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Structural flexibility of formally d^{10} [M(biphosphinine)$_2$]^q complexes†

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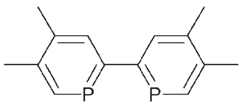
The potential energy curves associated with the interconversion between square planar (SP) and tetrahedral (Td) conformations of the formally d^{10} [M(biphosphinine)$_2$]^q complexes (M = Ni, Pt, Co, Rh and Ru) were obtained by means of DFT calculations with the B3LYP functional. In agreement with the experimental data, the complexes with M = Ni, Pt, Co and Rh were found to adopt a distorted tetrahedral conformation, the flatness of the computed potential energy curves accounting for the experimental characterization of several independent molecules and the fluxional behaviour observed in solution for M = Co and Rh. As expected for formal d^{10} complexes, the tetrahedral structure was always found to be more stable than the square planar structure. However, the computed energy difference is rather small (between 3.1 kcal mol^{-1} for M = Ru and 13.6 kcal mol^{-1} for M = Ni) and it is shown that, for a given column of the periodic table, the lower the d orbitals on the metal centre (Ni < Pt and Co < Rh), the less favoured the square planar conformation. Finally, for M = Ru, the slight preference for the tetrahedral conformation found in the isolated complex is not preserved in the presence of two counter cations (Na$^+$): in agreement with the experimental data for the uncryptated complex, the two cations were found to be located above and below the plane of a nearly square planar dianionic [Ru(biphosphinine)$_2$]$^{2-}$ unit.

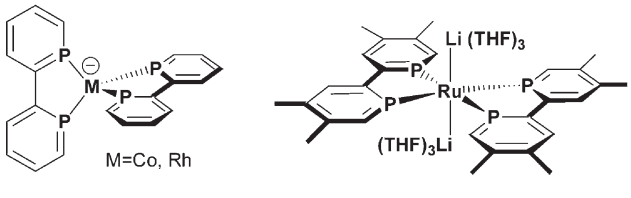
Introduction

It is now well-established that the replacement of nitrogen by phosphorus in aromatic ligands results in significant changes of the electronic properties.[1] Whereas divalent nitrogen-based ligands behave as strong σ-donors and good π-acceptors, their phosphorus counterparts act as poor σ-donors but display a powerful π-accepting capacity. The most striking examples are provided by the phosphorus equivalents of 2,2′-bipyridines, the 2,2′-biphosphinines, such as the easily available 4,4′,5,5′-tetramethyl derivative (tmbp;[2] Scheme 1).

Recent studies have demonstrated that these new phosphorus ligands can efficiently stabilize highly reduced transition metal centres such as Zr(2−),[3] Ti(2−),[3] Hf(2−),[3] Mn(1−),[4] Fe(2−),[5] Ru(2−),[5] Co(1−),[6] Rh(1−),[6] Ni(−)[7b]. Most of these complexes, which have been structurally characterized, exhibit very peculiar geometries that cannot be rationalized following classical electron-counting rules. Thus, homoleptic [M(tmbp)$_3$]$^{2-}$ (M = Ti, Zr, Hf) dianionic species, which are formally d^6, adopt a perfect trigonal prismatic geometry as usually encountered in complexes having the d^0 to d^2 electronic configuration. Interestingly, the neutral homoleptic [W(tmbp)$_3$] complex adopts quite a similar geometry.[8] On the other hand, the group 9 anionic complexes [Co(tmbp)$_2$]·[Na(2.2.2)] and [Rh(tmbp)$_2$]·[Na(2.2.2)] were characterized as a mixture of conformers that adopt a highly distorted tetrahedral geometry in the solid state. Indeed, the crystal cell of the Co complex featured two conformers ($\theta = 78°$ and 83°) and that of the Rh derivative three ($\theta = 59°$, 63° and 87°), with θ defining the interplane angle between the two biphosphinine ligands (Scheme 2, left-hand side). Nevertheless, the presence of different conformations is not observed in solution. These results led us to propose that the energetic barrier between tetrahedral (Td) and square planar (SP) geometries would probably be very weak in these Co and Rh derivatives.



Scheme 1 Tetramethylbiphosphinine (tmbp).



Scheme 2

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† Electronic supplementary information (ESI) available: main geometrical parameters optimized for the structures whose energies are reported in Fig. 1. See http://www.rsc.org/suppdata/nj/b3/b316684h/

Interestingly, a single conformer was found for the isoelectronic neutral Ni[7a] and Pt[7c] complexes with a distorted tetrahedral structure ($\theta = 74.4°$ and 59.4°, respectively). On the other hand, a striking result was also obtained during studies of group 8 dianionic complexes, which can also be considered as formally d^{10} species. Thus, the $[Ru(tmbp)_2]\cdot[Li(THF)_3]_2$ complex was found to adopt a nearly square planar geometry ($\theta = 7.3°$) when the two counter anions are not encapsulated (Scheme 2, right-hand side), the iron complex being assumed to have the same structure.[5] Unfortunately, the X-ray structures of the analogous complexes featuring a cryptated Li or Na cation could not be recorded, as well as that of uncryptated Co(1−) and Rh(1−) complexes.

All these observations on group 8 and 10 complexes reinforce the idea that the energetic barrier between different conformations in these formally d^{10} complexes is probably small and suggest that interaction with the counter cation(s) could play a role in fixing the equilibrium geometry of uncryptated complexes.

In order to shed some light on the role played by the biphosphinine ligands, the nature of the metal centre and its interaction with counter ions, we recently launched theoretical studies of $[M(biphosphinine)_2]^q$ type complexes. Herein we wish to report on results for the complexes with M = Ru ($q = -2$), Co and Rh ($q = -1$) and M = Ni and Pt ($q = 0$). The following main points will be addressed: (i) how does the energy of the complex depend on the relative orientation of the biphosphinine ligands? (ii) what is the influence of the nature of the metal centre on the energy difference between square planar and tetrahedral conformations? (iii) what is the role played by the counter cations in fixing the geometry of the uncryptated dianionic Ru complex?

Computational details

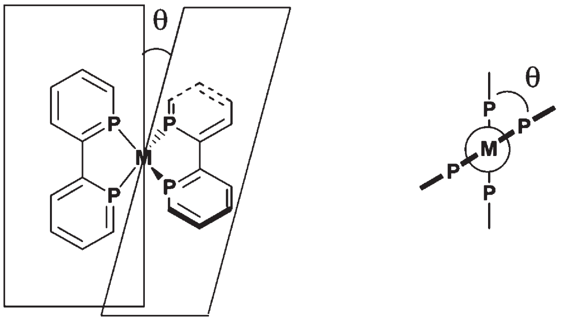
Geometry optimizations were performed with the GAUSSIAN 98 series of programs.[9] Density functional theory (DFT)[10,11] was applied with the B3LYP functional.[12–14] A quasi-relativistic effective core potential operator was used to represent the 10 innermost electrons of the cobalt and nickel atoms, the 28 innermost electrons of the ruthenium and rhodium atoms, the 60 innermost electrons of the platinum atom[15] as well as the electron core of the P atom.[16] The basis set for the metal was that associated with the pseudo-potential[15] with a standard double-ζ LANL2DZ contraction.[9] The basis set for the P atoms was that associated with the pseudo-potential[16] with a standard double-ζ LANL2DZ contraction[9] supplemented with a set of d-polarization functions.[17] The 6-31G* basis set was used for C atoms and the 6-31G basis set for the Na and H atoms.[18] For the single-point calculations on the SP and Td conformations the basis set for the metal atom was supplemented by a set of f-polarization functions[19] and the 6-31+G* basis set was used for C and P atoms.[18d]

Results and discussion

Conformational study of the $[M(bp)_2]^q$ complexes

The conformation of the $[M(bp)_2]^q$ complexes (bp = unsubstituted biphosphinine) is characterized by the dihedral angle θ between the P–M–P units of the two bp ligands (Scheme 3). In the following calculations, all the geometrical parameters are optimized within the D_2 symmetry group, a constraint that does not force the full bp ligands to be planar.

The conformation of the complexes with M = Ni and Pt ($q = 0$), Co and Rh ($q = -1$) and Ru ($q = -2$) was optimized and these structures were further characterized as minima by a vibrational frequencies calculation. The main optimized theoretical parameters are reported in Table 1 together with the experimental values. The flexibility of these complexes was then studied by varying the dihedral angle θ from 0° (structure called square planar in the following) to 90° (tetrahedral in the following) in steps of 15°. The computed energy profiles associated with this distortion away from the θ equilibrium value are given in Fig. 1.



Scheme 3 Definition of the angle θ in $[M(bp)_2]^q$ complexes: front view and side view (Newman convention).

Whatever the nature of the metal centre, the square planar conformation ($\theta = 0°$) was found to be the highest energy structure on the potential energy curves (Fig. 1). The energy difference with the tetrahedral conformation ($\theta = 90°$) is, however, not very large, lying between 3.1 (Ru) and 13.6 (Ni) kcal mol^{-1}.[20] Another common feature is the flatness of these curves for θ lying between 45° and 90°. The Ni and Pt complexes were found to adopt a distorted tetrahedral conformation, the equilibrium θ values [70.9° and 55°, respectively; Fig. 1(a)] being in good agreement with the experimental data (74.4° and 59.4°, respectively). The optimized angle for the Co complex (75.1°) is also close to the values found for the two independent molecules (78° and 83°). The agreement seems less satisfactory for the Rh complex [Table 1 and Fig. 1(b)], with $\theta_{eq} = 46.9°$ instead of $\theta = 59°$, 63° and 87° for the three experimental conformers. However, an important feature of the potential energy curve is the small energy change associated with a large displacement away from the equilibrium value of θ (1 kcal mol^{-1} between 30° and 70°), a result that can account for the experimental characterization of several independent molecules and the fluxional behaviour observed in solution. A similar behaviour is expected for the Ru complex [Fig. 1(c)] with an energy lowering of only 0.3 kcal mol^{-1} between $\theta = 45°$ and $\theta = 90°$ (minimum). Unfortunately, its cryptated experimental structure is not known. The most striking result for the Ru complex is, however, that the nearly square planar

Table 1 Main theoretical parameters of the P=C–C=P units in the $[M(biphosphinine)_2]^q$ complexes [M = Ni, Pt ($q = 0$), M = Co, Rh ($q = -1$) and Ru ($q = -2$)] optimized within the D_2 symmetry constraint Experimental values are given in parentheses.

M[a]	M–P/Å	P=C/Å	C–C/Å	P–M–P/°	θ/°
Ni[7a]	2.212	1.778	1.472	85.5	71.0
	(2.140)	(1.748)	(1.466)	(85.3)	(74.0)
Pt[7c]	2.358	1.779	1.462	81.3	53.5
	(2.264)	(1.748)	(1.46)	(81.4)	(59.4)
Co[6]	2.127	1.798	1.457	84.6	75.1
	(2.100)	(1.764)	(1.457)	(83.8)	(78, 83)
Rh[6]	2.293	1.798	1.455	80.9	46.9
	(2.219)	(1.763)	(1.456)	(81.1)	(59, 63, 87)
Ru[5]	2.255	1.824	1.447	79.1	90.0
	(2.215)	(1.770)	(1.437)	(79.2)	(7.3)

[a] References for the experimental values.

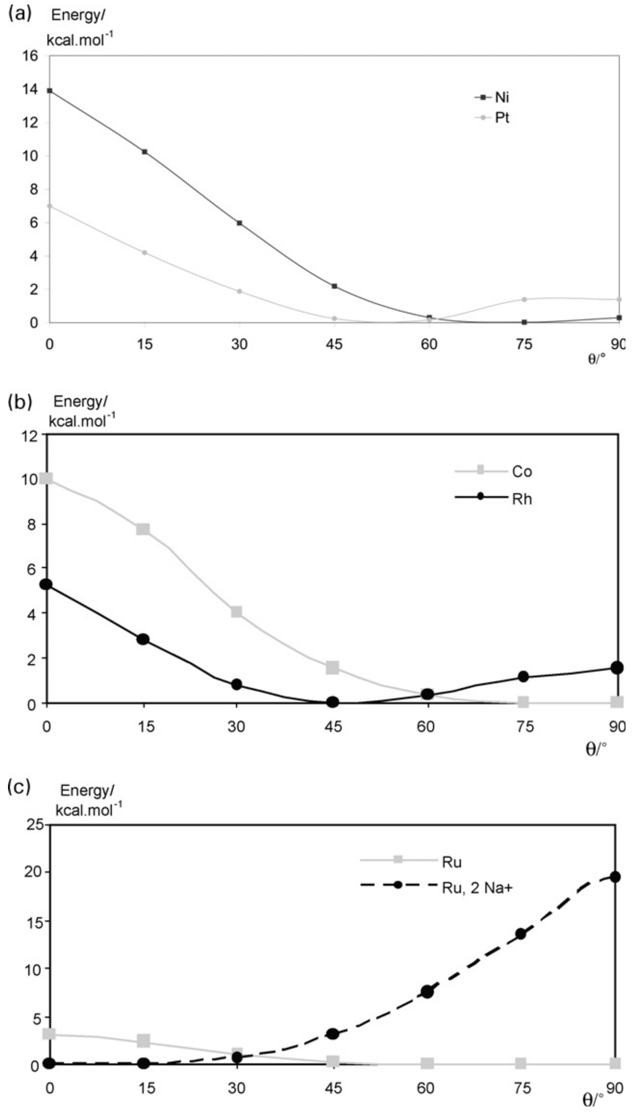


Fig. 1 Computed energy profiles as a function of the θ angle (see Scheme 3) in $[M(bp)_2]^q$ complexes: (a) M = Ni, Pt; (b) M = Co, Rh; (c) M = Ru with (dotted line) and without (solid line) Na^+ cations.

structure found for the uncryptated complex^5 corresponds to the highest energy structure on the computed potential energy curve reported in Fig. 1(c) (see last section).

Let us finally discuss briefly the details of the geometry around the metal centres (Table 1). The average overestimation of the M–P and P=C bonds is 0.061 and 0.037 Å, respectively, while the deviation for the central C–C bond connecting the two cycles is lower than 0.010 Å and the P–M–P bite angle is almost exactly reproduced. The optimized values for the P=C and C–C bond lengths in the P=C–C=P units are significantly different from those optimized in the isolated bp ligand (1.786 and 1.501 Å, respectively). There is a lengthening of the P=C bonds for M = Ru, Rh and Co and a shortening of the C–C bond whatever the nature of the metal centre. This trend is in agreement with that found in the experimental complexes (Table 1), the experimental values for the P=C and C–C bonds in the isolated tmbp ligand being equal to 1.736 and 1.490 Å, respectively. The largest variations were found for the Ru complex with Δ(P=C) = +0.038 Å (exptal: +0.034 Å) and Δ(C–C) = −0.054 Å (exptal: −0.053 Å), the smallest were for the Ni(0) complex with Δ(P=C) = −0.008 Å (exptal: +0.012 Å) and Δ(C–C) = −0.029 Å (exptal: −0.024 Å). Such changes in the internal bond distances of the bp ligand will be analyzed in the following section.

Energy difference between square planar and tetrahedral conformations

According to qualitative molecular orbital arguments,[21] such small energy changes between the square planar and the tetrahedral conformations might be surprising. With a formal electron count of ten electrons around the metal centre, the tetrahedral conformation with five low-lying d orbitals should be much more stable than the square planar conformation with four low-lying and one sigma antibonding d orbitals. Examination of the electronic structure of the Ru and Co complexes actually reveals that the two extra electrons in the square planar structure are located in an almost purely ligand-centred molecular orbital (the HOMO), the in-phase combination of the LUMO on each biphosphinine ligand [see Fig. 2(A), left-hand side, for the Ru complex]. Therefore, the rotation transforms a formally d^8 square planar complex into a formally d^{10} tetrahedral complex, that is, two structures with their usual formal electron counts. The double occupation of the π^* MO in the square planar conformation is not so unfavourable from an energetic point-of-view because of the low-lying energy level the LUMO of the bp ligands (strong π-acceptor). For instance, in the Ru complex, it is located only 14.9 kcal mol^{-1} above the metal-centred HOMO of the tetrahedral structure [Fig. 2(A), right-hand side].[22] Since a ligand-centred MO is being transformed in a metal-centred MO, an orbital crossing should be associated with this intramolecular redox process. It is actually an avoided orbital crossing since the ligand and the metal orbitals are of the same symmetry (b_1) in the D_2 group: the coefficient of the d orbital in the HOMO increases progressively as the rotation takes place from the square planar to the tetrahedral conformation [Fig. 2(A)]. Since no energy barrier was found between these two limiting structures, neither for the total energy (Fig. 1) nor for the energy of the HOMO, it can be described as a strongly avoided crossing. The orbital picture is a bit different, although basically similar, in the square planar structure of the Rh, Pt and Ni complexes because the bp ligands distort out of the plane defined by the MP_4 unit.[23] The HOMO remains mostly developed on the π^* orbital of the ligands (with a polarization of the p component on the P centres) but a d contribution appears which increases on going from the square planar to the tetrahedral conformation [Fig. 2(B), for Ni]. Again, no energy barrier is associated with this change in the location of the HOMO (Fig. 1). Note finally that the bite angle value (about 80°) is closer to the ideal value for a square planar (90°) than for a tetrahedral conformation (109°). These three

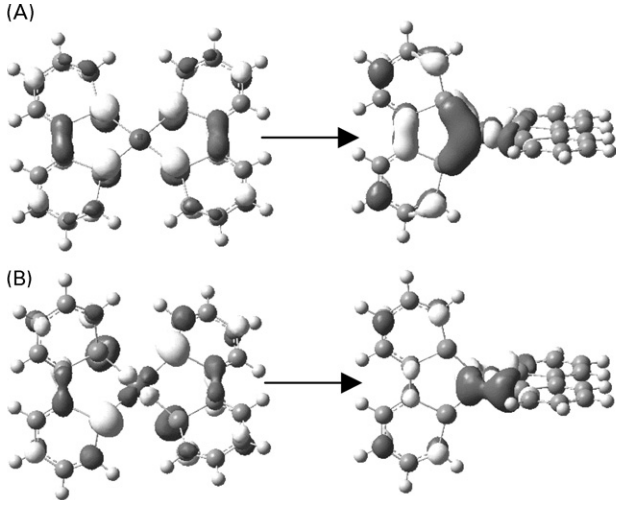


Fig. 2 HOMO of (A) dianionic $[Ru(bp)_2]^{-2}$ and (B) neutral $[Ni(bp)_2]$ complexes in the (left) square planar and (right) tetrahedral conformations.

factors (usual formal electron count, strong π-acceptor properties of the bp ligands and bite angle value) help to understand why the computed energy difference between these two limiting structures is rather small.

The large participation of the bp LUMO in the electronic structure entails an electron transfer from the metal centre to the ligands. Since this orbital is mainly P=C antibonding and C–C bonding in the P=C–C=P unit (Fig. 2) it results in a lengthening of the P=C bonds and a shortening of the C–C bond, as actually noticed in the previous section. It is noteworthy that in the Ru complex the optimized P=C and C–C bond lengths (1.824 and 1.447 Å, respectively, Table 1) are not far from those optimized in the isolated monoanionic $(bp)^-$ species (1.831 and 1.449 Å, respectively), so that this complex can be described approximately as a Ru(0) centre coordinated to two $(bp)^-$ monoanions.

The energy difference between the square planar conformation (the highest energy structure on the potential energy curves reported in Fig. 1) and the tetrahedral conformation (the lowest or close to the lowest energy structure) was found to depend on the nature of the metal centre. In particular, it decreases on going from the first to the second (third) series in a given column (from 10.0 to 3.7 kcal mol^{-1} for Co and Rh, from 13.6 to 4.7 kcal mol^{-1} for Ni and Pt). This trend correlates with the evolution of the d orbital energy[24] on the metal centre: the lower the d level the greater the preference for the tetrahedral conformation. The electronic structure of the two limiting conformations analyzed just above allows a simple rationalization of this result. In the square planar conformation, only four metal-centred orbitals are occupied while in the tetrahedral conformation the five d orbitals are occupied. Therefore, any lowering of the d orbital level is more efficient in stabilizing the tetrahedral conformation than the square planar one.

The role of the counter cations in the ruthenium complex

The largest discrepancy between the theoretical and the experimental conformations was found for the Ru complex. As a matter fact, a tetrahedral conformation is predicted while the experimental structure is nearly square planar ($\theta = 7.3°$). However, the latter has been characterized when the two counter cations are not encapsulated. The rotational energy curve from $\theta = 0$ (SP) to 90° (Td) was therefore recomputed in the presence of two Na^+ counter ions. For each value of θ, the geometry of the complex and the position of the cations were optimized within the C_2 symmetry constraint. The energy profile associated with the rotation in $[Ru(bp)_2]^{2-}{\cdot}[Na^+]_2$ is given in Fig. 1(c) together with for the isolated $[Ru(bp)_2]^{2-}$ species.

Although the optimized geometrical parameters are only slightly modified by the presence of the counter ions (see Electronic supplementary information), a dramatic change was found in the shape of the potential energy curve, the square planar conformation [Fig. 3(A)] being more stable than the tetrahedral one [Fig. 3(B)] by 19.5 kcal mol^{-1}. This result takes into account the basis set superposition error (BSSE), which was found to be almost independent of the rotational angle (between 4.0 and 5.6 kcal mol^{-1}). The minimum energy structure was actually characterized by a vibrational frequencies calculation for $\theta = 11.8°$ (the energy lowering with respect to $\theta = 0°$ being only 0.02 kcal mol^{-1}), a value in good agreement with the experimental data ($\theta = 7.3°$). Therefore, the presence of two counter cations was found to change the geometry around the metal centre from a tetrahedral to a nearly square planar conformation, the structure of the overall complex being a distorted octahedron.

The total energy (E_{tot}) can be defined as $E_{\text{tot}} = E_{\text{comp}} + E_{2\text{Na}+} + E_{\text{int}}$ where E_{comp} is the energy of the isolated $[Ru(bp)_2]^{2-}$ dianion unit, $E_{2\text{Na}+}$ that of the two counter ions and E_{int} their interaction energy. For the two former terms, the geometry used was that optimized in the full complex and the energies were corrected for the BSSE. Calculations were performed for θ varying from 0° to 90° in steps of 15° and the results are reported in Table 2. Both E_{comp} and $E_{2\text{Na}+}$ favour the tetrahedral conformation by 2.5 and 6.2 kcal mol^{-1}, respectively. For the former, the result is close to that found in the previous section (isolated dianion) and for the latter it comes from the larger distance between the cationic centres in the tetrahedral structure (5.94 instead of 5.34 Å in the square planar one). It thus appears that the stabilizing interaction between the two cations and the dianionic unit (E_{int}) favours the square planar conformation by 28.2 kcal mol^{-1}, a value large enough to change the conformational preference of the $[Ru(bp)_2]^{2-}$ unit.

This result can be related to the location of the cations in the two limiting structures. In the square planar conformation [Fig. 3(A)] there is a strong interaction with the metal centre (Ru···Na = 2.668 Å) and much weaker interactions with the phosphorus atoms (Na···P = 3.520 Å). In the tetrahedral conformation [Fig. 3(B)] the cations interact with both Ru and two P centres (Ru···Na = 2.970 Å and Ru···P = 2.823 Å). Therefore, the larger value found for E_{int} in the square planar structure is due to a stronger interaction of the Na^+ cations

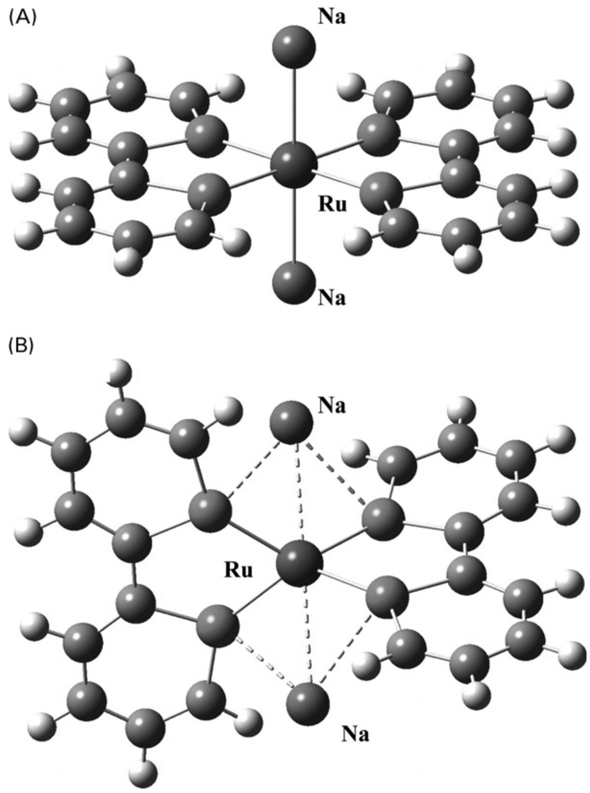


Fig. 3 Optimized structures of the $[Ru(bp)_2]{\cdot}Na_2$ complex in the (A) square planar and (B) tetrahedral conformations of the $[Ru(bp)_2]^{-2}$ dianionic unit.

Table 2 Decomposition of the energy (E_{tot}) of the $[Ru(biphosphinine)^{2-}{\cdot}2Na^+]$ complex into the E_{comp}, $E_{2\text{Na}+}$ and E_{int} components (see text) as a function of the angle θ. Energies, in kcal mol^{-1}, are given with respect to the values found in the tetrahedral conformation.

θ/°	0	15	30	45	60	75	90
E_{tot}	−19.5	−19.5	−18.8	−16.5	−12.0	−6.0	0.0
E_{comp}	2.5	1.8	0.8	0.0	−0.4	−0.5	0.0
$E_{2\text{Na}+}$	6.2	6.2	6.0	5.3	4.2	2.4	0.0
E_{int}	−28.2	−27.5	−25.6	−21.8	−15.8	−7.9	0.0

with the metal centre. This result can be traced to the larger negative charge carried by the metal centre in the SP conformation (−0.89 e instead of −0.76 e in the Td one, according to NBO calculations) and to a covalent interaction since the counter ions are located in the two vacant sites associated with the square planar complex. At this point, it must be recalled that naked cations have been used in these calculations while in the experimental complex the cations are solvated by three THF molecules. This simplified model might well be responsible for the short Ru···Na distance found in the planar conformation (2.668 Å), a value actually smaller than the sum of the covalent radii (2.80 Å). Such an underestimation of the Ru···Na distance could in turn favour this conformation with respect to the more encumbered tetrahedral one in which this distance is found to be significantly longer (2.970 Å). An additional calculation was thus performed, the square planar conformation being reoptimized with the Ru···Na distances held fixed to 2.970 Å, that is the optimized value in the tetrahedral conformation. As expected, the energy difference between the two conformations is reduced but the preference for the square planar conformation of the $[Ru(bp)_2]^{2-}$ unit is preserved by 7 kcal mol^{-1}.

Conclusion

The distorted tetrahedral conformation of the formally d^{10} $[M(bp)_2]^q$ complexes (M = Ni, Pt, Co and Rh) is well-reproduced by B3LYP calculations. The rather small energy difference between the square planar (SP) and the tetrahedral (Td) conformations, which accounts for the experimental characterization of several independent molecules and the fluxional behaviour observed in solution for M = Co and Rh, is mainly traced to the following factors: (i) the rotation in these formally d^{10} complexes actually connects two structures with their usual formal electron counts, d^8 (or nearly d^8) for SP, d^{10} for Td; (ii) the two remaining electrons in the SP conformation are located in a purely or mostly ligand-centred MO so that the strong π-acceptor properties of the bp ligands help to stabilize the SP conformation. On the other hand, it is shown that for a given column of the periodic table, the lower the d orbitals on the metal centre (Ni < Pt and Co < Rh) the less favoured the square planar conformation. Finally, the slight structural preference of the $[Ru(bp)]^{2-}$ complex for a tetrahedral conformation is reversed in the presence of two counter cations (Na^+). In agreement with the experimental data for the uncryptated complex, a nearly square planar conformation is favoured by the Na···Ru interactions.

Acknowledgements

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