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Note

Cationic 16-electron half-sandwich ruthenium complexes containing asymmetric diamines: understanding the stability and reactivity of coordinatively unsaturated two-legged piano stool complexes

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Abstract

The cationic 16e complexes $[RuCp^*(\eta^2(N,N)\text{-}Me_2NCH_2CH_2N(CH_2CHMe_2)_2)]^+$ (**1**) and $[RuCp^*(\eta^2(N,N)\text{-}Me_2NCH_2CH_2NCH_2CH_2OCH_2CH_2)]^+$ (**2**) as well as the 18e complex $[RuCp^*(\eta^6\text{-}C_6H_5\text{-}N(Me)NCH_2CH_2NMe_2)]^+$ (**3**) have been synthesized as the BAr'_4 ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) salts in one-pot reactions starting from $[RuCp^*(Cl)]_4$. For **1**, the X-ray crystal structure has also been determined showing the absence of any agostic interactions between ruthenium and the C–H bonds of the diamine ligand, and only minor deviations from the planar geometry despite the bulky diamine ligand. Based on EH model calculations, the extraordinary kinetic inertness of the planar 16e $[Cp^*Ru(NN)]^+$ structure is traced to a high HOMO–LUMO gap deriving from through-bond coupling through the intervening σ skeleton of the chelating diamine (NN) ligand (in contrast to the P analogs) and further to the high π donor strength of Cp* (relative to parent Cp). Possible ligand rearrangements to increase the chemical reactivity are analyzed.

Keywords: Crystal structures; Theoretical calculations; Ruthenium complexes; Half-sandwich complexes; Diamine complexes

1. Introduction

In recent years, there has been growing interest in coordinatively unsaturated two-legged piano stool (half-sandwich) transition metal complexes as appealing candidates for stoichiometric as well as catalytic applications in organic syntheses [1]. More specifically, compounds of the type $[MCp^*L^1L^2]$ with a d^6 electron count and predominant σ ligands have been found to favor a planar geometry (i.e. the Cp* plane is perpendicular to the $L^1\text{–}Ru\text{–}L^2$ plane) in a variety of complexes containing O, S, P, and N donor ligands [2]. Incidentally, the configurational stability of a potential catalyst is highly desirable with respect to achieving enantiomerically pure products [1c].

In the course of our efforts to synthesize and characterize coordinatively unsaturated ruthenium complexes, we recently reported on the first cationic 16-electron ruthenium complex $[RuCp^*(Me_2NCH_2CH_2NMe_2)]^+$ [3], a compound that has proven to be remarkably inert with respect to oxidative addition of H_2, $HSiEt_3$, and MeBr. Note that $Me_2NCH_2CH_2NMe_2$ neither has π-donor properties to stabilize the electron deficient ruthenium center nor is particularly bulky so as to prevent attack of incoming reagents. Beyond that, not

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even agostic interactions are apparent between $Me_2NCH_2CH_2NMe_2$ and the ruthenium center.

In this work we describe the synthesis of further cationic 16-electron complexes of the type [RuCp*-(η^2(N,N)-diamine)]$^+$ using diamine ligands with pendant alkyl substituents to facilitate agostic interactions. For bulky phosphines, such interactions have been demonstrated indeed [4]. In addition, we are undertaking comparative extended Hückel (EH) calculations so as to rationalize the differences in behavior between N and P donor ligands in RuCp* chemistry on a qualitative level.

2. Experimental

All reactions were performed under an inert atmosphere of purified argon by using Schlenk techniques unless otherwise stated. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp^*(Cl)]_4$ and $NaBAr'_4$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) were prepared according to the literature [5,6]. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalysis were done by the Microanalytical Laboratories, University of Vienna.

2.1. Synthesis of [RuCp*(η^2(N,N)-$Me_2NCH_2CH_2N$-$(CH_2CHMe_2)_2$]BAr'_4 (1)

A suspension of $[RuCp^*(Cl)]_4$ (300 mg, 0.276 mmol) in Et_2O (5 ml) was treated with $Me_2NCH_2CH_2N(CH_2CHMe_2)_2$ (222 mg, 1.104 mmol) and stirred for 1 h at room temperature. After that time, $NaBAr'_4$ (0.978 mg, 1.104 mmol) was added and the solution stirred for an additional 5 min. After removal of the solvent, the residue was dissolved in Et_2O (5 ml), insoluble materials were removed by filtration and the blue product was precipitated by addition of n-hexane. Yield: 1.30 g (91%). *Anal.* Calc. for $C_{54}H_{55}BF_{24}N_2Ru$: C, 49.89; H, 4.26; N, 2.15. Found: C, 49.77; H, 4.28; N, 2.24%. ^1H NMR (δ, CD_2Cl_2, 20°C): 7.72 (m, 8H), 7.57 (s, 4H), 3.41 (dd, 2H, NCH_2, $J = 13.4$ Hz, $J = 5.7$ Hz), 3.11 (dd, 2H, NCH_2, $J = 13.4$ Hz, $J = 5.7$ Hz), 2.90 (s, 6H, NMe_2), 2.20 (m, 2H, NCH_2CH_2N), 1.94 (m, 2H, CH), 1.89 (m, 2H, NCH_2CH_2N), 1.38 (s, 15H, C_5Me_5), 1.02 (d, 6H, Me, $J = 6.7$ Hz), 0.88 (d, 6H, Me, $J = 6.7$ Hz). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 161.5 (q, $J_{BC} = 49.7$ Hz, BAr'_4), 135.2 (BAr'_4), 127.1 (q, $J_{CF} = 31.3$ Hz, BAr'_4), 123.1 (q, $J_{CF} = 272.6$ Hz, BAr'_4), 117.9 (BAr'_4), 71.3 (C_5Me_5), 69.1, 62.9, 61.5, 51.7, 45.1 (NMe_2), 26.4 (CH), 24.7 (CH), 23.6 ($CHMe$), 19.7 ($CHMe$), 10.6 (C_5Me_5).

2.2. Synthesis of [RuCp*(η^2(N,N)-$Me_2NCH_2CH_2$-$\overline{NCH_2CH_2OCH_2CH_2}$)]$BAr'_4$ (2)

This compound was prepared analogously to **1** with $[RuCp^*(Cl)]_4$ and $Me_2NCH_2CH_2\overline{NCH_2CH_2OCH_2CH_2}$) as the starting materials. Yield: 90%. *Anal.* Calc. for $C_{50}H_{45}BF_{24}N_2ORu$: C, 47.75; H, 3.61; N, 2.22. Found: C, 47.77; H, 3.73; N, 2.14%. ^1H NMR (δ, CD_2Cl_2, 20°C): 7.75 (m, 8H), 7.58 (s, 4H), 4.61 (ddd, 2H, OCH_2, $J = 13.4$ Hz, $J = 12.4$ Hz, $J = 4.1$ Hz), 3.87 (dd, 2H, OCH_2, $J = 12.4$ Hz, $J = 12.8$ Hz), 3.89 (m, 2H, NCH_2), 2.87 (m, 2H, NCH_2), 2.85 (s, 6H, NMe_2), 2.30 (m, 2H, NCH_2CH_2N), 1.86 (m, 2H, NCH_2CH_2N), 1.45 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 161.5 (q, $J_{BC} = 49.7$ Hz, BAr'_4), 135.2 (BAr'_4), 127.1 (q, $J_{CF} = 31.3$ Hz, BAr'_4), 123.1 (q, $J_{CF} = 272.6$ Hz, BAr'_4), 117.9 (BAr'_4), 71.1 (C_5Me_5), 66.6, 60.5, 58.5, 56.6, 49.9, 49.2, 45.1, 10.4 (C_5Me_5).

2.3. Synthesis of [RuCp*(η^6-C_6H_5-$N(Me)CH_2CH_2$-NMe_2)]BAr'_4 (3)

This compound was prepared following the protocol above with $[RuCp^*(Cl)]_4$ and $Ph(Me)NCH_2CH_2NMe_2$) as the starting materials. Yield: 87%. *Anal.* Calc. for $C_{53}H_{45}BF_{24}N_2Ru$: C, 49.82; H, 3.55; N, 2.19. Found: C, 49.79; H, 3.43; N, 2.14%. ^1H NMR (δ, $CDCl_3$, 20°C): 7.79 (m, 8H), 7.60 (s, 4H), 5.37 (m, 2H), 5.16 (m, 3H), 3.31 (t, 2H), 2.89 (s, 3H, Me), 2.46 (t, 2H), 2.25 (s, 6H, NMe_2), 1.86 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 161.2 (q, $J_{BC} = 49.6$ Hz, BAr'_4), 135.1 (BAr'_4), 127.3 (q, $J_{CF} = 31.5$ Hz, BAr'_4), 123.1 (q, $J_{CF} = 272.8$ Hz, BAr'_4), 118.1 (BAr'_4), 95.6, 85.1, 82.3(C_5Me_5), 69.6, 57.0, 51.4, 46.2, 38.4, 11.2 (C_5Me_5).

2.4. X-ray structure determination for 1

Crystal data and experimental details are given in Table 1. X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), a nominal crystal-to-detector distance of 3.85 cm, 0.3° ω-scan frames). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. The structure was solved by Patterson methods using the program SHELXS86 [7]. Structure refinement on F^2 was carried out with the program SHELXL93 [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

Table 1
Crystallographic data for [RuCp*(η^2(N,N)-$Me_2NCH_2CH_2N(CH_2CHMe_2)_2$]$BAr'_4$ (**1**)

Formula	$C_{54}H_{55}BF_{24}N_2Ru$
Formula weight	1299.88
Crystal size (mm)	$0.60 \times 0.40 \times 0.40$
Space group	$P2_1/c$ (no. 14)
a (Å)	12.646(6)
b (Å)	18.798(8)
c (Å)	25.147(11)
β (°)	98.93(3)
V (Å^3)	5906(5)
F(000)	2632
Z	4
ρ_{calc} (g cm^{-3})	1.462
T (K)	293
μ (mm^{-1}) (Mo Kα)	0.378
Absorption correction	empirical
Transmission factor min./max.	0.4/0.8
θ_{max} (°)	21
Index ranges	$-15 \le h \le 14$, $-21 \le k \le 21$, $-15 \le l \le 30$
No. reflections measured	16257
No. unique reflections	6307
No. reflections $F > 4\sigma(F)$	3605
No. restraints/parameters	213/426
$R(F)$ ($F > 4\sigma(F)$)	0.094
$R(F)$ (all data)[a]	0.158
$wR(F^2)$ (all data)[b]	0.296
Difference Fourier peaks min./max. (e Å^{-3})	−0.55/0.70

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

2.5. Extended Hückel calculations

The extended Hückel molecular orbital calculations were conducted by using the program developed by Hoffmann and Lipscomb [9]. The atomic parameters used in this study were taken from the CACAO program [10]. All the bond lengths and angles of the complexes analyzed were those determined crystallographically.

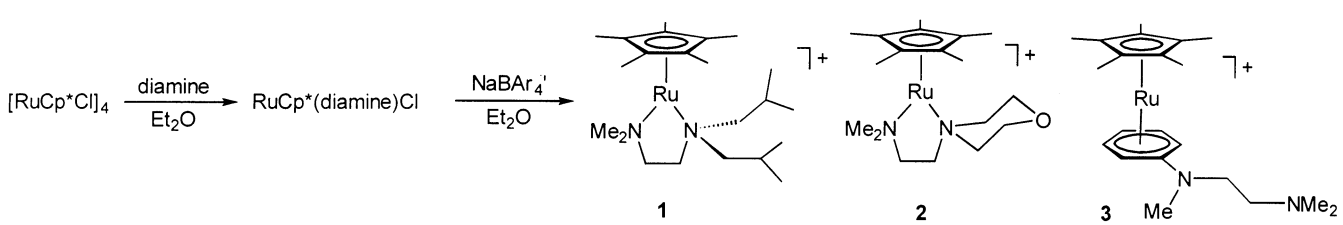
3. Results and discussion

3.1. Syntheses

The complexes **1**, **2** and **3**, as the BAr'_4 ($Ar' = 3,5$-$C_6H_3(CF_3)_2$) salts, were synthesized in a one-pot reaction with $[RuCp^*(Cl)]_4$ as the starting material. The intermediarily formed complexes RuCp*(η^2(N,N)-diamine)Cl have not been isolated. When $[RuCp^*(Cl)]_4$ is treated with the respective diamine (one equivalent) in Et_2O and the resulting orange–red solid was reacted with $NaBAr'_4$, complexes **1**–**3** are, on work-up, obtained in 91, 90 and 87% isolated yields, respectively (Scheme 1). Characterization of all complexes was achieved by elemental analysis, and ^1H and $^{13}C\{H\}$ NMR spectroscopies.

Complexes **1** and **2** are blue complexes which on exposure to air decompose to severeal intractable materials (cf. the isoelectronic complex [RuCp*(η^2(N,N)-$Me_2NCH_2CH_2NMe_2$)]$^+$ reacts with dioxygen to give the hydroxo tetramethylfulvene complex [Ru(η^6-$C_5Me_4CH_2$)($Me_2NCH_2CH_2NMe_2$)(OH)]$^+$ [3]). The ^1H NMR spectrum of **1** exhibits a singlet for the Cp* ring at 1.38 ppm. The CH_2CHMe_2 groups of the $Me_2NCH_2CH_2N(CH_2CHMe_2)_2$ ligand display two doublets of doublets centered at 3.41 and 3.11 ppm (CH_2), a multiplet at 1.94 ppm (CH), and two doublets centered at 1.06 and 0.88 ppm (Me), i.e. the CH_2CHMe_2 groups are diastereotopic. In the $^{13}C\{^1H\}$ NMR spectrum of **1** the resonances of the ring carbon atoms of the Cp* ligand give rise to a singlet at 71.3 ppm. Similar NMR spectra are obtained for **2**. Complex **3**, on the other hand, is a pale yellow air stable 18-electron sandwich complex with the C_6H_5-$N(Me)CH_2CH_2NMe_2$ coordinated in η^6-fashion. This reaction is perhaps not surprising taken into account the high affinity of the RuCp* fragment for arene ligands. Both ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** are unremarkable and are not discussed here.

The structure of **1** has been determined by X-ray crystallography. A structural view of **1** is shown in Fig. 1 with selected bond distances and angles given in the caption. The average Ru–C(Cp*) distance is 2.134(10) Å. The Ru–N(1) and Ru–N(2) distances are 2.177(13) and 2.213(13) Å, respectively. The angle between the planes defined by the Cp* ring and the atoms N(1), Ru, and N(2) is 78° indicating some pyramidalization at the metal center, compared with 89.3° found for the symmetrical analog [3]. However, this could well be a solid state effect since no agostic interactions between ruthenium and one of the C–H bonds of the diamine ligand are observed; the shortest distance between the ruthenium center and the carbon atoms of the $Me_2NCH_2CH_2N(CH_2CHMe_2)_2$ ligand is about 3.00 Å.



Scheme 1.

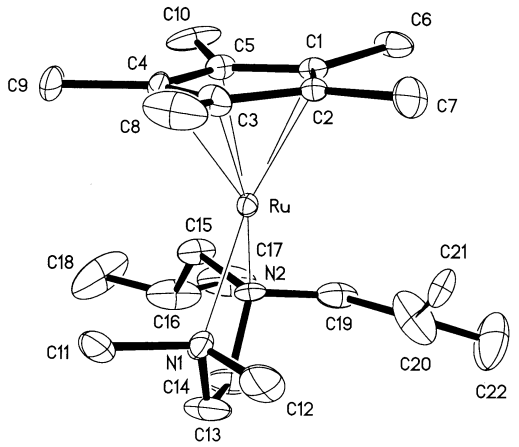


Fig. 1. Structural view of [RuCp*(η^2(N,N)-Me_2NCH_2-$CH_2N(CH_2$-$CHMe_2)_2$]BAr'_4 (**1**). Selected bond lengths (Å) and angles (°): Ru–$C(1-5)_{av}$ 2.134(10), Ru–N(1) 2.177(13), Ru–N(2) 2.214 (13), N(1)–Ru–N(2) 78.1(5).

A planar ground-state structure is consistent with MO calculations for diamagetic d^6 complexes of the types $CpML_2$ and CpMLL′ when L, L′ are pure or predominant σ-donor ligands. For instance, the planar geometry of monomeric [CpRu(acac)] is calculated to be favored by 6.9 kcal mol^{-1} (0.30 eV) over the bent one [1c].

3.2. Extended Hückel analyses

MO studies of half-sandwich $CpML^1L^2$ have been conducted in detail by several authors [11]. We here extend these studies to chelating ligands, thus allowing for through-bond effects in addition to through-space coupling [12]. Through-bond coupling is a result primarily of the filled–filled interaction between the symmetric combination of π or p orbitals with the σ bonding orbital, whereas little to no mixing occurs between the antisymmetric π or p combination with σ* [12a]. Since the σ-bonding orbital of C–C is more similar in size to that of the p orbitals of N relative to P, differences in behavior might be expected. The complexes [Cp*Ru(L^1–L^2)]$^+$ have been analyzed where L^1–L^2 = $Me_2NC_2H_4$-NMe_2 (NN), $Me_2PC_2H_4PMe_2$ (PP), and $Me_2NC_2H_4$-PMe_2 (NP).

The relevant MOs of the {RuCp*} fragment are well-known [11]. Thus, the interaction of the Cp* ligand and Ru occurs mainly through donation of the two filled π orbitals e''_1 of Cp* into the degenerate Ru d(π) orbitals d_{yz} and d_{xz}. The resulting antibonding π* orbitals are perpendicular to and pointing away from the Cp* plane. Further, the a''_2 orbital of Cp* interacts weakly with the Ru d_{z^2} orbital which, therefore, is slightly destabilized relative to the δ-symmetric $d_{x^2-y^2}$ and d_{xy} orbitals that are both coplanar to the Cp* ring plane.

In free bidentate L^1–L^2, the two lone pair σ orbitals interact through-space and couple to the central σ and σ* orbitals of the C–C bond in L^1–L^2, forming the new group orbitals φ'_a and φ'_s [12]. As is seen in Fig. 2, this p–σ–p through-bond coupling is strong in the case of (NN), but weak for (NP) and (PP), as expected, giving rise to a different order in energy levels.

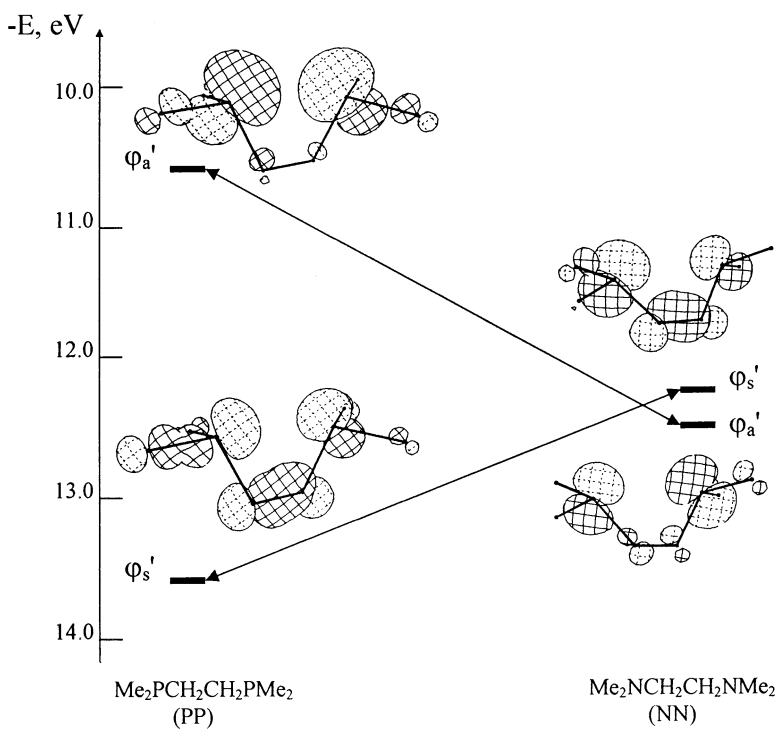


Fig. 2. Comparative orbital interaction diagram resulting from through-space and through-bond effects for free PP and NN.

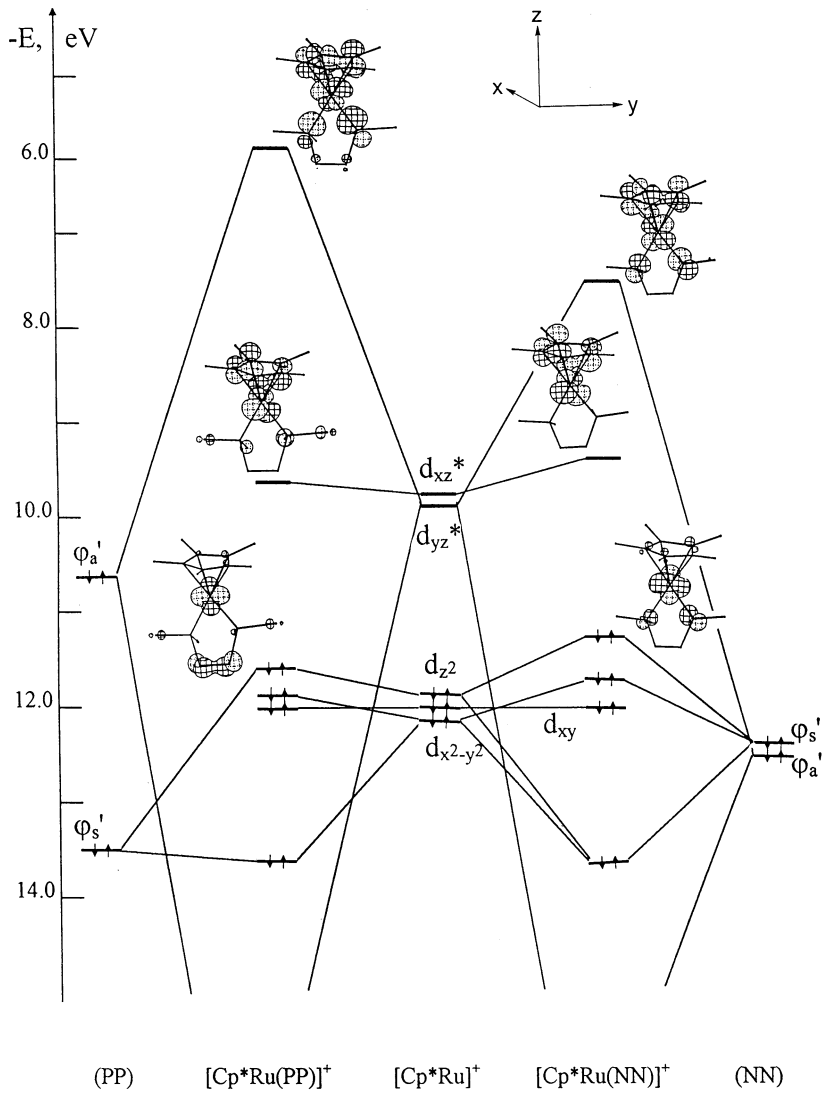


Fig. 3. Qualitative interaction diagram between $\{Cp^*Ru\}^+$ and PP and NN.

Fig. 3 shows a simplified interaction diagram between $\{RuCp^*\}^+$ fragment and L^1–L^2. The φ_a' orbital interacts strongly with the d_{yz}^* orbital, removing the degeneracy of the LUMO of $\{RuCp^*\}^+$ leaving behind the d_{xz}^* MO as the new LUMO and forming SLUMO. According to the φ_a' orbital energies, the SLUMO energy increases strongly in the series (NN) < (NP) < (PP), reflecting the force of coupling between the $\{RuCp^*\}^+$ fragment and L^1–L^2. On the other hand, the changes in LUMO are negligible. A slight destabilization of the HOMO (as d_{z^2}) and $d_{x^2-y^2}$ via the interaction with φ_s' is effective only in the case of the NN ligand. Because of the geometries of LUMO and HOMO (which is located in the Cp(O)–Ru–L^1–L^2 line) the complex $RuCp^*(L^1–L^2)^+$ is neither a good acceptor (neither σ nor π) nor a good donor (unless the geometry is changed).

What modes of activation of planar $[RuCp^*(L^1–L^2)]$ can be envisaged? A pyramidal distortion through bending of the Cp* and L^1–M–L^2 planes (from -20 to $+20°$) virtually does not activate the molecule, despite the rehybridization of the LUMO to point out toward the developing vacant site (Fig. 4). The reason is that the LUMO is pushed up in energy because φ_s' of L^1–L^2 now better interacts with d_{xz}^*. Conversely, the d_{z^2} MO is no longer destabilized as in the planar configuration rendering the HOMO going down. The resulting increase of the HOMO–LUMO gap (Fig. 4) is well-known [11]. We suggest that a raise in chemical reactivity may be achieved if there is additional $\eta^5 \rightarrow \eta^3$ Cp ring slippage. Such a process is known to have a low barrier [13] but pushes down the LUMO effectively. Along these lines the complex gradually not only becomes a better σ acceptor, but also the donor abilities are altered through a concomitant change in the (filled) d-orbital energetic ordering. In the quite general case of a two-legged piano stool metal(d^6) complex (Cp*MLX) with a chiral conformation, each of the orbitals d_{z^2},

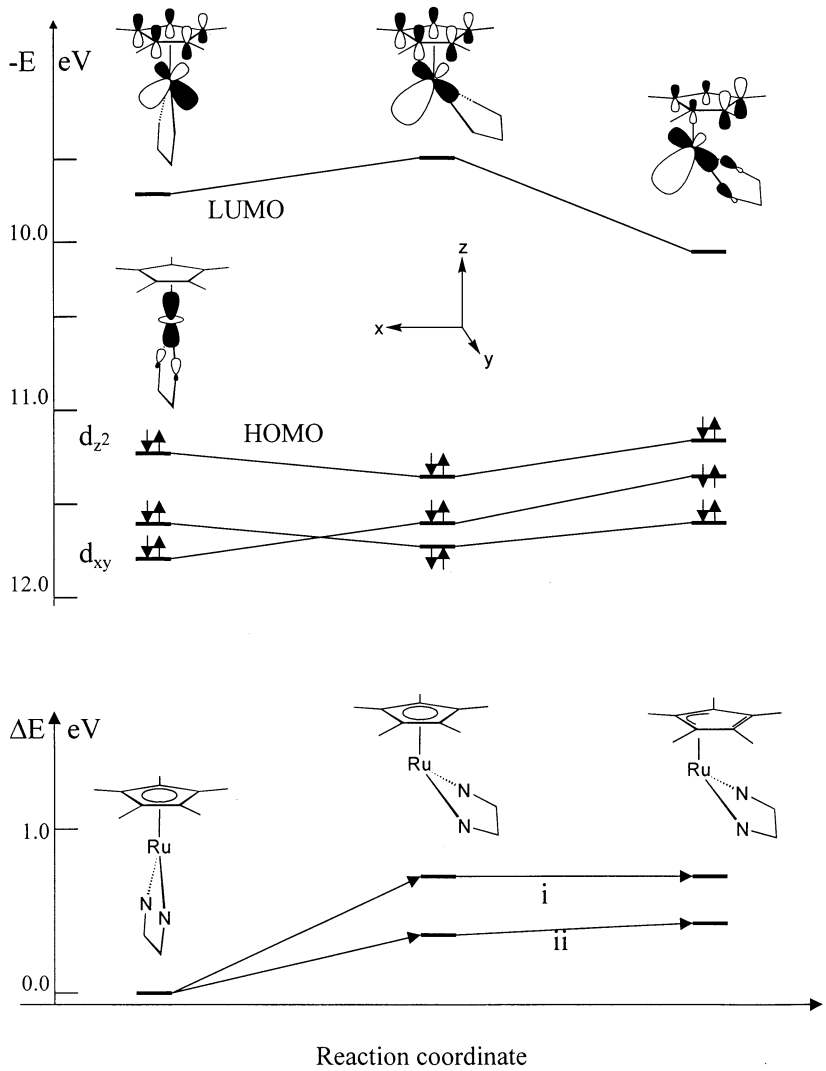


Fig. 4. Computed changes in energies of the HOMO and LUMO in $[Cp^*Ru(NN)]^+$ (upper part) and in the total energies for (i) $[Cp^*Ru(NN)]^+$ and (ii) $[Cp^*Ru(PP)]^+$ (lower part) for stepwise planar/pyramidal distortion, and $\eta^5 \rightarrow \eta^3$ Cp* ring slippage.

$d_{x^2-y^2}$, and d_{xy} can become the HOMO, depending on the nature of the ligands L and X, with eventually dramatic differences in chemical behavior [11c,14]. Thus, if d_{z^2} remains to be the HOMO, the complex will be a (weak) σ donor; but if d_{xy} becomes the HOMO, the complex will be more a π donor.

Independent of the subsequent reactions, a prior planar/pyramidal inversion appears to be mandatory implying that the barrier of this process would be part of the overall activation enthalpies. Planar/pyramidal rearrangement barriers may be high or low depending on the relative contributions of the gain in energy from the increased participation of φ'_s and loss in energy from the worsened conjugation between φ'_a and one of the e''_1 orbitals of Cp*. Although all three complexes under consideration are notably destabilized upon pyramidal distortion, this destabilizing effect is about twice as great for the (NN) complex compared with that of (PP) explaining the higher stability of the amine complexes over the phosphorus analogs. The smaller inversion barriers for (NP) and (PP) can be traced to the stronger interaction of φ'_a with π*-FMO of {RuCp*} fragment in the pyramidal configuration and the relatively small decrease in the corresponding $\langle e''_1 \mid \varphi'_a \rangle$ overlap. Furthermore, because of p–σ–p through-bond coupling, the loss in energy due to the interaction of d_{xy} with φ'_s is greater in the NN case compared with PP. It should be mentioned here that this overlap is also diminished when replacing Cp* with Cp. In fact, the related complexes of Cp are found to be much more reactive and detailed investigations in this respect are under way in our laboratories.

4. Supplementary material

X-ray structural data, including positional and thermal parameters, and bond distances and angles for

complex **1** may be ordered from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, referring to the deposition number CSD 408817, the names of the authors, and the citation of the present paper.

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