for 2b and 3–5

	complex			
	2b	**3**	**4**	**5**
Crystal Data				
formula	$C_{30}H_{34}IN_2PRu$	$C_{27}H_{30}N_5Ru{\cdot}Cl{\cdot}CH_2Cl_2$	$C_{20}H_{27}F_3N_2O_3RuS$	$C_{19}H_{27}ClN_2Ru$
M_r	681.56	646.02	533.58	419.96
cryst system	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$C2/c$ (No. 15)	$Fdd2$ (No. 43)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a, Å	33.722(3)	28.5405(13)	9.7428(7)	10.0105(10)
b, Å	10.1880(10)	32.042(2)	12.0561(8)	12.4130(10)
c, Å	15.778(2)	12.100(2)	18.1700(7)	14.023(2)
β, deg	92.199(10)			
V, Å^3	5416.5(10)	11065.2(18)	2134.3(2)	1742.5(3)
D_{calc}, g cm^{-3}	1.672	1.551	1.660	1.601
Z	8	16	4	4
F(000)	2720	5280	1088	864
μ, cm^{-1}	17.7	8.7	8.6	10.4
cryst size, mm	0.50 × 0.20 × 0.25	0.15 × 0.15 × 0.63	0.13 × 0.50 × 0.50	0.40 × 0.40 × 0.40
Data Collection				
T, K	150	150	150	295
θ_{min}, θ_{max}, deg	1.21, 27.5	1.9, 27.5	1.12, 27.5	1.45, 27.5
λ(Mo Kα), Å	0.710 73 (mon)	0.710 73 (mon)	0.710 73 (mon)	0.710 73 (Zr)
$\Delta\omega$, deg	$0.54 + 0.35 \tan \theta$	$0.86 + 0.35 \tan \theta$	$0.61 + 0.35 \tan \theta$	$0.54 + 0.35 \tan \theta$
hor, ver apert, mm	3.00, 4.00	2.73, 4.00	3.00, 4.00	3.00, 5.00
X-ray exposure, h	27.9	19.9	12.4	66.9
ref reflcns	2,−4,1; 6,2,−4; 12,0,2	0,−2,−10; 14,0,−2; -2,−4,−4	-2,−4,−3; −1,−2,−5; −3,3,0	2,3,3; 3,2,−1; 1,5,2
data set	−43:43, 0:13, −20:20	−36:37, −41:0, −15:0	−8:15, −12:12, −23:0	0:12, 0:16, −18:18
tot. data	13364	6645	5464	4874
tot. unique data	6219	3329	4887	3990
obsd data				
$I > 2.5\sigma(I)$	5696		4710	3810
$I > 2.0\sigma(I)$		2306		
difabs corr range	0.903, 1.209		0.94, 1.100	0.933, 1.045
Refinement				
no. of refined params	330	311	297	233
final R^a	0.0230	0.0515	0.0187	0.0189
$R_w{}^b$	0.0271		0.0261	0.0194
w$R2^c$		0.0980		
S	2.85	0.92	0.75	0.77
$w^{-1\,d}$	$[\sigma^2(F)]$	$[\sigma^2(F_o{}^2) + (0.0336P)^2]$	$[\sigma^2(F) + 0.000605F^2]$	$[\sigma^2(F)]$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.026, 0.606	0.000, 0.001	0.015, 0.24	0.036, 0.528
min and max resid density, e Å^{-3}	−0.85, 0.67	−0.55, 0.79	−0.71, 0.99	−0.49, 0.36

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

during the preparation). However, with Cp*, the sterically less demanding ligand trimethylphosphine affords the bis(phosphine) complex [Ru(Cp*)(PMe$_3$)$_2$Cl],[21] and we are currently investigating the use of less bulky phosphines to prepare analogous bis(phosphine) ruthenium complexes with $C_6H_3(CH_2NMe_2)_2$-2,6$^-$. It should be noted that, in ruthenium(II) phosphine complexes with the Cp ligand, only coordinatively saturated 18-electron complexes with two phosphines are known, *e.g.* [Ru(Cp)(PR$_3$)$_2$Cl] (R = Ph, Me).[22] Compared to Cp, the superior ability of the $(C_5Me_5)^-$ anion and $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ to stabilize unsaturated 16-electron complexes may be attributed to both greater steric bulk and better electron donor capabilities.

The similarity suggested here between Cp* and $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ may be of use in developing future chemistry of ruthenium complexes of the latter ligand. We are now investigating not only the relative importance of steric and electronic factors in such complexes but also their reactivity in catalytic processes where we have found complex **2b** to be an effective hydrogen transfer catalyst.[23]

Conclusion

In this first investigation of the organoruthenium chemistry of the $C_6H_3(CH_2NMe_2)_2$-2,6$^-$ ligand system we have found that it can exhibit considerable flexibility in its coordination geometry. In terms of the complexes we have isolated, analogy may be drawn between this ligand and the classical ligand Cp*.

Experimental Section

General Comments. All experiments were conducted under 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); ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 298 K on Bruker AC200 or AC300 spectrometers unless otherwise stated. Starting materials [Li{$C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$, **1**,[24] [RuCl$_2$(PPh$_3$)$_4$],[25] and [RuCl$_2$(nbd)]$_n$[26] were prepared according to literature procedures. RuCl$_3$·3H$_2$O was obtained from Degussa.

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2b and 3−5 (Esd's in Parentheses)

	2b	**3**	**4**	**5**		**2b**	**3**	**4**	**5**
Bond Lengths									
Ru−N(1)	2.2063(19)	2.199(7)	2.3381(19)	2.3171(17)	Ru−O				2.2327(16)
Ru−N(2)	2.1635(18)	2.192(7)	2.349(2)	2.2977(17)	Ru−C(13)			2.155(3)	
Ru−N(3)		2.077(6)			Ru−C(14)			2.150(3)	2.165(2)
Ru−N(4)		2.007(6)			Ru−C(15)				2.170(2)
Ru−N(5)		2.088(6)			Ru−C(16)			2.137(3)	
Ru−I	2.8025(4)				Ru−C(17)			2.168(2)	2.174(2)
Ru−P	2.1757(7)				Ru−C(18)				2.153(2)
Ru−Cl			2.4747(8)		Ru−C(1)	1.967(2)	1.982(7)	2.060(2)	2.027(2)
Bond Angles									
N(1)−Ru−N(2)	147.59(7)	156.2(2)	110.09(7)	109.35(6)	C(1)−Ru−C(14)			122.81(9)	121.91(8)
N(1)−Ru−C(1)	79.50(8)	77.9(3)	74.15(8)	74.91(7)	C(1)−Ru−C(15)				85.15(7)
N(2)−Ru−C(1)	79.56(8)	78.3(3)	73.80(8)	74.62(7)	C(1)−Ru−C(16)			122.96(9)	
C(1)−Ru−P	92.19(6)				C(1)−Ru−C(17)			86.02(9)	84.91(7)
C(1)−Ru−I	160.44(6)				C(1)−Ru−C(18)				121.92(7)
N(1)−Ru−P	105.07(6)				C(1)−C(2)−C(3)	120.1(2)	119.3(8)	119.7(2)	120.69(18)
N(2)−Ru−P	100.18(5)				C(2)−C(3)−C(4)	119.9(2)	120.5(9)	120.4(2)	119.91(19)
N(1)−Ru−I	93.51(5)				C(3)−C(4)−C(5)	120.9(2)	121.4(9)	119.7(2)	119.56(18)
N(2)−Ru−I	98.09(5)				C(4)−C(5)−C(6)	119.3(2)	119.1(8)	120.1(2)	119.76(18)
N(1)−Ru−N(3)		94.2(3)			C(1)−C(6)−C(5)	120.0(2)	119.3(7)	120.8(2)	120.33(18)
N(1)−Ru−N(4)		100.9(2)			C(1)−C(2)−C(7)		113.3(8)		
N(1)−Ru−N(5)		89.4(2)			C(1)−C(2)−C(10)	113.80(18)		116.07(19)	115.14(17)
N(2)−Ru−N(3)		89.8(3)			C(1)−C(6)−C(10)		112.4(6)		
N(2)−Ru−N(4)		102.9(2)			C(1)−C(6)−C(7)	114.35(18)		115.65(19)	115.21(17)
N(2)−Ru−N(5)		96.1(3)			N(2)−C(7)−C(2)		110.1(7)		
N(3)−Ru−N(4)		78.6(2)			N(2)−C(10)−C(2)	109.11(18)			
N(3)−Ru−N(5)		156.9(3)			N(2)−C(7)−C(6)			107.69(18)	107.06(16)
N(4)−Ru−N(5)		78.3(2)			N(1)−C(7)−C(6)	109.43(18)			
C(1)−Ru−N(3)		100.4(3)			N(1)−C(10)−C(2)			107.19(18)	107.91(16)
C(1)−Ru−N(4)		178.4(3)			N(1)−C(10)−C(6)		109.4(7)		
C(1)−Ru−N(5)		102.7(3)			N(1)−Ru−Cl			86.72(5)	
C(1)−Ru−Cl			145.44(6)		N(2)−Ru−Cl			86.70(5)	
C(1)−Ru−O(1)				142.24(6)	N(1)−Ru−O(1)				83.69(6)
C(1)−Ru−C(13)			85.72(9)		N(2)−Ru−O(1)				83.95(6)
Torsion Angles (deg)									
C(1)−C(2)−C(3)−C(4)	−0.4(3)	1.5(13)	4.0(4)	−2.6(3)	C(4)−C(3)−C(2)−C(10)	−178.9(2)		163.6(2)	−167.19(18)
C(2)−C(3)−C(4)−C(5)	1.2(4)	−2.0(14)	5.4(4)	−7.9(3)	C(6)−C(1)−C(2)−C(10)	179.48(18)			3.2(2)
C(3)−C(4)−C(5)−C(6)	−0.5(4)	0.8(14)	−6.3(4)	6.6(3)	C(4)−C(5)−C(6)−C(7)	179.7(2)		167.0(3)	−164.93(19)
C(4)−C(5)−C(6)−C(1)	−1.0(4)	0.8(13)	−2.3(4)	5.1(3)	C(4)−C(5)−C(6)−C(10)		−176.2(9)		
C(6)−C(1)−C(2)−C(3)	−1.1(3)	0.2(13)	−12.3(4)	14.0(3)	C(2)−C(1)−C(6)−C(7)	−178.8(2)		−158.5(2)	155.66(18)
C(4)−C(3)−C(2)−C(7)		175.4(9)			C(2)−C(1)−C(6)−C(10)		176.1(8)	156.1(2)	

Synthesis of [RuCl{$C_6H_3(CH_2NMe_2)_2$-2,6}(PPh_3)] (2a). A solution of [Li{$C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$, **1** (0.86 g, 2.17 mmol), in THF (30 mL) was added dropwise to a suspension of [$RuCl_2(PPh_3)_4$] (5.23 g, 4.28 mmol) in THF (60 mL). After 1 h the solvent was removed *in vacuo* from the deep blue reaction mixture and the residue washed with a Et_2O/hexane (2:1) mixture (100 mL). The remaining blue solid was extracted with CH_2Cl_2. After the solution was concentrated and layered with hexane, complex **2a** was obtained as a deep blue microcrystalline solid (1.52 g, 60%).

^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 7.80 (m, 6 H, Ar H), 6.96 (m, 10 H, Ar H), 6.83 (d, 2 H, $^3J_{HH} = 7.3$ Hz, Ar H), 2.54 and 2.48 (AB pattern, 4 H, $^2J_{HH} = 13.8$ Hz, CH_2N), 2.18 and 2.01 (2 s, 12 H, NMe_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 185.8 (d, $^2J_{PC} = 15$ Hz, C *ipso*), 148.8 (C *ortho*), 136.8 (d, $^1J_{PC} = 46$ Hz, PPh_3), 134.5 (d, $^2J_{PC} = 10$ Hz, PPh_3), 128.8 (d, $^4J_{PC} = 2$ Hz, PPh_3), 127.3 (d, $^3J_{PC} = 10$ Hz, PPh_3), 120.0 (C *para*), 119.6 (C *meta*), 74.3 (CH_2N), 52.4 and 48.6 (NMe_2). ^{31}P NMR ($CDCl_3$, 81 MHz): δ (ppm) 91.1 (s, PPh_3). Anal. Calcd for $C_{30}H_{34}N_2PClRu$: C, 61.06; H, 5.81; N, 4.75. Found: C, 60.8; H, 5.8; N, 4.8.

Synthesis of [RuI{$C_6H_3(CH_2NMe_2)_2$-2,6}(PPh_3)] (2b). To solution of **2a** (0.50 g, 8.5 mmol) in methanol (30 mL) was added KI (0.99 g, 59.5 mmol) and the resulting solution stirred for 5 h. The solvent was removed *in vacuo* and the residue extracted with benzene. The benzene solution was concentrated to 5 mL and hexane added to induce precipitation. The blue solid was collected and dried *in vacuo* (0.463 g, 68%). Analytically pure samples were obtained by slow evaporation of a benzene solution and included 0.25 C_6H_6.

^{1}H NMR (C_6D_6, 200 MHz): δ (ppm) 7.78 (m, 6 H, Ar H), 6.91 (m, 10 H, Ar H), 6.75 (d, 2 H, $^3J_{HH} = 7.3$ Hz, Ar H), 2.69 and 2.49 (AB pattern, 4 H, $^2J_{HH} = 13.9$ Hz, CH_2N), 2.13 and 2.03 (2 s, 12 H, NMe_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 187.2 (d, $^2J_{PC} = 14$ Hz, C *ipso*), 148.6 (C *ortho*), 136.5 (d, $^1J_{PC} = 47$ Hz, PPh_3), 134.6 (d, $^2J_{PC} = 10$ Hz, PPh_3), 128.8 (d, $^4J_{PC} = 2$ Hz, PPh_3), 127.1 (d, $^3J_{PC} = 10$ Hz, PPh_3), 120.3 (C *para*), 120.2 (C *meta*), 74.0 (CH_2N), 53.7 and 48.5 (NMe_2). ^{31}P NMR ($CDCl_3$, 81 MHz): δ (ppm) 89.0 (s, PPh_3). Anal. Calcd for $C_{30}H_{34}N_2PIRu \cdot 0.25C_6H_6$: C, 55.60; H, 5.08; N, 4.03. Found: C, 54.52; H, 5.08; N, 4.03.

Synthesis of [Ru{$C_6H_3(CH_2NMe_2)_2$-2,6}(terpy)]Cl (3). A solution of **2a** (1.30 g, 2.20 mmol) and 2,2′:6′,2″-terpyridine (0.52 g, 2.20 mmol) in MeOH (40 mL) was heated at reflux for 3 h. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (10 mL) and toluene (60 mL) was added. The blue precipitate was filtered off, washed with Et_2O, and dried *in vacuo* to yield **3** (1.14 g, 92%). Analytically pure crystals of **3** were obtained by slow concentration of a CH_2Cl_2/toluene solution.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 8.99 (d, 2 H, $^3J_{HH} = 8.0$ Hz, Ar H), 8.85 (d, 2 H, $^3J_{HH} = 8.0$ Hz, Ar H), 8.17 (d, 2 H, $^3J_{HH} = 5.4$ Hz, Ar H), 8.11 (t, 1 H, $^3J_{HH} = 8.0$ Hz, Ar H), 7.98 (t, 2 H, $^3J_{HH} = 7.8$ Hz, Ar), 7.39 (m, 2 H, Ar), 7.26 (d, 2 H, Ar, $^3J_{HH} = 7.4$ Hz), 7.03 (t, 1 H, Ar), 3.64 (s, 4 H, CH_2N), 1.22 (s, 12 H, NMe_2). ^{13}C ($CDCl_3$, 75 MHz): δ (ppm) 220.2, 160.3, 154.2, 151.9, 141.9, 134.9, 129.4, 126.3, 124.0, 122.5, 120.7, 120.4, 74.8 and 51.7. Anal. Calcd for [$C_{27}H_{30}N_5ClRu + CH_2Cl_2$]: C, 52.06; H, 4.99; N, 10.84. Found: C, 54.78; H, 5.71; N, 11.37.

Synthesis of [RuCl{$C_6H_3(CH_2NMe_2)_2$-2,6}(C_7H_8)] (4). A suspension of [$RuCl_2$(nbd)]$_n$ (1.80 g, 6.8 mmol) and [Li{$C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$, **1** (2.86 g, 3.6 mmol), in THF (60 mL) was stirred at room temperature for 24 h. After removal of the solvent *in vacuo*, the residue was washed with Et_2O and then extracted with CH_2Cl_2 (2 × 30 mL). The solvent was removed to leave a yellow-brown solid. This residue was stirred with THF (15 mL) and then left to stand at −30 °C for 18 h. The yellow solid **4** was collected and dried *in vacuo* (0.855 g, 30%). An analytically pure sample was crystallized from CH_2Cl_2.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.97 (s, 3 H, Ar H), 3.98 and 2.92 (2d, 4 H, $^2J_{HH} = 14.0$ Hz, CH_2N), 3.87 and 3.46 (2m, 4 H, HC=), 3.55 and 3.30 (2 br s, 2 H, CH), 1.99 and 1.95 (2 s, 12 H, NMe_2), 1.24 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 178.5 (C *ipso*), 146.0 (C *ortho*), 122.5 (C *para*), 122.2 (C *meta*), 71.6 (CH_2N), 57.1 (CH_2), 54.7 and 45.0 (HC=), 49.8 and 48.2 (NMe_2), 49.4 and 47.0 (CH). Anal. Calcd for [$C_{19}H_{27}N_2ClRu + 0.25CH_2Cl_2$]: C, 52.40; H, 6.28; N, 6.35. Found: C, 52.40; H, 6.24; N, 6.40.

Synthesis of [Ru(SO_3CF_3){$C_6H_3(CH_2NMe_2)_2$-2,6)(C_7H_8)] (5). $AgSO_3CF_3 \cdot C_6H_6$ (0.27 g, 0.80 mmol) was added to a solution of **3** (0.31 g, 0.73 mmol) in CH_2Cl_2 (15 mL) and SMe_2 (0.2 mL). After 20 min the reaction mixture was centrifuged and the yellow supernatant removed and evaporated to dryness. The residue was extracted with Et_2O (3 × 20 mL) and the resulting solution concentrated to approximately 15 mL and layered with hexane to yield **3** as yellow crystals (0.21 g, 53%).

^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 6.89 (t, 1 H, $^3J_{HH} = 7.3$, Ar H), 6.66 (d, 2 H, $^3J_{HH} = 7.3$ Hz, Ar H), 4.39 and 3.17 (2 m, 4 H, =CH), 4.04 and 2.90 (2 br s, 2 H, CH), 3.20 and 2.17 (2 d, 4 H, $^2J_{HH} = 14.3$, CH_2N), 1.59 and 1.58 (2 s, 12 H, NMe_2), 1.21 (t, 2 H, $^3J_{HH} = 1.4$, CH_2). ^{13}C (C_6D_6, 75 MHz): δ (ppm) 173.4, 145.5, 123.2, 122.6, 70.5, 59.1, 58.3, 50.9, 50.7, 49.9, 48.5, and 47.3. Anal. Calcd for $C_{20}H_{27}F_3N_2O_3RuS$: C, 45.04; H, 5.06; N, 5.25. Found: C, 44.92; H, 5.10; N, 5.29.

X-ray Structure Determination of 2b and 3−5. Suitable crystals for X-ray structure determination were glued on a Lindemann glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer with rotating anode for **2b, 3**, and **4** and on an Enraf-Nonius sealed-tube CAD4 for **5**. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 reflections (set4) in the ranges 13.5° < θ < 16.1° for **4** and 11.5° < θ < 14.1° for the other compounds. Reduced-cell calculations did not indicate higher lattice symmetry.[27]

Crystal data and details on data collection and refinement of **2b** and **3**−**5** are given in Table 1. Data were collected in the $\omega/2\theta$ scan mode. Data were corrected for *Lp* effects and for the linear decay of the reference reflections (0%, 8%, 2%, and 3%, respectively). Standard deviations of the intensities are based on counting statistics,[28] except for **3**. For **2b**, **4**, and **5** an empirical absorption/extinction correction was applied (DIFABS[29]). The structures **2b**, **4**, and **5** were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[30]), and **3** was solved by automated direct methods (SHELXS86).[31] For **2b**, **4**, and **5** refinement on *F* was carried out by full-matrix least-squares techniques (SHELX76[32]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93[33]) for **3**; no observance criterion was applied during refinement. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of **2b**, **4**, and **5** were included in the refinement on calculated positions (C−H = 0.98 Å) riding on their carrier atoms, except for the hydrogens on C(13), C(14), C(16), and C(17) (**4**) and on C(14), C(15), C(17), and C(18) (**5**) of the norbornadiene, which were located on a difference Fourier map and subsequently included in the refinement. The hydrogen atoms of **3** were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms, by a factor of 1.5 for the methyl and 1.2 for the other hydrogen atoms, respectively. Hydrogen atoms of **2b** and **4** were refined with one overall isotropic thermal parameters of 0.0276(13) and 0.0441(15) Å^2, respectively. Hydrogen atoms of **5** were refined with two overall isotropic thermal parameters of 0.0269(17) and 0.0318(19) Å^2 for the methylenic and the remaining atoms, respectively. The refinement of **2b** included an empirical absorption correction parameter (0.00018(1));[29] one reflection was omitted in view of experimental errors. Weights were introduced in the final refinement cycles.

The correct enantiomorphic structures were determined for **4** and **5**. Final refinements of **4** and **5** were performed in their absolute structure, giving the lowest *R*-values (Flack parameters −0.05(3), −0.02(3)[35]).

The structure of **3** contains two CH_2Cl_2 molecules disordered over an inversion center. No satisfactory solvent model could be refined. The SQUEEZE[36] procedure from PLATON[34] was used to take this electron density into account. Neutral atom scattering factors taken from Cromer and Mann[37] and anomalous dispersion corrections from Cromer and Liberman[38] were used for **2b**, **4**, and **5**. For **3** neutral atom scattering factors and anomalous dispersion corrections were taken from ref 39. Geometrical calculations and illustrations were performed with PLATON;[34] all calculations were performed on a DECstation 5000 cluster.

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Supporting Information Available: Tables listing further details of the structure determinations, atomic coordinates, bond lengths and angles, and thermal parameters for **2b** and **3**−**5** (39 pages). Ordering information is given on any current masthead page.

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