Organometallics **2008,** *27,* 2873–2876

Notes

Influence of the Nature of the Ligand on Dirhodium(II) Carbene Species: A Theoretical Analysis

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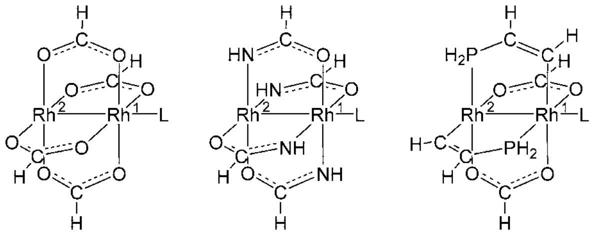
Received January 31, 2008

Summary: The influence of three prototypic families of bridging ligands (carboxylate, carboxamidate, and ortho-metalated arylphosphines) on the electronic structure of dirhodium(II) carbene complexes was theoretically analyzed. The calculations indicated that the electron donation of the ligand to the Rh atom, rather than the chelating ability or the metal−ligand orbital mixing, was responsible for tuning carbene charge via back-donation, which can influence the reactivity and selectivity of the dirhodium complexes in catalytic carbene transfer reactions.

Dirhodium complexes are widely known as effective and selective catalysts for Lewis acid catalyzed processes, carbene transfer reactions, and chemical oxidations.[1] The most fruitful research involves metal carbene species, which are generated from the extrusion of nitrogen in the reaction of diazo compounds with metal complexes. Once formed, carbenoids can undergo a large spectrum of transformations, such as cyclopropanation, dipolar cycloaddition, ylide formation, and C−H insertion, among others.[2] A number of experimental studies have shown that the chemoselectivity of the dirhodium carbenoids is greatly affected by the nature of the bridging ligand attached to the metal.[3–8] The selectivity of carboxylate and carbamidate dirhodium catalysts has been correlated with their oxidation potential, which may reflect the degree of electron deficiency and, hence, the electrophilicity of the Rh_2 carbenoid intermediate.[8] However, complexes bearing ortho-metalated phosphine ligands exhibit similar selectivity in carbene-transfer reactions to Rh_2(caprolactamate)$_4$, in spite of the much more positive oxidation potential of the former (∼1000 mV vs ∼10 mV, respectively).[4] Pirrung et al.[7] have suggested that modulation of electronic properties of the bridging ligands in carboxylate type complexes could increase their selectivity by increasing the back-donation from the metal complex to the carbene moiety. The stretching frequency for the CO bound to Rh complexes suggests a π-back-bonding ability of the carboxamidate and ortho-metalated phosphine dirhodium complexes higher than that of dirhodium tetraacetate.[5]

Chart 1. Model Dirhodium Catalysts



1a **1b** **1c** L = ∅

2a **2b** **2c** L = $CH(CO_2Me)$

Experimental results show intriguing variations on the selectivity of the Rh complexes upon modification of bridging ligands, and it would be useful to determine the influence of

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10.1021/om800089k CCC: $40.75

Table 1. Description of Some Occupied Molecular Orbitals and NPA Atomic Charges (au) in Tetraformate (1a), Tetraformamide (1b), and Ortho-Bis-Cyclometalated Phosphine (1c) Complexes[a]

	1a			**1b**			**1c**		
orbital	*E* (eV)	L(p)[b]	Rh(d)[c]	*E* (eV)	L(p)[b]	Rh(d)[b]	*E* (eV)	L(p)[b]	Rh(d)[b]
δ^* (HOMO)	−6.69	30	65	−5.17	37	59	−6.27	34[d]	51
π^*	−6.98	14	80	−6.10	8	90	−6.39	9	86
π^*	−6.98	14	80	−6.12	8	91	−6.42	11	86
q_{NPA} (Rh)		0.92			0.81			0.45	

[a] Only contributions >7% are reported. [b] Contribution of the atomic p orbitals of the bridging ligands. [c] Contribution of the d orbitals of the Rh atoms to the corresponding molecular orbital. [d] Contribution of the formate and ortho-metalated phosphine ligands to the metal−ligand orbital: the contribution represents 22% for the formate ligands, whereas it could be labeled as a nonbonding contribution for the ortho-metalated phosphine moieties.

the nature of the ligand, not only on the electronic structure of the Rh complex but also on the key rhodium carbene intermediate. To date, theoretical studies on the influence of the ligands in ortho-metalated dirhodium phosphine complexes have been limited to determining to what extent the acidity of the complex is affected by modification of its bridging ligands or by a Lewis base attached to one of its axial positions.[9] Here, we report density functional theory (DFT) studies[10] of three prototypic ligand families, namely tetracarboxylate, tetracarboxamidate, and ortho-metalated phosphines (**1a**−**c** in Chart 1). The influence of the ligand on the dirhodium carbene properties was studied on the methoxycarbonyl carbene complexes **2a**−**c** (Chart 1).

Initially, we optimized the structure of the dirhodium formate complex **1a**, dirhodium formamidate complex **1b**, and ortho-bis-cyclometalated phosphine dirhodium complex **1c**, in order to analyze how the geometry and the electronic structure of the Rh_2 core are affected by the different ligands. The Rh−Rh computed distances follow this order: **1a** < **1b** < **1c** (2.40, 2.44, and 2.51 Å, respectively). These distances can be directly correlated to the calculated nonbonded distances between the two chelating atoms in the free ligands: O···O (2.30 Å), O···N (2.33 Å), and C···P (2.73 Å).

The Rh−Rh bonding interaction in $Rh_2(O_2CR_3)_4$ complexes has been already analyzed.[11−13] However, it is interesting to examine how the electronic structure of the Rh−Rh bond varies when the bridging formate groups in **1a** are changed by formamidate groups, as well as when two formate groups in **1a** are replaced by two ortho-metalated phosphine ligands. The ground-state ordering of molecular orbitals found for the Rh−Rh bond in **1a** at the B3LYP level ($\sigma^2 \approx \pi^4 > \delta^2 > \pi^{*4} \approx \delta^{*2} > \sigma^*$) agrees with early SCF-Xα calculations.[13] The two highest occupied orbitals of **1a** are the Rh−Rh δ^* and π^*, δ^* being only 0.29 eV higher in energy than π^*. For **1b**,**c**, the ordering is the same as in complex **1a**, but the energy of δ^* (HOMO) in **1b** is significantly higher than in **1a**,**c** (>1 eV). Since oxidation potentials should give a good approximation of the HOMO energy levels, we should note the correlation between the computed energies for the δ^* orbitals (Table 1) and the experimental oxidation potentials for analogous dirhodium compounds.[4,10,14] Thus, while a reversible oxidation is observed at 1170 and ∼1000 mV for $Rh_2(OAc)_4$ and $Rh_2(O_2CMe)_2[PPh_2(C_6H_4)]_2$, respectively, the potential of $Rh_2(HNOCMe)_4$ shifts to a significantly less positive value (150 mV).

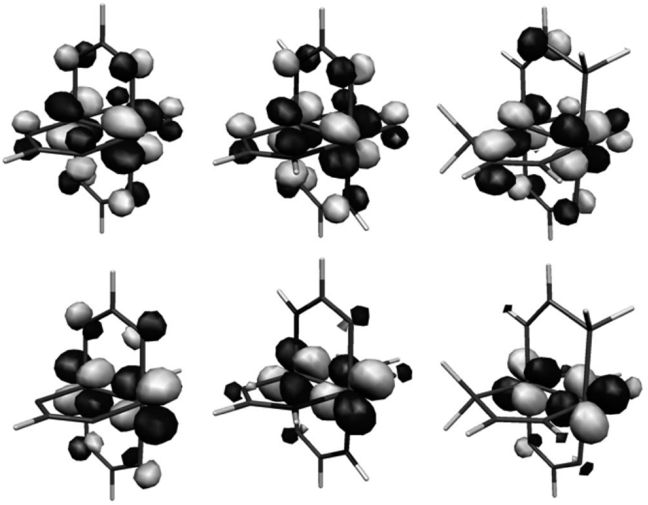

Figure 1. Representation of selected frontier orbitals δ^* (HOMO) (up) and π^* (HOMO-1) (down) for **1a** (left), **1b** (middle) and **1c** (right).

Table 1 collects the calculated frontier orbital energies, the most important atomic orbital contributions, and the natural population analysis (NPA) charges[15] at the rhodium atoms for **1a**−**c**. Figure 1 shows the Rh−Rh δ^* and π^* molecular orbitals. The variations in electronic structure can be discussed according to different types of ligand effects, such as chelating, orbital mixing, and electron density donation. First, one may expect a decrease of the π^* and δ^* orbital energies with the lengthening of the Rh−Rh distance, due to the release of the antibonding interaction of the metal orbitals. Nevertheless, we did not observe any correlation between Rh−Rh distances and orbital energies (Table 1). This feature is in agreement with a single-bond character between the rhodium atoms, leading to weak π and δ interactions. Another possible factor responsible for the HOMO energy differences is the metal−ligand orbital mixing (Table 1). The acetate ligand,[12] and also amidate, possesses $p^{\perp}$ orbitals of appropriate symmetry to combine with the δ^* Rh−Rh orbital, forming an antibonding combination in the HOMO labeled as δ^*. Among the series of dirhodium complexes,

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(10) Calculations were carried out with the Gaussian03 series of programs using the B3LYP functional. The basis set for Rh and P atoms was LANL2DZ, which in the case of P was supplemented by a d shell. For the atoms O and N directly attached to rhodium and the ester group of the carbene we used the 6-31G(d) basis set; for the rest of the atoms the 6-31G basis set was used. See the Supporting Information for further details.

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(14) The calculations on experimentally closer complexes with two $NCCH_3$ ligands axially bound to **1a**−**c** show the same ordering of frontier molecular orbitals and an analogous correlation between the HOMO energies and the oxidation potentials (see Table S5 and Figure S2 in the Supporting Information).

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Table 2. NPA Atomic Charges (au), Rhodium−Carbene Bond Distances (Å), and Interaction Energies (kcal mol^{-1}) in Methoxycarbonyl Carbene Complexes 2a−c and C−O Stretching Frequencies (ν_{CO} in cm^{-1}) for CO Bound to 1a−c

	2a	2b	2c
q_{NPA} (Rh$_1$, Rh$_2$)	0.92, 0.72	0.84, 0.59	0.49, 0.24
d (Rh−C$_{carbene}$)	1.940	1.917	1.901
ΔE_{int}	−46.2	−51.5	−54.4
ν_{CO} (exptl)	2104 (2098)[a]	2060 (2046)[b]	2062 (2041)[a]

[a] Experimentally determined values for the analogous complexes $Rh_2(CH_3CO_2)_4 \cdot CO$ and $Rh_2(C_6H_4P(C_6H_5)_2)_2(CH_3CO_2)_2 \cdot CO$; taken from ref 5. [b] Value for $Rh_2(CH_3CONH)_4 \cdot CO$ taken from ref 18.

complex **1b** has the largest antibonding metal−ligand orbital mixing (37% of p$^{\perp}$ ligand orbital in **1b** versus 30% in **1a** and 34% in **1c**), and consequently its δ* (HOMO) orbital possesses the highest energy, indicating the relevance of this effect in the oxidation potentials. On the other hand, there is a very little ligand character in the second highest occupied π* orbital, being mainly localized at the rhodium atoms. We also calculated the NPA charges[15] of the rhodium atoms to acquire more information on the electron-transfer properties of the ligands (see Table 1). On going from the tetraformate complex **1a** to the ortho-metalated phosphine complex **1c**, the electron density at the metal center increases, clearly manifesting the larger donation capability of the ortho-metalated phosphine ligand.

As we mentioned above, one of the most outstanding reactions catalyzed by these dirhodium complexes involves formation of metallocarbene species, which are postulated as the crucial intermediates in carbene transfer reactions. Therefore, we analyzed the effect of the nature of the ligand on the dirhodium−carbene bond, using the methoxycarbonyl carbene complexes **2a−c** as models (Chart 1, Table 2). Initially, we systematically searched for all possible isomers resulting from rotations around the Rh−C$_{carbene}$ bond and the carbene carbon−carbon σ bond.[16] No significant variations in energies and geometries along the rotational isomers series were found (see the Supporting Information for details).

As previously reported for **2a**,[17] we found that the methoxycarbonyl moiety is nearly orthogonal to the carbene plane, which prevents conjugation of the carbene 2p orbital and the CO π bond. The same feature is observed for the other two carbene complexes **2b**,**c**, for which we calculated that the dihedral angle deviates from planarity by 83 and 54°, respectively. Upon coordination of the carbene ligand, the Rh−Rh bond is only slightly elongated with respect to the parent dimer (by 0.074, 0.073, and 0.102 Å in **2a−c**, respectively). Accompanying Rh−Rh bond weakening, the positive charge at the Rh(L) metal center drops 0.20 (**2a**), 0.22 (**2b**), and 0.21 au (**2c**) (compare the charge of Rh in Table 1 with that of Rh(L) in Table 2). More interestingly, the calculated Rh−carbene bond distances were 1.940 (**2a**), 1.917 (**2b**), and 1.901 Å (**2c**), and an evident correlation between them and the rhodium−carbene bond strength (ΔE_{int}) was found (see Table 2). The computed energy values for the formation of compound **2** from the respective compound **1**, of −46.2 (**a**), −51.5 (**b**), and −54.4 kcal mol^{-1} (**c**), would reflect how the bridging ligand nature modifies the interaction of the dimetallic fragment with the carbene moiety. These bond energy values lay between those previously computed for model carbenoids arising from the interaction of **1a** with other carbenes, such as CH_2 (−57.7 kcal mol^{-1}) and imidazole 2-ylidene (−45.5 kcal mol^{-1}).[18c]

Previous investigations[17,18] have shown that the Rh−carbene binding in dirhodium complexes can be characterized by two types of interactions: C$_{carbene}$ → Rh$_2$ σ donation and C$_{carbene}$ ← Rh$_2$ π back-donation. The σ donation can be described as the interaction between the filled nonbonding in-plane carbene orbital and the Rh−Rh σ* orbitals, C$_{carbene}$(sp^2) → Rh(σ*), while the π back-donation is the interaction between the Rh−Rh π* orbital and the vacant p carbene orbital, C$_{carbene}$(p) ← Rh(π*) (see Scheme 1). The results of natural bonding orbital (NBO) analysis[15] on the rhodium−carbene bond are summarized in Table 3. The population at the p$^{\perp}$ orbital of carbene carbon (C$_{carbene}$(p)) can be used to gauge the amount of back-donation and, therefore, the electrophilicity of the carbene center. On going from **2a** to **2c**, the population increases, indicating a reduction of the electrophilicity of the carbene carbon. In turn, the population of the sp^2 lone pair orbital involved in the σ rhodium−carbene bond (C$_{carbene}$(sp^2)) decreases in the order **2a** > **2b** > **2c**, in agreement with the synergic nature of donation/back-donation interactions. The stabilization energy of the interaction between the filled Rh(d) and the empty C$_{carbene}$(p) NBO orbitals follows the same trend: the greater the back-donation, the greater the stabilization energy (Table 3).

Scheme 1. Model of the Orbital Interaction between the Rh$_2$ Core and the Carbene Fragment

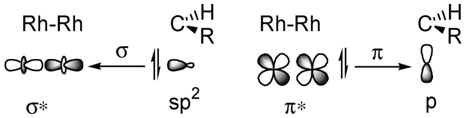

Table 3. NBO Analysis of the Dirhodium Methoxycarbonyl Carbene Complexes 2a−c

		2a	2b	2c
C$_{carbene}$ population (au)	p(π)	0.47	0.53	0.58
	sp^2(σ)	1.39	1.38	1.35
E_{stab}[a] (kcal mol^{-1})	Rh(d) → p(π)	39.4	52.5	59.0
	sp^2(σ) → Rh(d)	217.6	235.8	260.7

[a] NBO stabilization energies between the donor and acceptor NBO orbitals.

At this point, we analyzed the effect of the metallated aromatic ring in the *ortho*-metallated phosphine complexes, comparing the results of model **2c** with those of an enlarged model including the aromatic ring [$Rh_2(OOCH)_2\{(C_6H_4)PH_2\}_2$(carbene)] **2c'**. We did not found appreciable variation on the geometric and electronic features upon introduction of the aromatic ring.

Experimentally, the stretching frequency (ν_{CO}) for the CO bound to the rhodium complex has been also used as an indication of metal fragment back-donation capability. They roughly decrease in the order $Rh_2(OOCCH_3)_4$[5] > $Rh_2(HNCOCH_3)_4$[19] ≈ $Rh_2(OOCCH_3)_2(PC)_2$ (PC = ortho-metalated phosphines),[5] indicating the order of increasing π-back-bonding ability of the catalysts. The computed frequencies for the CO bound to **1a−c** (Table 2) approximately follow the same trend as the experimental ones for the analogous compounds and correlate with the estimated back-donation values (see p(π) population in Table 3). It is worth mentioning that experimental results have shown that $Rh_2(OOCCH_3)_2(PC)_2$ and carboxamidate complexes are more selective (chemo- and regioselective) in carbene transfer reactions than the tetraacetate complex.[5,20] For example, for competitive intramolecular cyclopropanation versus aromatic substitution with a diazo ketone, use of $Rh_2(OAc)_4$ results in similar amounts of products arising from both type of transformations, while Rh(II) caprolactamate and $Rh_2(OOCCH_3)_2(PC)_2$ catalysts provide only the cyclopropanation product.[5,19] It is not the focus of this paper to quantitatively assess the selectivity of any specific transformation, just to evaluate the different influence of three prototypic ligand families on dirhodium carbene intermediates. An assumption in this correlation between the amount of back-donation and the selectivity is that the considered reactions are electrophilic processes, in which nucleophilic groups such as C═C double, aromatic C−H, or aliphatic C−H bonds compete for the electrophilic carbene carbon with a vacant 2p orbital.[17] Thus, the increasing back-donation makes the carbene less electrophilic via partial population of the 2p orbital and therefore less reactive toward the poorer nucleophiles.

The origin of increased back-donation, and as a consequence a higher selectivity, in amidates and ortho-metalated phosphine complexes with respect to those of carboxylates merits further discussion. The chelation effect could shorten the rhodium−rhodium distance and raise the energy of the π^* orbitals of the metal fragment, favoring back-donation to the carbene. However, carboxylate complex **1a**, which possesses the shortest rhodium−rhodium distance, has the lowest carbene binding energy in the series. Concerning the metal−ligand orbital mixing factor, unlike the δ^* orbital, the π^* orbitals show little metal−ligand antibonding character for all the complexes. Therefore, neither ligand chelation nor metal−ligand orbital mixing seems to be the predominant factor for the carbenoid stability. A correlation between the NPA charges at the rhodium atoms in the metal complex (Table 1) and the amount of back-donation at the carbene carbon (Table 3) is observed; the higher the ligand electron density donation ability (which follows this order: O,O < N,O < P,C), the larger the back-donation from the metal fragment to the carbene. Additionally, the amidate complex **1b** has π^* orbitals with the highest energy among the series, which can also contribute to an increase in the back-donation ability of the metal complex to the carbene.

We can summarize that the lower oxidation potential of the complex **1b** compared with those of **1a**,**c** is a consequence of the destabilization of the HOMO (δ^*) arising from the metal−ligand orbital mixing. The higher selectivity observed for the amidate **1b** and the ortho-metalated phosphine complex **1c** in outstanding reactions involving the formation of Rh carbene species can be explained as being due to the capacity of amidate and ortho-metalated phosphine ligands to donate electron density to the rhodium center, which increases $\mathrm{Rh} \rightarrow \mathrm{C}_{\mathrm{carbene}}$ π back-donation and reduces the electrophilicity of the carbene carbon.

Acknowledgment. This work was supported by the Spanish Ministry of Science and Technology (No. CTQ2005-06909-C02-01/BQU) and by the Generalitat de Catalunya (No. 2005GR-00104).

Supporting Information Available: Text, tables, and figures giving computational details, results of the conformational analysis of carbene complexes **2a**−**c**, calculated structural parameters of **1a**−**c**, **2a**−**c**, and carbonyl complexes, and 3D representations of frontier molecular orbitals for **1a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The rotational barriers are expected to be very low because there are two filled Rh $4d_{xz}$ and $4d_{xy}$ orbitals available for back-donation to the carbene vacant 2p orbital.[17] Thus, for the sake of simplicity, we base our discussion only on the lowest energy minimum for each ligand.

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