Electronic structure of organobis(dimethylglyoximato)triphenylphosphinerhodium(III) complexes

Roman Boča*, Michal Dunaj-Jurčo, Ivan Potočňák

Department of Inorganic Chemistry, Slovak Technical University, SK-812 37 Bratislava, Slovakia

Dirk Steinborn, Maik Ludwig

Institute of Inorganic Chemistry, Martin Luther University Halle-Wittenberg, D-06099 Halle/S, Germany

Abstract

Three metal complexes of general composition [Rh(PPh$_3$)(dmgH)$_2$R] (dmgH$^-$ = monoanion of dimethylglyoxime, R$^-$ = CH$_3$–CH$_2^-$, CH$_2$=CH$^-$ and C$_6$H$_5$C≡C$^-$) have been investigated by the quasirelativistic INDO/1 method. Geometric models of the complexes were taken from X-ray structure analysis. The bonding situation has been analyzed in terms of bond-multiplicity indices and bicentric increments to the total energy. A decreasing *trans* influence of the organo group evidenced from the X-ray data was not confirmed by the corresponding stabilization of the Rh–P bond.

1. Introduction

A characterization of electronic properties of ligands in metal complexes is important to understand stability and reactivity of metal complexes as well as their activity in homogeneous catalysis [1]. This work is part of a series aimed at improving the understanding of the mutual electronic influence of ligands in organometallic compounds [2].

The *trans* influence of σ-organo ligands is of a particular interest. The *trans* influence of R can be established in compounds with a linear structural fragment R–M–L by means of the NMR coupling

constants ^1J(M–L). For example, in organomercury compounds of the RHgCH$_2$CHMe$_2$ type it was found that the coupling constant ^1J(^{199}Hg–^{13}C$_{i-Bu}$) reflects the *trans* influence of R correctly [3]. The coupling constant ^1J(^{103}Rh–^{31}P) in complexes of [Rh(dmgH)$_2$(PPh$_3$)R] type (dmgH$^-$ = dimethylglyoximato anion) can be assumed to be a measure for the *trans* influence of R [2].

To compare the NMR data with structural data of these complexes the crystal structures with R = CH$_3$–CH$_2$– (ethyl), CH$_2$=CH– (vinyl) and PhC≡C– (phenylacetylide) as representatives for sp^3-, sp^2- and sp-hybridized, respectively, σ-organo ligands have been reported recently [4–6]. The complexes under study consist of discrete
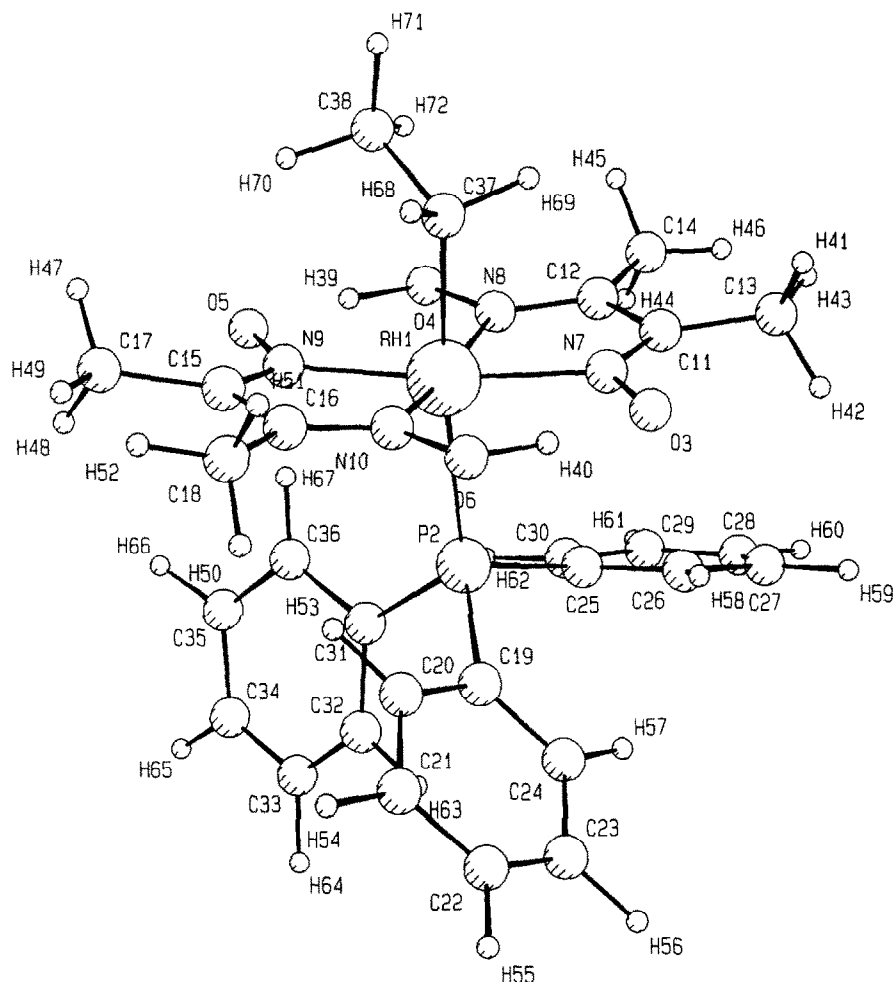
*Corresponding author.

Fig. 1. Structure of [Rh(PPh₃)(dmgH)₂(CH₂–CH₃)] complex.

molecules in which the rhodium atom displays a distorted octahedral coordination pattern (Figs. 1–3). The two dimethylglyoximato ligands define an equatorial plane and triphenylphosphine and the organo groups occupy the axial positions. The rhodium atom is slightly displaced from the mean plane of equatorial donor atoms towards the phosphorus atom. The Rh–P distances are 246.1, 244.7 and 240.9 pm for R = CH₃–CH₂–, CH₂=CH– and PhC≡C–, respectively.

Results of the X-ray structure analysis are in agreement with NMR investigations of the above mentioned complexes: both the R(Rh–P) bond lengths and the NMR coupling constants $^1J(^{103}\text{Rh}–^{31}\text{P}) = 61$, 63 and 80 Hz indicate that the *trans* influence of the organo group R is nearly

the same for the sp³- and sp²-hybridized ethyl and vinyl group, respectively. The *trans* influence of the sp-hybridized phenylacetylide group is considerably weaker [2,6]. On the other hand the series of *trans* influence, sp³ (ethyl) > sp² (vinyl) > sp (alkinyl), has been found in organomercury [3] and in other organometallic [7,8] compounds. Thus we would like to analyze the electronic structure of the above complexes in more detail by quantum-chemical calculations.

2. Calculations

For the molecular orbital study a quasirelativistic (non-empirical) version of the INDO/1
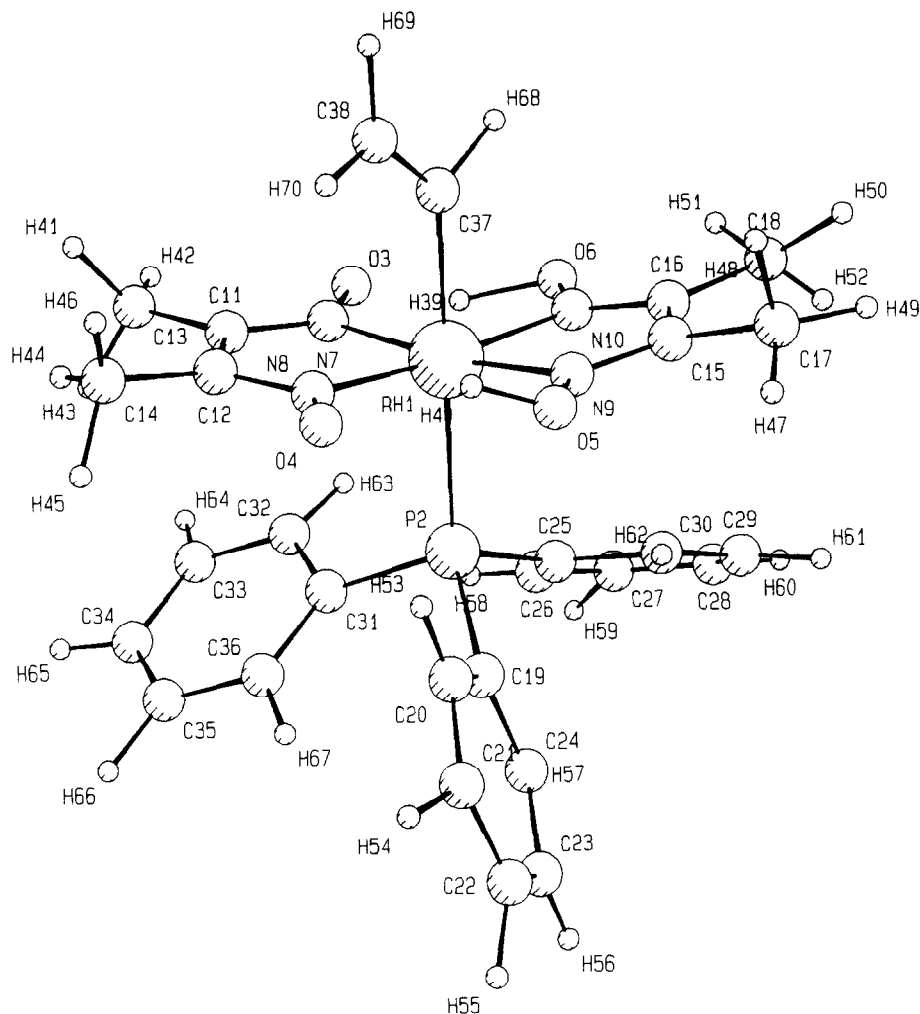
Fig. 2. Structure of [Rh(PPh₃)(dmgH)₂(CH=CH₂)] complex.

method was applied [9,10]. This method of the MO–LCAO–SCF level accounts for dominant relativistic effects which cannot be omitted for heavy atoms like rhodium. The above effects mostly are covered by the 5s- and 5p-orbital contraction (stabilization) which appears side-by-side with the 4d-orbital expansion (destabilization). The reference electron configuration of $4d^8 5s^1 5p^0$ has been used for the rhodium atom unless explicitly mentioned. An alternative choice of $4d^7 5s^2 5p^0$ (with an appropriate set of parameters generated via interpolation [9]) gave a higher total molecular energy. The systems under study contain 73, 70 and 78 atoms and 191, 189 and 215 valence orbitals for $R^- = CH_3–CH_2^-$, $CH_2=CH^-$ and

$PhC≡C^-$ groups, respectively. The atomic coordinates have been taken from the X-ray data [4–6].

Inspection of Fig. 2 shows that the complex **2** (with $R = CH_2=CH^-$) exhibits a decrease of symmetry relative to the other two complexes, **1** and **3**. Quite an unexpected localization of the hydrogen atoms with the O...H–O moiety of the dmgH⁻ ligands was found leading rather to dmg²⁻ and dmgH₂ assignment. Note that N8...H70 and O4...H70 contacts are not negligible (H70 being a part of the $CH_2=CH–$ group) and thus they may induce such a decrease of symmetry. In order to clarify this particular point we reconstructed the molecular geometry using the
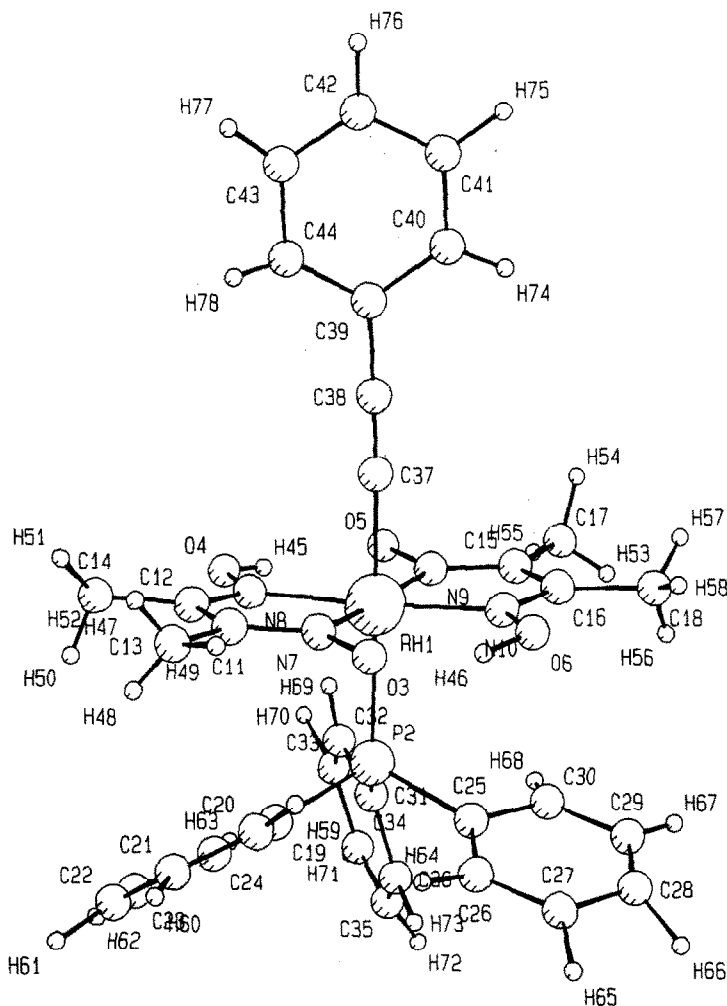
Fig. 3. Structure of [Rh(PPh$_3$)(dmgH)$_2$(C≡CPh)] complex.

averaged bonding coordinates (bond lengths, bond and dihedral angles) and assuming two possible localizations of the hydrogen atoms within the dimethylglyoximato groups: the former, **2a**, being O3...H39–O6 (as in **2**) and the latter, **2b**, being O3–H39...O6 (like in **1** and **3**). A limited geometry optimization restricted to four geometry parameters gave **2b** only slightly more stable (by 0.18 eV) with R(O3–H39) = R(O5–H40) = 109.6 pm and ϑ(N7–O3–H39) = ϑ(N9–O5–H40) = 106.0°. The geometry of **2a** relaxed to R(O6–H39) = 111.4, R(O5–H40) = 111.2 pm, ϑ(N10–O6–H39) = 105.4 and ϑ(N9–O5–H40) = 105.5°. Thus the less symmetrical struc-

ture **2a** is not energetically discriminated over the **2b** alternative.

3. Results and discussion

The bonding situation has been characterized by two quantitites: (i) the Wiberg (bond-strength) index W_{A-B} reflects the multiplicity of the chemical bond A–B; (ii) the bicentric part of the total energy E_{A-B} measures the degree of the stabilization interaction for a pair of atoms. According to the data in Table 1, the {RhPN$_4$C} chromophores contain ordinary (weaker than single) Rh–P, Rh–N and Rh–C bonds.

Table 1
Calculated bonding and atomic characteristics[a]

	CH_3–CH_2			CH_2=CH			PhC≡C		
	R_{A-B}	W_{A-B}	E_{A-B}	R_{A-B}	W_{A-B}	E_{A-B}	R_{A-B}	W_{A-B}	E_{A-B}
Bond A–B									
Rh1–P2	2.461	0.48	−16.1	2.447	0.52	−16.2	2.409	0.49	−16.1
C37–C38	1.518	1.07	−44.0	1.270	2.03	−67.7	1.183	2.68	−84.2
Rh1–C37	2.065	0.80	−21.4	2.036	0.80	−22.6	1.991	0.88	−24.5
Rh1–N7	1.989	0.56	−18.0	1.961	0.62	−19.0	1.978	0.57	−18.4
Rh1–N8	1.971	0.55	−17.9	1.951	0.63	−19.3	1.972	0.56	−17.8
Rh1–N9	1.962	0.57	−18.4	1.961	0.52	−17.3	1.980	0.59	−18.9
Rh1–N10	1.913	0.59	−18.2	1.956	0.52	−17.4	1.957	0.60	−18.4
Atom A	Q_A	d^n		Q_A	d^n		Q_A	d^n	
P2	+0.26			+0.27			+0.28		
Rh1	−0.78	8.18		−0.79	8.18		−0.77	8.10	
C37	−0.18			−0.12			−0.18		
C38	−0.13			−0.08			+0.02		
N7	+0.33			+0.28			+0.35		
N8	+0.17			+0.32			+0.14		
N9	+0.33			+0.19			+0.36		
N10	+0.20			+0.23			+0.17		

[a]Numbering of atoms according to Figs. 1–3. Distances in 10^{-10} m, energies in eV, charges in e.

Within the series of ligands $R^- = CH_3$–CH_2^-, CH_2=CH^- and PhC≡C^- the following trends are evident:

(i) the bond length C37–C38 decreases as 152, 127 and 118 pm, respectively;

(ii) the corresponding Wiberg index increases as 1.07, 2.03 and 2.68;

(iii) the bicentric part of the total energy changes as −44.0, −67.7 and −84.2 eV.

All these data confirm the increasing multiple character of the C–C bond. For the last system a remarkable weakening relative to the free acetylene molecule is probably caused by a participation of the triple bond in the conjugated system of the phenyl ring. This point has been clarified by calculation for the free PhC≡CH molecule. After the full geometry optimization the R_{A-B}, W_{A-B} and E_{A-B} parameters relaxed to 143 pm, 1.10 and −47.4 eV for the Ph–C bond and 120 pm, 2.83 and −88.0 eV for the C–C bond.

Passing from the ethyl to the vinyl and phenylacetylide complex both the Rh1–C37 and Rh1–P2 distances decrease. The latter change reflects a decreasing *trans* influence of the organo group.

From the molecular orbital study point of view this fact is followed only by the interaction energy $E_{Rh1-C37}$ (−21.4, −22.6 and −24.5 eV, respectively). Neither Wiberg indices $W_{Rh1-C37}$ (0.80, 0.80 and 0.88) and W_{Rh1-P2} (0.48, 0.52 and 0.49)
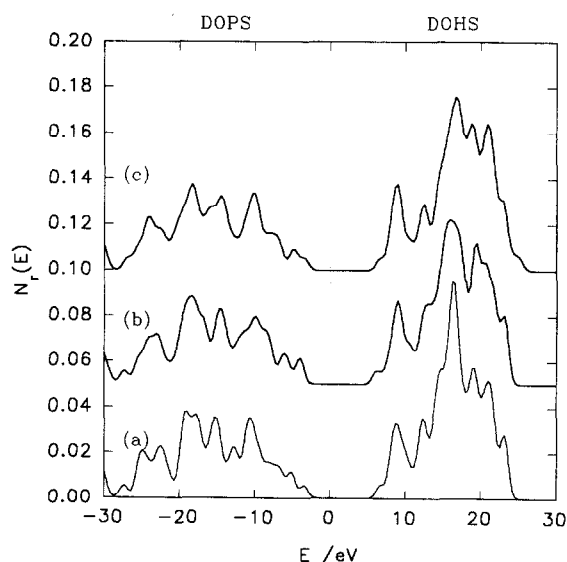

Fig. 4. Calculated total DOPS and DOHS functions: (a) $R^- = CH_3$–CH_2^-, (b) $R^- = CH_2$=CH^-, (c) $R^- = PhC$≡C^-.

nor bicentric parts E_{Rh1-P2} (-16.1, -16.2 and -16.1 eV) reflect the results of the crystal structure analysis. Effective atomic charges Q_{Rh1} (-0.78, -0.79 and -0.77 e) and Q_{P2} ($+0.26$, $+0.27$ and $+0.28$) are rather intact within the above series.

Inspection of the matrix of LCAO coefficients (191×191, 189×189 and 215×215 matrix elements, respectively) shows that molecular orbitals exhibit a great degree of delocalization in these systems. For this reason level interaction diagrams are almost impossible to construct. Moreover, a single molecular orbital loses its significance in such extended systems and the electronic structure is better characterized by the density of state (DOS) function. This is generated from the set of orbital energies of molecular orbitals via equation

$$N(\epsilon) = (2\pi\sigma)^{-1/2} \sum_i P_i \exp[-(\epsilon - \epsilon_i)^2 / 2\sigma^2]$$

where σ is a broadening parameter (typically $\sigma = 0.04$ Rydberg $= 0.544$ eV); ϵ_i is the orbital energy of the ith MO and P_i stands for the projection weight when projected DOS are generated.
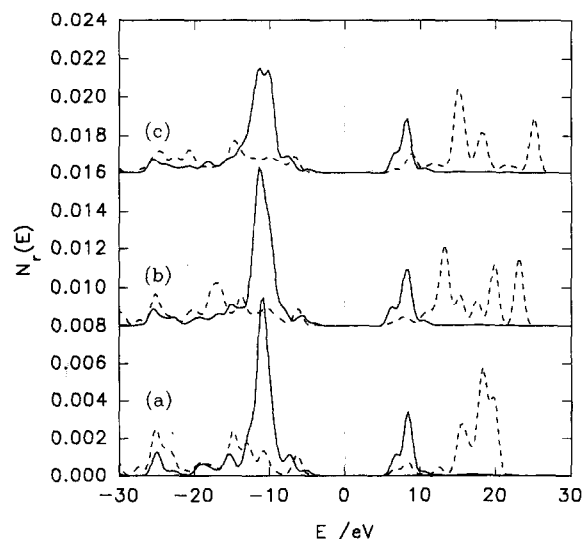
The latter quantity may be a net orbital population (e.g. a portion of Rh(4d) or C(2p) atomic orbitals) with the ith MO. The density of particle states (DOPS) function covers the occupied orbitals (below the Fermi level) whereas the density of hole states (DOHS) function embraces the unoccupied MOs. Actually the normalized density functions, $N_r(E) = N(E)/n_{AO}$, have been plotted, n_{AO} being the number of atomic (molecular) orbitals in the system.

The calculated DOPS and DOHS functions are presented in Figs. 4 and 5 within the energy interval of -30 to $+30$ eV. The Rh(4d) projection of DOPS indicates that the metal levels ($d^{8.1}$) do not enter the highest occupied MOs but they are situated below a set of ligand orbitals. The rest of them ($d^{1.9}$) are situated within the set of the lowest unoccupied MOs as seen from DOHS. The C(2p) projection of DOPS for organic group R exhibits only a small overlap with Rh(4d) projection of DOPS below -10 eV (this is enlarged in Fig. 5 to be better visible). It indicates a slight C(2p)– Rh(4d) mixing within the corresponding MO and consequently only a slight degree of activation of the C–C bonds within the R groups. The last finding agrees with the above assignment of the C–C bond multiplicity.

Fig. 5. Projected DOPS and DOHS functions: (———) Rh(4d) projection; (- - -) C_2(2p) projection. (a) $R^- = CH_3-CH_2^-$, (b) $R^- = CH_2=CH^-$, (c) $R^- = PhC \equiv C^-$.

References

[1] R. Boča, J. Kožíšek and D. Steinborn, J. Mol. Catal., 84 (1993) 261.
[2] D. Steinborn and M. Ludwig, J. Organomet. Chem., 463 (1993) 65.
[3] D. Steinborn, R. Taube, R. Ragelia and W. Höbold, J. Organomet. Chem., 210 (1981) 139.
[4] V. Kettmann, M. Dunaj-Jurčo, D. Steinborn and M. Ludwig, Acta Crystallogr., C, 50 (1994) 1239.
[5] M. Dunaj-Jurčo, V. Kettmann, D. Steinborn and M. Ludwig, Acta Crystallogr., in press.
[6] M. Dunaj-Jurčo, V. Kettmann, D. Steinborn and M. Ludwig, Acta Crystallogr., in press.
[7] T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
[8] D. Steinborn, Angew. Chem., Int. Ed. Engl., 31 (1992) 401.
[9] R. Boča, Int. J. Quantum Chem., 34 (1988) 385.
[10] R. Boča, Program MOSEM7. Slovak Technical University, Bratislava 1988, unpublished.