# *Articles*

# C−H Bond Activation of Methane Promoted by ($\eta^5$-Phospholyl)Rh(CO)$_2$: A Theoretical Perspective

Eder S. Xavier,[†] Wagner B. De Almeida,[†] Júlio Cosme S. da Silva,[‡] and
Willian R. Rocha*[,‡]

*Laboratório de Química Computacional e Modelagem Molecular (LQC-MM),
Departamento de Química-ICEX, Universidade Federal de Minas Gerais, 31270-901,
Belo Horizonte, MG, Brazil, and Departamento de Química Fundamental-CCEN,
Universidade Federal de Pernambuco, 50670-901, Cidade Universitária, Recife, PE, Brazil*

*Received December 7, 2004*

Quantum mechanical calculations at the MP4(SDQ)//MP2 were carried out to evaluate, a priori, the reactivity of [($\eta^5$-phospholyl)Rh(CO)$_2$] toward C−H bond activation of methane. The compound [($\eta^5$-phospholyl)Rh(CO)$_2$] is an analogue of [(Cp)Rh(CO)$_2$], which is well known to activate alkanes of moderate sizes. Our results show that compound [($\eta^5$-phospholyl)Rh(CO)$_2$] has a singlet ground state, with the lowest triplet state lying 55.1 kcal/mol above it. The calculation of the electronic spectrum of this compound revealed that the MLCT charge transfer band (M → CO) that leads to CO dissociation occurs at much higher energy (5.28 and 5.54 eV) than the value for the parent Cp compound. The methane substrate interacts with the monocarbonyl compound, generated after CO dissociation, forming a $\eta^2$ adduct, which is stabilized by 11.7 kcal/mol. The C−H bond activation of methane proceeds through a three-center transition state with a small activation enthalpy of 6.1 kcal/mol, relative to the $\eta^2$ adduct intermediate. Comparisons with the [(Cp)Rh(CO)$_2$] analogue are made and discussed. The results presented in this work suggest that the compound [($\eta^5$-phospholyl)Rh(CO)$_2$] can be used to activate the C−H bond of alkanes.

## Introduction

Over the past years, the intermolecular C−H bond activation of alkanes, promoted by transition metal complexes, by an oxidative addition mechanism, has attracted much attention from the chemical community.[1] This is in part motivated by the fact that the cleavage (or activation) and selective functionalization of an “unreactive” C−H bond of an alkane molecule would lead to the generation of compounds with direct economic impact, since alkanes are the main constituents of natural gas. The activation of a C−H bond of alkanes by an oxidative addition mechanism is an intriguing event because alkanes are poor electron donors and poor electron acceptors,[2] which would make its coordination to a transition metal complex, to undergo an addition of the metal into the C−H bond, an unlikely process. However, in a pioneering work, Janowicz and Bergman[3] and also Graham and coworkers[4] showed that metallocene-like complexes of the type [(Cp)M(CO)$_2$] (Cp = $\eta^5$-C$_5$H$_5$ and M = Ir or Rh) are able to activate the C−H bond of alkanes of moderate size, leading to isolable products, in which new metal−carbon and metal−hydrogen bonds are formed. The reaction is initiated by photoinduced loss of CO, forming a coordinatively unsaturated intermediate [(Cp)M(CO)] species, which in the presence of alkane (R−H) undergoes oxidative addition reaction, leading to the formation of a new, isolable, species, [(Cp)M(CO)(H)(R)], as can be seen in Scheme 1.

The oxidative addition mechanism and the nature of the intermediated involved in this reaction were confirmed by various experiments including low-temperature matrix isolation,[5] pulsed laser photolysis,[6] and time-resolved infrared experiments.[7] Despite the understanding of the first step of this reaction (CO loss

---

* To whom correspondence should be addressed. Fax: +55 81 2126-8442. E-mail: wrocha@ufpe.br.

[†] Universidade Federal de Minas Gerais.

[‡] Universidade Federal de Pernambuco.

(1) For reviews on this subject, see: (a) Muetterties, E. L. *Chem. Soc. Rev*. **1983**, *12*, 283. (b) Bergman, R. G. *Science* **1984**, *223*, 902. (c) Crabtree, R. H. *Chem. Rev*. **1985**, *85*, 245. (d) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (e) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315. (f) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res*. **1995**, *28*, 154. (g) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev*. **1997**, *97*, 2879, references therein.

(2) Hall, C.; Perutz, R. N. *Chem. Rev*. **1996** *96*, 3125.

(3) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc*. **1982**, *104*, 352. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc*. **1983**, *105*, 3929.

(4) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc*. **1982**, *104*, 3723. (b) Hoyano, J. A.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc*. **1983**, *105*, 7190.

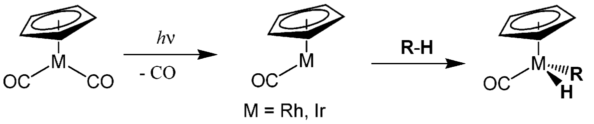
(5) Haddleton, D. M.; McCramley, A.; Perutz, R. N. *J. Am. Chem Soc*. **1988**, *110*, 1810.

(6) Belt, S. T., Grevels, F. W., Klotzbücher, W. E.; McCramley, A.; Perutz, R. N. *J. Am. Chem. Soc*. **1989**, *111*, 8373.

(7) Yang, H.; Kotz, K. T.; Asplund, M. C.; Wilkens, M. J.; Harris, C. B. *Acc. Chem. Res*. **1999**, *32*, 551.

10.1021/om049036g CCC: $30.25

**Scheme 1**



from the dicarbonyl complex by photoexcitation), the fast reaction kinetics and generation of short-lived intermediates along the reaction pathway make the understanding of the detailed mechanism a difficult task. In this regard, quantum mechanical calculations may help to elucidate the nature of the intermediates, reaction mechanism, and energy barriers involved in this reaction. In fact, since the publication of the pioneering experimental results,[3,4] this C−H activation reaction has been studied extensively by theoretical methods.[8−15] These theoretical studies have contributed to the understanding of the reaction mechanism and nature of the intermediates involved,[8−11,15] the exothermicity of the reaction,[12] the origin of the low quantum yield for the C−H activation, and the inertness of [Co(Cp)(CO)] toward alkane activation, in contrast with its Rh and Ir congeners.[11,13]

In this work we report a perspective, based on quantum mechanical calculations, on the use of the [($\eta^5$-phospholyl)Rh(CO)$_2$] compound to promote C−H activation of methane. The five-membered-ring phospholyl ligand, [C$_4$H$_4$P]$^-$, hereafter called **Pp**, is an analogue of cyclopentadienyl, in which a C−H unit is replaced by phosphorus. This ligand exhibit a rich coordination chemistry, which has been the subject of several review articles.[16] In recent years phospholyl and its derivatives have been successfully employed as an alternative ligand to replace cyclopentadienyl in some metallocene-based catalytic cycles, for example, olefin polymerization[17−19] and asymmetric catalysis.[20,21] These studies have shown that the activity and stereo- and regioselectivity of metallocene-based catalyst can be changed by replacing one or both Cp's by phospholyl ligands. Very recently[22] we have studied the structure and nature of the metal−ligand interactions in mixed iron(II) compounds of the type Fe(Cp)(**L**), where **L** stands for the ligands [C$_5$H$_5$], [C$_4$H$_4$P]$^-$, [1,3-P$_2$C$_3$H$_3$]$^-$, and [1,2,4-P$_3$C$_2$H$_2$]$^-$. We have found, at the MP4(SDQ)//B3LYP level of theory, that changing a CH group of the cyclopentadienyl ligand by phosphorus changes drastically the electronic structure of the resulting phosphametallocene and, thus, the reactivity of these compounds. These results prompted us to further investigate the reactivity of phospholyl complexes, and so, in the present work we investigate the reactivity of ($\eta^5$-phospholyl)dicarbonylrhodium, [($\eta^5$-phospholyl)Rh(CO)$_2$], toward C−H activation of methane. The compound [($\eta^5$-phospholyl)Rh(CO)$_2$] is a model of [(2,5-di-*tert*-butylphospholyl)Rh(CO)$_2$], synthesized by Mathey and co-workers,[23] in which the bulky *tert*-butyl groups have been replaced by hydrogen. In this work quantum mechanical calculations, at the MP4(SDQ)//MP2 level, were carried out to investigate the structures, excited states, nature of the intermediates, energetics, and reaction mechanism for the methane activation promoted by [($\eta^5$-phospholyl)Rh(CO)$_2$]. The results obtained are compared with the reported values for the cyclopentadienyl analogue in order to see the efficiency of the phospholyl compound in this kind of reaction.

## Theoretical Details

Full unconstrained geometry optimization and frequency calculations were performed at the Møller−Plesset perturbation (MP2) level of theory.[24] The inner shell electrons (1s, 2s, 2p, 3s, 3p, and 3d) of rhodium were treated by the effective core potential of Hay and Wadt (LANL2DZ),[25] and the valence electrons (4s, 4p, 4d, and 5s) were included explicitly in the calculations, using the associated double-$\zeta$ basis set with the original [55/5/5] contraction scheme. The C, P, H, and O atoms of the ligands were described by the correlated consistent polarized valence double-$\zeta$ basis set (cc-pVDZ) of Woon and Dunning.[26] The transition state structure obtained on the potential energy surface for the C−H bond activation was located using the quadratic synchronous approach of Schlegel and co-workers,[27] starting with a low level computed Hessian matrix for a suitable guess transition state structure. To obtain better energetic results, single-point energy calculations on the MP2 optimized geometries were performed using fourth-order Møller−Plesset perturbation theory (MP4), with single, double, and quadruple excitations, called MP4(SDQ)//MP2, which is our standard method for the study of catalytic reactions promoted by organometallic catalysts.[28]

All stationary points located on the potential energy surfaces were characterized as minima (no imaginary frequencies) or first-order transition state (characterized by having one imaginary frequency) through harmonic frequency calculations. To better understand the reaction mechanism for the C−H bond activation of methane, the intrinsic reaction pathway (IRC)[29]

---

(8) Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177.

(9) Song, J.; Hall, M. B. *Organometallics* **1993**, *12*, 3118.

(10) Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 799.

(11) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487.

(12) Couty, M.; Bayse, C. A.; Jiménez-Cataño, R.; Hall, M. B. *J. Phys. Chem.* **1996**, *100*, 13976.

(13) (a) Su, M.-D, Chu, S.-Y. *Organometallics* **1997**, *16*, 1621. (b) Su, M.-D, Chu, S.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 5373. (c) Su, M.-D, Chu, S.-Y. *J. Phys. Chem. A* **1997**, *101*, 6798. (d) Su, M.-D, Chu, S.-Y. *J. Phys. Chem. A* **2001**, *105*, 3591.

(14) Hu, Z.; Boyd, R. J.; Nakatsuji, H. *J. Am. Chem. Soc.* **2002**, *124*, 2664.

(15) Bergman, R. G.; Cundari, T. R.; Gillespie, A. M.; Gunnoe, T. B.; Harman, W. D.; Klinckman, T. R.; Temple, M. D.; White, D. P. *Organometallics* **2003**, *22*, 2331.

(16) For recent reviews see: (a) Mathey, F. *J. Organomet. Chem.* **2002**, *646*, 15. (b) Carmichael, D.; Mathey, F. *Top. Curr. Chem.* **2002**, *220*, 27. (c) Weber, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 563. (d) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578.

(17) Janiak, C.; Versteeg U.; Lange K. C. H.; Weimann, R.; Hahn E. *J. Organomet. Chem.* **1995**, *501*, 219.

(18) De Boer, E. J. M.; Gilmore, I. J.; Korndorffer, F. M.; Horton, A. D.; van der Linden, A.; Royan, B. W.; Ruisch, B. J.; Schoon, L.; Shaw, R. W. *J. Mol. Catal. A* **1998**, *128*, 155.

(19) Brown, S. J.; Gao, X.; Harrison, D. G.; Koch, L.; v. H. Spence, R. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5445.

(20) Garrett, C. E.; Fu, G. C. *J. Org. Chem.***1998**, *63*, 4168.

(21) Ganter, C.; Brassat, L.; Glinsböckel, C.; Ganter, B. *Organometallics* **1997**, *18*, 5444.

(22) Bruce, E. D. V.; Rocha, W. R. *Organometallics* **2004**, *23*, 5308.

(23) (a) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1167. (b) Charrier, C.; Bonnard, H.; Mathey, F.; Neibecker, D. *J. Organomet. Chem.* **1982**, *231*, 361. (c) Caffyn, A. J. M.; Carmichael, D.; Mathey, F.; Ricard, L. *Organometallics* **1997**, *16*, 2049.

(24) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

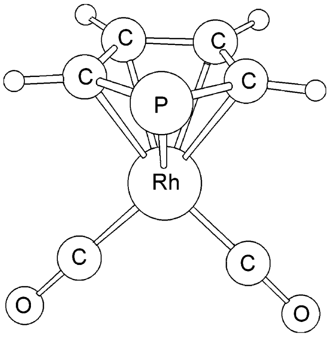
(25) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(26) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(27) Peng, C.; Schlegel, H. B. *Isr. J. Chem.***1993**, *33*, 449.

(28) (a) Rocha, W. R.; De Almeida, W. B. *Organometallics* **1998**, *17*, 1961. (b) Rocha, W. R.; De Almeida, W. B. *J. Braz. Chem. Soc.* **2000**, *11*, 112. (c) Rocha, W. R.; De Almeida, W. B. *J. Comput. Chem.* **2000**, *21*, 668. (d) Rocha, W. R. *J. Mol. Struct.* (*THEOCHEM*) **2004**, *677*, 133.

(29) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.



**PpCO2**

| Parameter | Singlet | Triplet |
|---|---|---|
| r (Rh-CO) | 1.831 | 1.922 |
| r (CO) | 1.166 | 1.160 |
| r (Rh-XX) | 1.901 | 2.116 |
| r (Rh-P) | 2.558 | 2.617 |
| r (Rh-$C_{ring}$)$_{av.}$ | 2.266 | 2.473 |
| ∠ (CO-Rh-CO) | 89.9 | 101.2 |
| ∠ (CO-Rh-XX) | 135.1 | 123.5 |
| ∠ (C-P-C) | 86.1 | 88.6 |
| ∠ (C-C-C)$_{av.}$ | 111.1 | 112.2 |

**Figure 1.** MP2 optimized structural parameters for the singlet and triplet electronic states of the [($\eta^5$-phospholyl)-Rh(CO)$_2$], **PpCO2**, compound.

was computed, using the Gonzalez–Schlegel second-order path following,[30] starting from the optimized transition state structure, with a steplength of 0.100 (amu)$^{1/2}$·bohr. All ab initio calculations reported in this work were performed using the Gaussian 98 program.[31]

## Results and Discussion

**Structure and Excited States of [($\eta^5$-phospholyl)Rh(CO)$_2$].** The [($\eta^5$-phospholyl)Rh(CO)$_2$], **PpCO2**, complex was optimized in the singlet and triplet electronic states, and the optimized MP2 structural parameters are shown in Figure 1. In the singlet state the Rh–CO bond has a value of 1.831 Å, the coordinated CO ligand has a bond length of 1.166 Å, and the distance between the rhodium atom and the center of the phospholyl ligand, *r*(Rh–XX), has a value of 1.901 Å. The ∠CO–Rh–CO angle and the angle ∠CO–Rh–XX, formed between the carbonyl ligand, the rhodium atom, and the center of the **Pp** ring, has values of 89.9° and 135.1°, respectively. The singlet state of the [(Cp)Rh-(CO)$_2$] analogue has essentially the same structural values, with the main deviations coming from the Rh–XX distance, which is increased 0.032 Å, and the Rh–CO bond, which is reduced 0.007 Å. These structural parameter values, obtained at the MP2 level of theory, are close to those computed at the B3LYP level of theory for the singlet state of [(Cp)Rh(CO)$_2$].[14] As can be seen in Figure 1, the structural parameters for the triplet excited state are greater than those computed for the singlet state. As an example, the Rh–CO bond in the triplet state is 0.091 Å greater than the value for the singlet state, the angle ∠CO–Rh–CO opens 11.3°, and ∠CO–Rh–XX angle decreases 11.6° as compared with the values for the singlet state. In the triplet state the interaction between the rhodium and the **Pp** ligand should be less effective since the *r*(Rh–XX) distance in the triplet state is augmented, compared with the value for the singlet state, changing from 1.901 to 2.116 Å. The triplet state has a spin density located at the rhodium atom, and at the MP2 level of theory, the energy of the triplet state is calculated to be much higher than the singlet state. The singlet–triplet splitting energy ($\Delta E_{st} = E_{triplet} - E_{singlet}$) for the **PpCO2** complex is 55.1 kcal/mol. This $\Delta E_{st}$ is 21.7 kcal/mol higher than the reported value of 33.4 kcal/mol for the [(Cp)Rh(CO)$_2$] compound, computed at the B3LYP level of theory.[14] This is an interesting result since the existence of low-lying triplet states may play an important role in the primary photophysical process that takes place before the photoinduced CO loss from [(**Pp**)-Rh(CO)$_2$]. According to the work of Bromberg and coworkers,[32] the low quantum yield for the C–H activation reaction promoted by the [(Cp)Rh(CO)$_2$] complex may be related with the primary photophysical process that takes place before the photoinduced CO dissociation from the [(**Pp**)Rh(CO)$_2$] complex. The existence of low-lying excited states below the MLCT bands, which lead to the M–CO bond breaking, originates a competition in which the UV excitation of the [(Cp)Rh(CO)$_2$] populates excited states that do not lead to CO loss and, thus, reduces the quantum yield. The molecular structures and excited states of [(Cp)Rh(CO)$_2$] were recently investigated theoretically by Hu and co-workers[14] using the B3LYP and the symmetry-adapted cluster-configuration interaction (SAC-CI) methods. The authors found a strong ligand Cp to metal and CO charge transfer, which lies in the same energy range as the MLCT excitation bands, and they proposed a competitive charge transfer mechanism as the origin of the low quantum yield observed experimentally.

To compare the changes in the excited states and excitation energies accompanying the replacement of Cp in the compound [(Cp)Rh(CO)$_2$] by the phospholyl ligand **Pp**, generating the complex [(**Pp**)Rh(CO)$_2$], we have calculated the electronic spectrum of [(**Pp**)Rh(CO)$_2$] in the gas phase, within the semiempirical intermediate neglect of differential overlap (INDO) approach, with singly excited configuration interaction (CIS), named INDO/CIS,[33] using the parameters for the Rh atom reported by Anderson, Cundari, and Zerner.[34] The active space employed for the electronic spectrum calculations was composed of the 10 highest occupied and the 10 lowest unoccupied molecular orbitals. The calculated excitation energies, main configuration, and oscillator

---

(30) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, *Revision A.6*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(32) Bromberg, S. E.; Lian, T.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 2069.

(33) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111.

(34) Anderson, W. P.; Cundari, T. R.; Zerner, M. C. *Int. J. Quantum Chem.* **1991**, *39* 31.

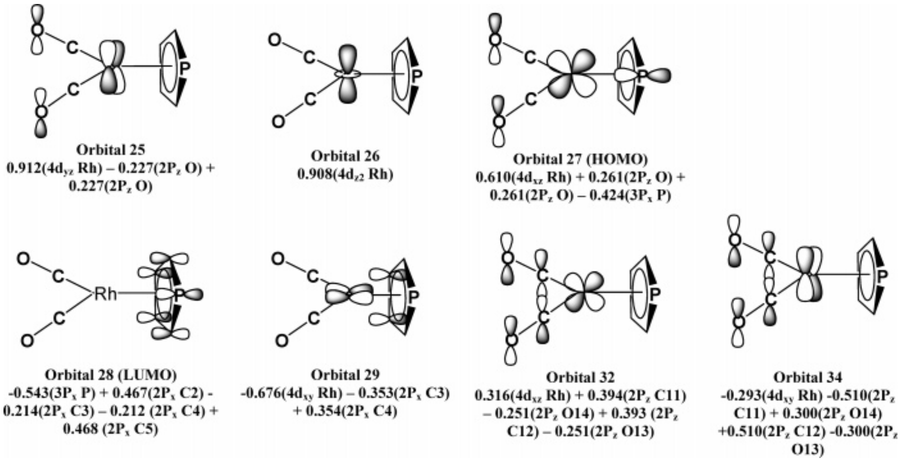


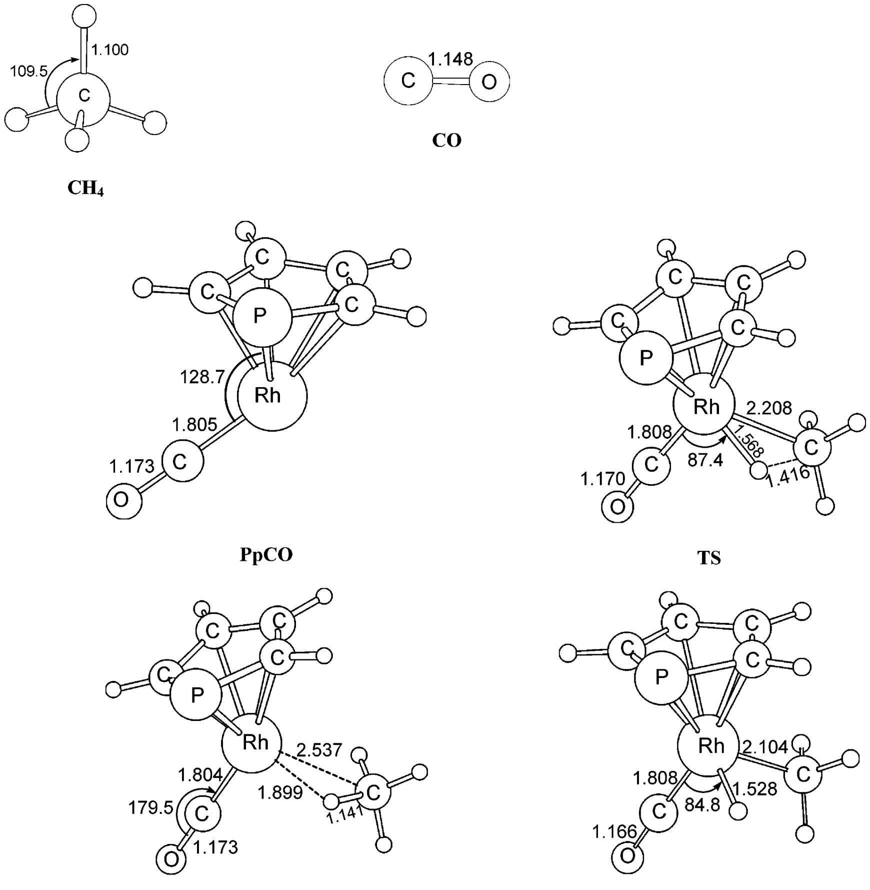
**Figure 2.** Diagram of the most important orbitals involved in the electronic transitions of **PpCO2**.

**Table 1. INDO/CIS Results for the [$\eta^5$-phosphilyl)Rh(CO)$_2$], PpCO2, Compound**

| main configuration | excitation energy (eV) | oscillator strength |
|---|---|---|
| $0.92(27 \rightarrow 28)$ | 3.40 | 0.00000 |
| $0.33(25 \rightarrow 29) - 0.90(27 \rightarrow 28)$ | 4.10 | 0.07317 |
| $0.87(25 \rightarrow 29) + 0.34(27 \rightarrow 28)$ | 4.35 | 0.01328 |
| $-0.88(26 \rightarrow 28)$ | 4.73 | 0.12227 |
| $0.64(27 \rightarrow 31) - 0.51(27 \rightarrow 32) - 0.41(27 \rightarrow 33)$ | 4.84 | 0.01365 |
| $-0.44(27 \rightarrow 31) - 0.79(27 \rightarrow 33)$ | 5.03 | 0.04048 |
| $-0.96(25 \rightarrow 28)$ | 5.25 | 0.01444 |
| $0.47(26 \rightarrow 32) - 0.35(26 \rightarrow 33) - 0.41(27 \rightarrow 31) - 0.58(27 \rightarrow 32)$ | 5.28 | 0.10009 |
| $0.83(26 \rightarrow 32) + 0.39(27 \rightarrow 32)$ | 5.54 | 0.04301 |
| $0.82(27 \rightarrow 34)$ | 5.68 | 0.08838 |

strength for the [(**Pp**)Rh(CO)$_2$] compound are shown in Table 1, and the schematic representation of the most important orbitals involved in the electronic transitions is shown in Figure 2. The lowest computed excitation energy for the [(**Pp**)Rh(CO)$_2$] compound occurs at 3.40 eV (364 nm), with zero oscillator strength. This is essentially a HOMO → LUMO transition. As can be seen in Figure 2, the HOMO has contributions coming from the metal 4d$_{xz}$, the phosphorus lone pair, and the oxygen 2p$_z$ nonbonding orbitals, with a major contribution of the 4d$_{xz}$ metal orbital. The LUMO orbital is centered at the **Pp** ligand, with $\pi$-antibonding character. Excitation at this wavelength does not lead to CO dissociation. There are two strong absorptions occurring at 4.73 eV (262 nm) with oscillator strength 0.12227 and at 5.28 eV (234 nm) with oscillator strength 0.10009. The transition occurring at 4.73 eV involves the occupied orbital 26 and the LUMO. As can be seen in Figure 2, this is a charge transfer transition from the metal 4d$_{z^2}$ orbital to the $\pi$-antibonding orbital of the **Pp** ligand. The electronic transition at 5.28 eV has major contribution from excitations starting at the occupied orbitals 26 and HOMO and ending at the unoccupied orbital 32, which has an Rh−CO antibonding character. The absorption occurring at 5.54 eV (224 nm) also involves the excitation of orbital 26 (Rh 4d$_{z^2}$) to orbital 32 with Rh−CO antibonding character. As a result, excitations at 5.28 and 5.54 eV will correspond to the MLCT (M → CO) band, which leads to the dissociation of CO from the coordination sphere of the rhodium atom in the [(Pp)Rh(CO)$_2$] compound. The experimental MLCT band[32] for the [(Cp*)Rh(CO)$_2$] compound occurs at 4.20 eV. Our results indicate that when Cp is replaced by phospholyl, the resulting compound, [(**Pp**)Rh(CO)$_2$], has a singlet ground state, with the lowest triplet state lying 55.1 kcal/mol above it. The M → CO charge transfer band occurs at much higher energy (5.28 and 5.54 eV) than the value for the parent Cp compound. Other kinds of MLCT charge transfer bands that do not lead to CO dissociation occur in a different energy range, contrary to the case of the Cp analogue, predicted theoretically.[14]

**Structures of the Species Obtained along the Reaction Pathway.** The MP2 optimized geometries for the monocarbonyl species, **PpCO**, the adduct formed upon interaction of **PpCO** with methane, **ADDUCT**, and the alkyl-hydride, **PROD**, generated along the intrinsic reaction coordinate for the oxidative addition reaction, are shown in Figure 3. Figure 3 also shows the optimized geometries for the free **CH$_4$** and **CO** ligands. When the [(**Pp**)Rh(CO)$_2$] compound loses a carbonyl ligand, generating the monocarbonyl species **PpCO**, the main structural changes occurring involve the Rh−CO, Rh−XX, and CO bond distances. As can be seen in Figures 3 and 2, the Rh−CO bond length is reduced by 0.026 Å on going from **PpCO2** to **PpCO**, and the CO distance is increased, varying from 1.166 Å in **PpCO2** to 1.173 Å in **PpCO**. The distance between the rhodium and the center of the **Pp** ring decreases from 1.901 Å to 1.868 Å when the CO dissociation occurs. This structural result can be explained by the fact that when a strong $\pi$-acceptor ligand such as CO leaves the coordination sphere of the metal, the remaining $\pi$-acceptor ligands interact more effectively with the metal, reducing the M−L bond. The small increase of 0.007 Å of the CO bond may be attributed to the *trans* effect of the **Pp** ligand, which weakens the CO bond. This small increase of the CO bond is manifested in the vibrational spectrum of the compounds. At the MP2 level of theory, the **PpCO2** complex shows an asymmetric stretching of the carbonyl ligand at 1980 cm$^{-1}$.



**$CH_4$** **CO** **PpCO** **TS** **ADDUCT** **PROD**

**Figure 3.** MP2 optimized structures of the main species obtained along the reaction path of the methane oxidative addition. Bond lengths are given in Å and bond angles in degrees.

After CO dissociation, the asymmetric stretching of the remaining carbonyl in the **PpCO** compound is 1957 cm$^{-1}$. Interaction of methane with the monocarbonyl species generates the **ADDUCT** intermediate. As can be seen in Figure 3, the interaction of methane with the monocarbonyl species **PpCO** does not change appreciably the structure of this compound, indicating the weak nature of this interaction. The methane interacts with **PpCO** in a $\eta^2$ fashion through the C−H bond. The distance of the metal to the carbon atom is computed as 2.537 Å, and the Rh−H distance is 1.899 Å. The C−H bond of methane increases 0.041 Å upon interaction with the rhodium atom, varying from 1.100 Å in the free ligand to 1.141 Å in the **ADDUCT**. This adduct structure has a CO stretching frequency of 1964 cm$^{-1}$, computed at the MP2 level of theory, and the C−H bond interacting with the metal has an asymmetric C−H stretching of 2672 cm$^{-1}$, which, compared with the value for the free methane ligand (3080 cm$^{-1}$), represents a reduction of 408 cm$^{-1}$ due to the interaction with the rhodium atom. The bending frequency of the methane ligand increases from 1338 cm$^{-1}$ in the free ligand to 1618 cm$^{-1}$ in the adduct. The appearance of these new vibrations involving the methane ligand can be used to monitor the formation of the **ADDUCT** species. The transition state structure, **TS** (Figure 3), obtained for the oxidative addition has an imaginary frequency of 857i cm$^{-1}$. The nuclear displacement associated with this normal mode displays a concerted mechanism in which the C−H bond is breaking and, at the same time, the Rh−C bond is forming. The C−H bond distance of 1.416 Å is even more elongated as compared with the C−H bond distance of 1.141 Å in the $\eta^2$ **ADDUCT**, representing an increase of 24%. The Rh−H and Rh−C bonds start to form, with distances of 1.568 and 2.208 Å, respectively. The other structural parameters remain unchanged as compared with the **ADDUCT** structure. Further interaction between the incoming methane molecule with the metallic fragment generates the methyl-hydride compound, **PROD**, in which the C−H bond is completely dissociated, with a C−H distance of 2.287 Å. The new Rh−C and Rh−H bonds formed have the values 2.104 and 1.528 Å, respectively. The variation of the main structural changes occurring along the reaction pathway for the C−H bond activation of methane is show in Figure 4, in which the concerted nature of the reaction can be seen.

**Reaction Energetics.** The intrinsic reaction coordination (IRC) profile for the oxidative addition reaction is shown in Figure 4, and the energetic results are summarized in Table 2. As can be seen from Figure 4 and Table 2, the enthalpy variation associated with the CO dissociation process **PpCO2** → **PpCO** + **CO** is 57.9 kcal/mol at the MP2 level of theory. At the MP4(SDQ)//MP2 level this value reduces to 52.1 kcal/mol. This result is of the same order of magnitude as compared with the computed value for the Cp analogue[14] and shows that the CO dissociation is a very demanding energy process. The interaction of methane with the monocarbonyl compound **PpCO** is an exothermic pro-

**Table 2. Computed Energies (in kcal·mol$^{-1}$) for the Overall Process of C−H Activation of Methane**

| process | | MP2 | | MP4(SDQ)//MP2$^a$ | |
|---|---|---|---|---|---|
| | | $\Delta E_{ZPE}$ | $\Delta H$ | $\Delta E_{ZPE}$ | $\Delta H$ |
| CO dissociation | **PpCO2 → PpCO + CO** | 57.1 | 57.9 | 51.2 | 52.1 |
| adduct formation | **PpCO + $CH_4$ → ADDUCT** | −12.9 | −13.2 | −11.5 | −11.7 |
| C−H activation | **ADDUCT → TS** | 4.2 | 3.5 | 6.8 | 6.1 |
| product formation | **TS → PROD** | −10.8 | −10.8 | −6.3 | −6.3 |

$^a$ Zero-point energy and thermal corrections computed at the MP2 level of theory.

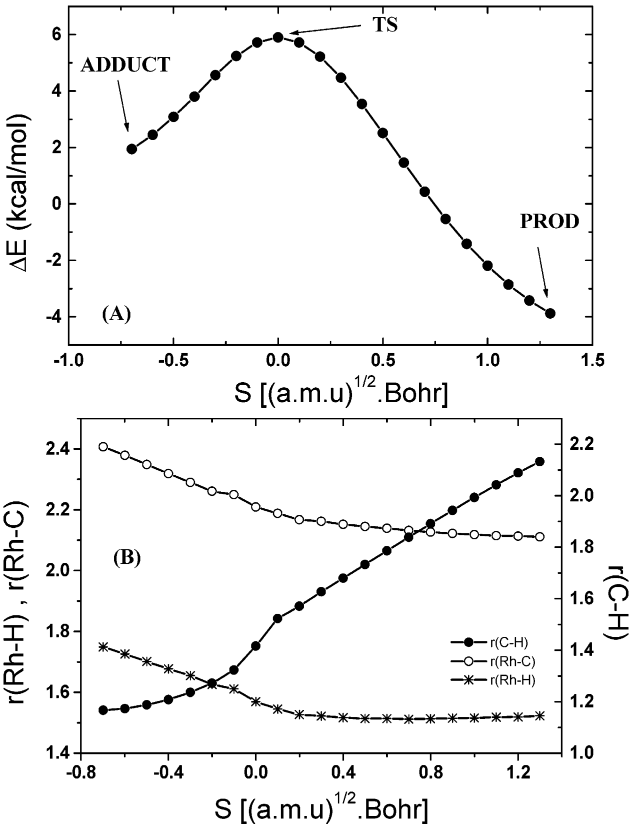


**Figure 4.** (A) Intrinsic reaction coordinate (IRC) for the C−H bond activation of methane. (B) Variation of the C−H, Rh−H, and Rh−C bonds along the reaction coordinate. Values are given in Å.

cess, releasing 13.2 kcal/mol at the MP2 level of theory, and at the MP4(SDQ)//MP2 level the computed enthalpy for this process, **$CH_4$ + PpCO → ADDUCT**, is −11.7 kcal/mol. This result indicated that methane forms a weak interaction with the metallic fragment, which stabilizes the resulting complex (**ADDUCT**). The nature of this weak interaction can be attributed to a small electron density donation from the $\sigma$(C−H) molecular orbital of methane to the metal.[2] At the MP2 level of theory, the activation parameters $\Delta E^{\#}$ and $\Delta H^{\#}$ for the process **ADDUCT → TS** are 4.2 and 3.5 kcal/mol, respectively. At the MP4(SDQ)//MP2 level the values for $\Delta E^{\#}$ and $\Delta H^{\#}$ increase to 6.8 and 6.1 kcal/mol, respectively. The activation enthalpy for the C−H bond activation for the Cp analogue [(Cp*)Rh(CO)$_2$] has been estimated in liquid noble gases to be approximately 6 kcal/mol.[35] Our results indicate that the activation parameters for the compound [(**Pp**)Rh(CO)$_2$] are of the same order of magnitude as the value found for the Cp analogue, and so, the C−H activated product should form with a half-life of the same order of the Cp analogue of about 200 ns.[32] The formation of the alkyl hydride compound from the transition state, **TS**, is an exothermic process, with a $\Delta H$ of −10.8 kcal/mol computed at the MP2 level of theory. However, at the MP4(SDQ)//MP2 level, the $\Delta H$ is −6.3 kcal/mol, which corresponds to an increase of 4.5 kcal/mol. So, as can be seen in Table 2, we may conclude that the effect of the of inclusion of a higher correlated level, for the process **ADDUCT → PROD**, is more pronounced in the relative stability of the species involved than in the activation energies parameter, since the effect of a higher level of electron correlation is to reduce by 2.6 kcal/mol the $\Delta E^{\#}$ and $\Delta H^{\#}$, while this effect increases the $\Delta E$ and $\Delta H$ by 4.5 kcal/mol.

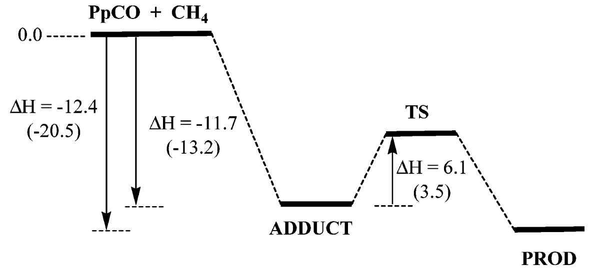


**Figure 5.** Overall MP4(SDQ)//MP2 enthalpy profile (in units of kcal/mol) for the methane activation reaction, relative to the isolated species **PpCO** and **$CH_4$**. The MP2 values are given in parentheses.

Figure 5 summarizes the $\Delta H$ profile for the activation of methane by the [($\eta^5$-phospholyl)Rh(CO)$_2$] compound, relative to the isolated monocarbonyl, **PpCO**, and methane. As can be seen, the overall exothermicity of the reaction (**PpCO + $CH_4$ → PROD**) is −12.4 kcal/mol at the MP4(SDQ)//MP2 level of theory. At the MP2 level of theory, the exothermicity of the reaction is overestimated, being −20.5 kcal/mol, which represents a difference of 8.1 kcal/mol. This controversial exothermicity for the C−H bond activation of methane was also found for the Cp analogue [(Cp)Rh(CO)$_2$] reported by Couty and co-workers,[12] who calculated the $\Delta E$ for this reaction, without thermal corrections to the enthalpy, and showed that the MP2 results, with a different basis set, are only qualitative. As can be seen in Figure 5, relative to the initial reactants, the reaction proceeds without energy barrier, which is also observed for the Cp analogue.[1e] The small activation enthalpy of 6.1 kcal/mol, at the MP4(SDQ)//MP2 level of theory is relative to the $\eta^2$ adduct intermediate, **ADDUCT**, formed by the interaction of **PpCO** with methane.

## Summary and Conclusions

In this work, quantum mechanical calculations at the MP4(SDQ)//MP2 level were carried out to evaluate, a

---

(35) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369.

priori, the reactivity of [($\eta^5$-phospholyl)Rh(CO)$_2$], **PpCO2**, toward C−H bond activation of methane. The study of the catalyst precursor **PpCO2** revealed that it has a singlet ground state, with the lowest triplet state lying 55.1 kcal/mol above it. This singlet−triplet splitting energy is 21.7 kcal/mol higher than the reported value for the [(Cp)Rh(CO)$_2$] compound. INDO/CIS calculations revealed that the M → CO charge transfer band which leads to CO dissociation occurs at much higher energy (5.28 and 5.54 eV) than the value for the parent Cp compound. Other kinds of MLCT charge transfer bands that do not lead to CO dissociation occur in a different energy range, contrary to the case of the Cp analogue, predicted theoretically. The CO dissociation from the dicarbonyl species, **PpCO2**, to generate the active catalyst **PpCO**, has an activation enthalpy of 52.1 kcal/mol. The methane substrate interacts with the monocarbonyl compound **PpCO**, forming a $\eta^2$ adduct, which is stabilized by 11.7 kcal/mol. In this $\eta^2$ adduct, the frequencies associated with the asymmetric C−H stretching and bending vibrations of the methane are drastically changed when compared with the free ligand. The stretching vibration reduces of 408 cm$^{-1}$ due to the interaction with the rhodium atom, and the bending frequency of the methane ligand increases from 280 cm$^{-1}$. These vibrations can be used to monitor the adduct formation along the reaction path. The C−H bond activation of methane proceeds through a three-center transition state with a small activation enthalpy of 6.1 kcal/mol, relative to the $\eta^2$ adduct intermediate, **ADDUCT**, formed by the interaction of the monocarbonyl species, **PpCO**, with methane. This computed activation enthalpy is of the same order as that predicted experimentally for the Cp analogue. This work presents theoretical evidence that the replacement of cyclopentadiene in the compound [(Cp)Rh(CO)$_2$] by the phospholyl ligand generates a compound, [($\eta^5$-phospholyl)Rh(CO)$_2$], which can be used to activate the C−H bond of alkanes, which awaits future experimental work.

**Acknowledgment.** The authors would like to thank the Brazilian agencies CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for financial support. We also thank Dr. Vinícius Caliman for the stimulating discussion on the subject of this work. W.R.R would like to thank the IMMC (Instituto do Milênio de Materiais Complexos) for financial support.

**Supporting Information Available:** Tables containing total energies, zero-point vibrational energies, and thermal corrections to the energy and enthalpy computed for the free ligands (**CH$_4$** and **CO**) and the complexes (**PpCO2**, **PpCO**, **ADDUCT**, **PROD**), in Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049036G