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Ability of N-Heterocyclic Carbene Ligands to Promote Intermolecular Oxidative Addition Reactions at Unsaturated Ruthenium Centers

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We report the results of density functional calculations on the reactivity of a series of coordinatively unsaturated mixed phosphine/N-heterocyclic carbene complexes of ruthenium of the type $Ru(CO)(IR)_{3-n}(PH_3)_n$, where $n = 1-3$ and R = H (1,3-imidazol-2-ylidene) and R = Me (1,3-dimethylimidazol-2-ylidene). The oxidative addition reactions of H_2 and CH_4 and the C−C bond activation of C_2H_6 have been studied. For all three processes, substitution of PH_3 by IH results in minimal changes in the reaction energetics. In all cases H_2 oxidative addition is barrierless and is downhill by around 120 kJ/mol. With CH_4 activation barriers of around 75 kJ/mol are computed and the reaction is approximately thermoneutral. With C_2H_6 activation barriers increase to around 260 kJ/mol and the reaction is disfavored by about + 35 kJ/mol. Introduction of the IMe ligand disfavors oxidative addition, especially for the C_2H_6 reaction, and this trend is linked to increased steric bulk of the IMe ligand compared to IH. Computed Ru−PH_3 and Ru−IR bond strengths and CO stretching frequencies indicate that PH_3/IR substitution does create a more electron-rich metal center, and yet this does not facilitate oxidative addition with these Ru species. A fragment analysis reveals that, as expected, PH_3/IH substitution enhances the Lewis basicity of the metal reactant. However, a more important effect is a reduction in Lewis acidity, and this factor lies behind the similar reaction energetics computed for analogous PH_3- and IH-containing species.

Introduction

Over the past decade N-heterocyclic carbenes (NHCs, Scheme 1) have found an ever-widening role as auxiliary ligands in organometallic chemistry.[1] As with phosphines, substituent groups can allow tuning of the steric and electronic properties of the NHC ligand.[2] In addition, NHCs are generally thought to exhibit enhanced thermal stability compared to phosphines, as the latter are prone to P−C bond rupture and metalation processes at higher temperatures.[3] As a consequence of this, NHCs have been extensively exploited in homogeneous catalysis, and in many cases the replacement of phosphines by NHC ligands confers greater reactivity on transition metal catalysts, most notably in Grubb's type systems for alkene metathesis and ROMP/RCM[4] and Pd-based catalysts for C−C bond coupling.[5] Late transition metal−NHC bonds have been shown to be more stable thermodynamically than similar metal−phosphine bonds, and this has been attributed to the strongly nucleophilic (σ-donating) nature of NHC ligands.[2,6] π-Back-bonding on the other hand is thought to be of minor importance in transition metal−NHC bonds.[7] Overall the introduction of NHC ligands should make metal centers more electron-rich, and this could have a significant effect on bond activation processes that are central to many catalytic schemes. We have been investigating the chemistry of the mixed Ru-NHC/phosphine complexes $Ru(H)_2(CO)(IMes)_{3-n}(PPh_3)_n$ ($n = 1-2$, IMes as shown in Scheme 1) and have shown that these systems promote H−H, C−H, and C−C bond activation reactions.[8a,b] The closely related Ru-NHC/arsine system $Ru(H)_2(AsPh_3)(CO)(IMes)_2$ allows facile

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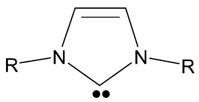
10.1021/om034391c CCC: $27.50

Scheme 1



R = H (1,3-imidazol-2-ylidene, IH),
R = Me (1,3-dimethylimidazol-2-ylidene, IMe),
R = mesityl (1,3-dimesitylimidazol-2-ylidene, IMes)

access to solvent-stabilized systems Ru(H)$_2$(CO)(IMes)$_2$(S) (S = H$_2$O, EtOH, H$_2$S, SH^{n}Pr), which can undergo subsequent heteroatom−H bond activation reactions.[8c,d] In the former case, the coordinatively unsaturated 16e species Ru(CO)(IMes)$_{3-n}$(PPh$_3$)$_n$ are assumed to play a key role. To assess the idea that strongly donating NHC ligands promote bond activation reactions by such intermediates, we have undertaken a computational study of the intermolecular oxidative addition reactions of Ru(CO)(IR)$_{3-n}$(PH$_3$)$_n$ (R = H or Me, n = 1−3) model species with H$_2$, CH$_4$, and the C−C bond of C$_2$H$_6$. In this study the IMes ligand used experimentally has been simplified to either IH or IMe, allowing us to probe primarily the electronic influence of these ligands in the absence of gross steric effects. However, as we show below, the major consequence of introducing a methyl substituent in place of hydrogen is steric in origin. This work adds to the growing computational literature[9] on the reactivity of transition metal NHC complexes but is one of relatively few studies to compare NHCs directly with phosphines,[10] in this case the traditional phosphine of computational chemistry, PH$_3$. The structure and reactivity of four-coordinate 16e Ru(0) species have been studied previously, both theoretically and experimentally. Thus, the isolable species Ru(CO)$_2$(P^{t}Bu$_2$Me)$_2$ adopts a bent C_{2v} geometry, which calculations suggest is promoted by strong π-back-donation to the CO ligands from the electron-rich Ru center.[11] When such an arrangement is denied by using a chelating diphosphine, a near square-planar geometry is seen.[12] The reaction of H$_2$ with the model complex Ru(PH$_3$)$_4$ has been computed to be barrierless, consistent with the very rapid reaction of the transient Ru(dmpe)$_2$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) with H$_2$.[13] Ru(PH$_3$)$_4$ was computed to have a distorted square-planar geometry.[14]

Computational Details

The majority of the calculations in this paper employed the Gaussian 98 program.[15] Ru and P centers were described using

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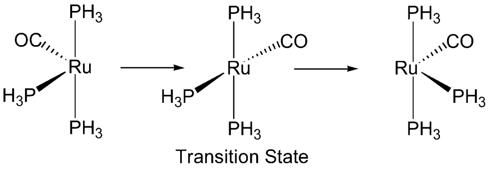
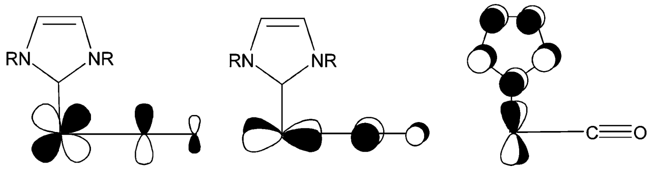
the Stuttgart RECPs and the associated basis sets,[16] while for P an extra set of polarization functions was added ($\zeta = 0.387$).[17] 6-31G** basis sets were used for C, N, O, and H atoms.[18] The performance of a range of pure and hybrid density functionals was assessed for the reactions of the $Ru(CO)(IH)_{3-n}(PH_3)_n$ systems, and it was found that although the absolute values obtained for reaction energetics could vary quite widely, the computed trends, either as a function of the number of NHC ligands present or in terms of the energetics of H_2, CH_4, and C_2H_6 oxidative addition to a given complex, varied little with the choice of functional. Results in the text are computed with the BP86 functional unless specified otherwise. This choice was based on the good performance of this functional in reproducing the geometry of *mer*-$Ru(H)_2(CO)(PPh_3)_3$ (see Results section) as well as it being more efficient computationally than hybrid functionals such as B3LYP, which gave comparable results in this respect. All stationary points were characterized by computation of the Hessian matrix to be either minima (all positive eigenvalues) or transition states (one imaginary eigenvalue). Transition states were further characterized by IRC calculations, which in all cases led to the expected local minima. All energies include a correction for zero-point energies. Only the formation of *mer*-isomer of $Ru(H)_2(CO)(PH_3)_3$ was considered, as it is the PPh_3 analogue of this species that is observed experimentally. In addition, only reaction profiles for oxidative addition in the plane containing trans CO and PH_3 ligands of the $Ru(CO)(IR)_{3-n}(PH_3)_n$ reactants were studied. This places the model NHC ligands in a trans arrangement in the six-coordinate products, as observed in the analogous experimental systems $Ru(H)_2(CO)(IMes)(PPh_3)_2$ and $Ru(H)_2(CO)(IMes)_2(PPh_3)$.[8a] Moreover, test calculations on the oxidative addition of CH_4 in the IH−Ru−IH plane of $Ru(CO)(IH)_2(PH_3)$ showed this process to be significantly less favorable both kinetically and thermodynamically than the results obtained when the approach of the substrate is in the $H_3P{-}Ru{-}CO$ plane.

In the analysis of our results we have exploited the energy decomposition analysis available within the Amsterdam Density Functional program, ADF1999.[19] For these calculations a triple-ζ-STO basis set was employed for Ru, and all other atoms were described by a double-ζ plus polarization STO basis set. The frozen core approximation was employed for the 1s electrons of C and O and up to and including the 3d electrons of Ru. Geometry optimizations used the procedure developed by Versluis and Ziegler[20] and employed the BP86 functional. The quasi-relativistic corrections of Snijders and co-workers were also included.[21]

Scheme 2



Scheme 3



Results

Structures of Unsaturated $Ru(CO)(IR)_{3-n}(PH_3)_n$ Species ($R = H, Me$; $n = 1-3$) The structure of 16e $Ru(CO)(PH_3)_3$ computed with the BP86 functional exhibits a slightly bent C_{2v} shape with an equatorial $OC{-}Ru{-}PH_3$ angle of 168°. In fact the computed value for this angle varies by as much as 25° depending on which functional was employed, and the potential energy surface associated with this angle was therefore investigated. With the BP86 functional, inversion at the Ru center entailed a minimal activation barrier of only 1.4 kJ/mol (Scheme 2). This ease of deformation of the equatorial $OC{-}Ru{-}PH_3$ angle not only accounts for it being sensitive to the functional employed but also indicates that the effect of this variation on the relative energy of the $Ru(CO)(PH_3)_3$ reactant will be minor.

The computed geometries of $Ru(CO)(IH)(PH_3)_2$ and $Ru(CO)(IH)_2(PH_3)$ are much less functional-dependent, with the $OC{-}Ru{-}PH_3$ angle being around 140° in all cases. The activation barriers for inversion at the metal also increase, to 11.5 kJ/mol for $Ru(CO)(IH)(PH_3)_2$ and 20.5 kJ/mol for $Ru(CO)(IH)_2(PH_3)$. Substitution of PH_3 with IH causes a lengthening of the trans Ru−ligand bond distance by about 0.02−0.03 Å. An interesting feature of these systems is that the IH ligand always eclipses the Ru−CO bond, despite the presumably unfavorable steric effect of this arrangement. This result can be rationalized in terms of maximizing Ru→NHC π-back-donation into a vacant π orbital on the NHC ring. Alternative orientations would result in direct competition for metal electron density with the strong π-acid CO ligand (Scheme 3). This electronic effect is weak however, consistent with the generally held view that NHC ligands are poor π-acceptors. Thus, rotation of the IH ligand to a position staggering the equatorial $OC{-}Ru{-}PH_3$ angle costs only 6 kJ/mol. Furthermore the introduction of greater, although still minimal, steric bulk through the use of IMe ligands is sufficient to drive the NHC ligand to this staggered position, overcoming any electronic preference for the orientation over the Ru−CO bond. In addition, the IMe complexes also exhibit a tilting of the NHC ligand into the vacant space on one side of the Ru center, once again presumably due to steric reasons. These features apart, the structures of analogous IH and IMe species are very similar.

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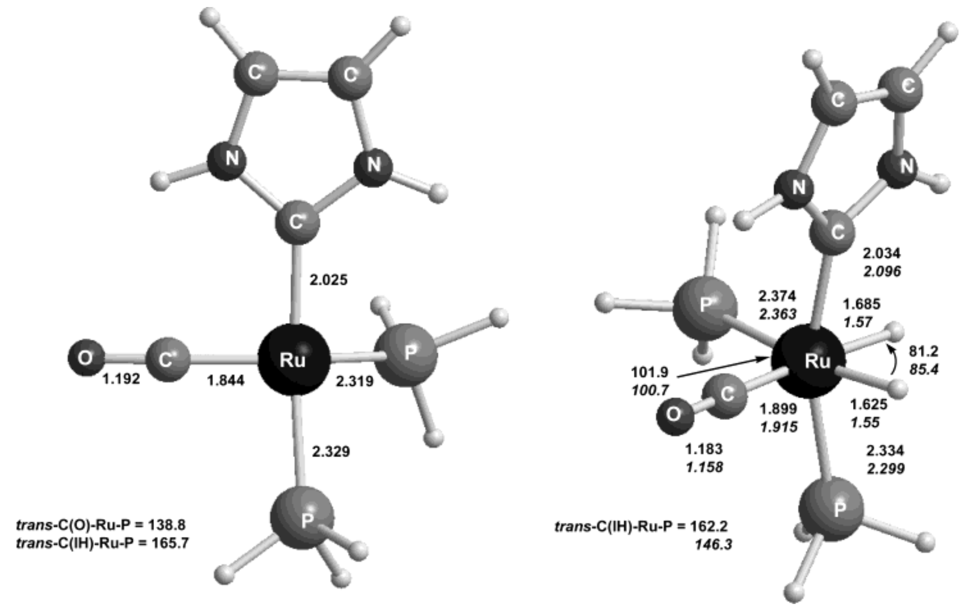

Figure 1. Selected computed geometric parameters (Å, deg) for $Ru(CO)(IH)(PH_3)_2$ and $Ru(H)_2(CO)(IH)(PH_3)_2$. Experimental data for $Ru(H)_2(CO)(IMes)(PPh_3)_2$ are given in italics.[24]

Reactivity of $Ru(CO)(IR)_{3-n}(PH_3)_n$ (R = H, Me; n = 1−3). (i) Oxidative Addition of H_2. For $Ru(CO)(PH_3)_3$, $Ru(CO)(IH)(PH_3)_2$, and $Ru(CO)(IH)_2(PH_3)$ reaction profiles indicate that H_2 oxidative addition occurs without an activation barrier.[22] This is a result similar to that found previously for $Ru(PH_3)_4$ and, as in that case, H_2 is found to adopt an end-on, η^1-orientation at long Ru···H_2 separations (>2.0 Å). At shorter distances the H_2 moiety progressively swings round and cleaves to give ultimately the dihydride products, $Ru(H)_2(CO)(IH)_{3-n}(PH_3)_n$. The structure of the tris-phosphine product, *mer*-$Ru(H)_2(CO)(PH_3)_3$, can be compared with the experimental structure of *mer*-$Ru(H)_2(CO)(PPh_3)_3$,[23] and the BP86 functional gives especially good agreement, with bond distances deviating on average by only 0.02 Å from experiment. As with their 16e precursors, both $Ru(H)_2(CO)(IH)(PH_3)_2$ and $Ru(H)_2(CO)(IH)_2(PH_3)$ display structures in which the IH ligands lie directly over the Ru−CO bond. The computed structures of $Ru(CO)(IH)(PH_3)_2$ and $Ru(H)_2(CO)(IH)(PH_3)_2$ are shown in Figure 1, where the latter is also compared with the experimental structure of $Ru(H)_2(CO)(IMes)(PPh_3)_2$.[24] In general, agreement with the distances between heavy atoms is good, the major discrepancy being for the Ru−C_{IMes} distance, which is 0.06 Å longer than the computed Ru−C_{IH} distance. This may result from the greater steric encumbrance with the IMes ligand, and the resultant weakening of the Ru−C_{IMes} interaction could also account for the fact that the trans Ru−PPh_3 distance is shorter than the computed Ru−PH_3 distance (2.2985(5) Å cf. 2.334 Å). As with their Ru(0) precursors, we find that in all cases the introduction of the IH ligands (and IMe ligands; see below) causes a lengthening of the trans-Ru−L bond of about 0.02 Å. In general, we have found the structures of the various $Ru(CO)(IR)_n(PH_3)_{3-n}$ species and their related stationary points along the oxidative addition profiles to be rather similar, and so only the monosubstituted family will be illustrated here in the figures. Sets of Cartesian coordinates for the reactions of all $Ru(CO)(IR)_n(PH_3)_{3-n}$ species are given as Supporting Information.

Table 1. Computed Energetics (kJ/mol) for the Oxidative Addition of H_2 to $Ru(CO)(IR)_{3-n}(PH_3)_n$ Species (R = H, Me; n = 1−3)

metal species	ΔE_{act}	ΔE_{oxadd}
$Ru(CO)(PH_3)_3$		−120.7
$Ru(CO)(IH)(PH_3)_2$		−117.1
$Ru(CO)(IH)_2(PH_3)$		−115.9
$Ru(CO)(IMe)(PH_3)_2$	+11.3	−102.0
$Ru(CO)(IMe)_2(PH_3)$	+17.3	−96.2

H_2 oxidative addition to $Ru(CO)(PH_3)_3$ is strongly favored, with the energy change (ΔE_{oxadd}) being −120.7 kJ/mol (Table 1). More of a surprise to us was the fact that ΔE_{oxadd} changes little as the IH ligands are introduced, with ΔE_{oxadd} = −117.1 kJ/mol and −115.9 kJ/mol for the formation of $Ru(H)_2(CO)(IH)(PH_3)_2$ and $Ru(H)_2(CO)(IH)_2(PH_3)$, respectively. Overall it must be concluded that PH_3/IH substitution does not have a significant effect on the overall energetics of H_2 oxidative addition to $Ru(CO)(IH)_{3-n}(PH_3)_n$ species. The introduction of Me substituents on the NHC ligands results in small activation barriers for H_2 oxidative addition to $Ru(CO)(IMe)(PH_3)_2$ and $Ru(CO)(IMe)_2(PH_3)$ of 11.3 and 17.3 kJ/mol respectively. The transition states for these processes occur at Ru···H_2 separations of over 2.0 Å, and their associated imaginary frequencies suggest the activation barriers are linked to the movement of the IMe ligands to accommodate the entering H_2 substrate. For $Ru(CO)(IMe)(PH_3)_2$ this corresponds to rotation of one Me substituent, while for $Ru(CO)(IMe)_2(PH_3)$ the IMe ligands are forced to lie closer to CO. Once H_2 can access the metal center, cleavage can proceed without any further activation barrier. The presence of these small activation barriers therefore reflects steric rather than electronic factors.

The structures of $Ru(H)_2(CO)(IMe)(PH_3)_2$ and $Ru(H)_2(CO)(IMe)_2(PH_3)$ are similar to their IH analogues

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(22) H_2 oxidative addition to $Ru(CO)(PPh_3)_3$ has been shown to occur extremely rapidly with a rate constant of 8.4×10^7 M^{-1} s^{-1}. Colombo, M.; George, M. W.; Moore, J. N.; Pattison, D. I.; Perutz, R. N.; Virrels, I. G.; Ye, T.-Q. *J. Chem. Soc., Dalton Trans.* **1997**, 2857.

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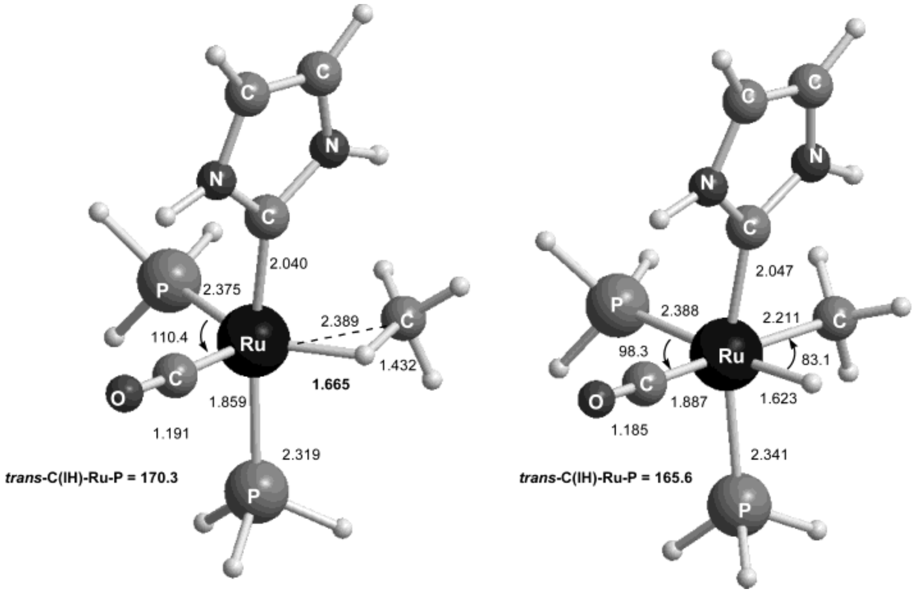

Figure 2. Selected computed geometric parameters (Å, deg) for the transition state and the product for the oxidative addition of CH_4 to $Ru(CO)(IH)(PH_3)_2$.

Table 2. Computed Energetics (kJ/mol) for the Oxidative Addition of CH_4 to $Ru(CO)(IR)_{3-n}(PH_3)_n$ Species (R = H, Me; *n* = 1−3)

metal species	ΔE_{act}	ΔE_{oxadd}
$Ru(CO)(PH_3)_3$	+70.8	−9.3
$Ru(CO)(IH)(PH_3)_2$	+73.7	−9.0
$Ru(CO)(IH)_2(PH_3)$	+78.4	−7.3
$Ru(CO)(IMe)(PH_3)_2$	+98.0	+16.8
$Ru(CO)(IMe)_2(PH_3)$	+111.8	+28.3

except that the increased steric bulk of the IMe ligands once again causes these ligands to adopt a staggered orientation with respect to the H−Ru−H angle (see Supporting Information). The introduction of the IMe ligands reduces ΔE_{oxadd} to −102.0 kJ/mol in $Ru(H)_2(CO)(PH_3)_2(IMe)$ and to −96.2 kJ/mol in $Ru(H)_2(CO)(IMe)_2(PH_3)$. The most likely cause of this seems to be the increased steric encumbrance experienced in the product molecules upon introduction of the Me substituents into the NHC ligands.

(ii) Oxidative Addition of CH_4. Two pathways are possible for this process, with the new Ru−H bond being formed either trans to CO or trans to PH_3. In all cases the latter scenario entailed a lower activation barrier (by about 15 kJ/mol) and was more favorable (by about 10 kJ/mol). We ascribe this greater stability to the fact that it avoids a trans configuration of the high trans influence H and CO ligands. In the following, therefore, we discuss only those reaction profiles leading to the isomers placing H trans to PH_3 (see data in Table 2).

The stationary points for the reactions of all the $Ru(CO)(IH)_{3-n}(PH_3)_n$ systems with CH_4 turn out to be very similar, and the geometries for the $Ru(CO)(IH)(PH_3)_2$ system shown in Figure 2 are representative of these. The oxidative addition transition state is typical for this process and features an η^2-C,H orientation for CH_4 and a short, product-like Ru⋯H distance of 1.67 Å.[25] Throughout the approach of CH_4 to the 16e intermediate, and in the product, the IH ligand is able to retain its preferred electronic orientation over the Ru−CO bond. For these Ru systems we have been unable to find any evidence for a minimum corresponding to a precursor CH_4 complex formed prior to C−H bond activation.

The oxidative addition of CH_4 to $Ru(CO)(PH_3)_3$ was found to be only slightly downhill (ΔE_{oxadd} = −9.3 kJ/mol) and becomes marginally less so upon the introduction of the IH ligands. A similar trend is seen in the activation barriers, with the value of 70.8 kJ/mol computed for $Ru(CO)(PH_3)_3$ increasing to 73.7 and 78.4 kJ/mol for $Ru(CO)(IH)(PH_3)_2$ and $Ru(CO)(IH)_2(PH_3)$, respectively. Although these trends may reflect the less accommodating steric nature of the IH ligands compared to PH_3, overall it can be concluded that IH and PH_3 ligands have very similar effects on the CH_4 oxidative addition process. With the $Ru(CO)(IMe)_{3-n}(PH_3)_n$ reactants the CH_4 oxidative addition process becomes significantly disfavored and activation barriers increase as first one and then two IMe ligands are included. Although this represents the same general effect of the IMe ligands on the H_2 oxidative addition reaction, in this case the energetics are more sensitive to the IH/IMe substitution, confirming the predominantly steric origin of this trend. The greater steric crowding in the hydrido-methyl systems is reflected in a new orientation of the IMe ligands, with the plane of the NHC ring now bisecting the $H_3P-Ru-CH_3$ angle in both transition states and products.

(iii) Oxidative Addition of the C−C Bond of C_2H_6. The results for this reaction confirm the trends highlighted above for the H_2 and CH_4 oxidative addition reactions. As expected, C−C oxidative addition to $Ru(CO)(PH_3)_3$ is an intrinsically difficult process entailing a high activation barrier (260.9 kJ/mol) and being significantly uphill (+38.8 kJ/mol, Table 3). Similar values are computed for the $Ru(CO)(IH)(PH_3)_2$ and Ru-

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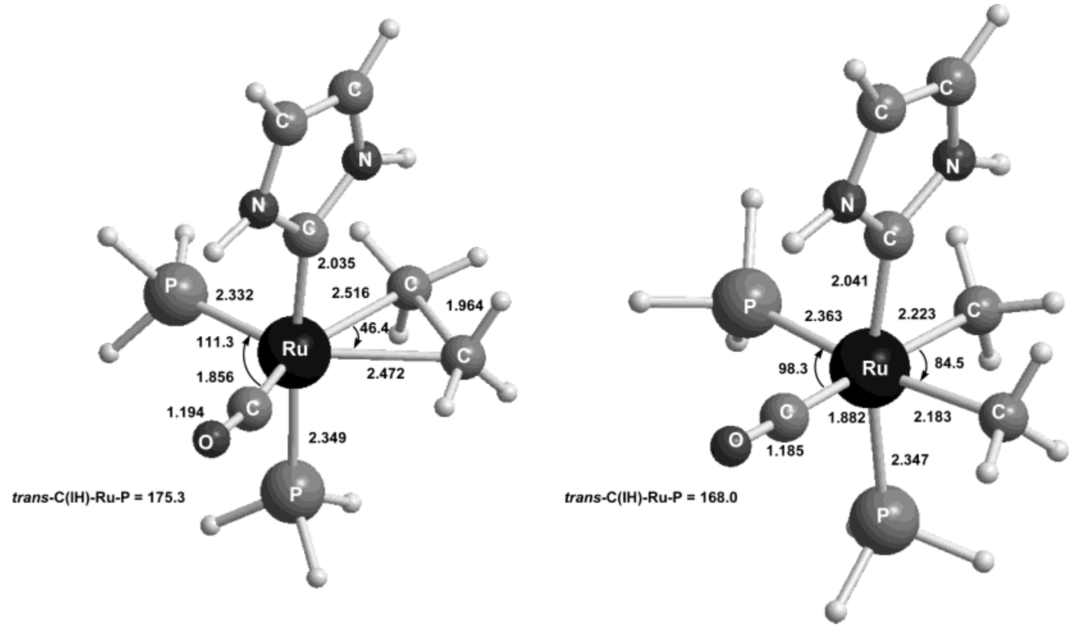

Figure 3. Selected computed geometric parameters (Å, deg) for the transition state and the product for the oxidative addition of C_2H_6 to $Ru(CO)(IH)(PH_3)_2$.

Table 3. Computed Energetics (kJ/mol) for the C−C Bond Oxidative Addition of C_2H_6 to $Ru(CO)(IR)_{3-n}(PH_3)_n$ Species (R = H, Me; $n = 1-3$)

metal species	ΔE_{act}	ΔE_{oxadd}
$Ru(CO)(PH_3)_3$	+260.9	+38.8
$Ru(CO)(IH)(PH_3)_2$	+260.2	+35.4
$Ru(CO)(IH)_2(PH_3)$	+265.7	+32.8
$Ru(CO)(IMe)(PH_3)_2$	+294.1	+70.4
$Ru(CO)(IMe)_2(PH_3)$	+307.5	+93.6

$(CO)(IH)_2(PH_3)$ systems, indicating once again that PH_3/IH substutution has a limited effect on oxidative addition reactions to these systems. The C−C activation transition states all feature a staggered ethane moiety in which the Ru···C contacts are about 0.05 Å shorter trans to PH_3 (Figure 3). The introduction of IMe ligands again disfavors oxidative addition, and the greater steric demands of the methyl substitutes make them particularly sensitive. Thus activation barriers increase by 33 and 42 kJ/mol respectively upon substitution of the IH ligands in $Ru(CO)(IH)(PH_3)_2$ and $Ru(CO)(IH)_2(PH_3)$ with IMe. The same substitutions further disfavor reaction, with ΔE_{oxadd} increasing by +35 and +62 kJ/mol, respectively. A correlation between reaction energetics and the transition state and product geometries is again seen. As before, there is still sufficient room around the Ru center for the IH ligands to adopt their (electronically) preferred orientation over the Ru−CO bond in these structures. When IMe is present, the sterically least encumbered conformer is accessed and the NHC ring again bisects the $H_3P-Ru-CH_3$ angle. Otherwise the stationary points computed for the IMe systems are again very similar to their IH analogues.

Discussion

Drawing together the results in Tables 1−3 shows that, for a given unsaturated Ru species, the oxidative addition of H_2 is considerably more favorable both thermodynamically and kinetically than that of CH_4. Activation of the C−C bond of C_2H_6 is even more difficult, particularly kinetically. These results are consistent with numerous previous theoretical studies on these reactions with other unsaturated metal fragments,[25,26−33] although there are relatively few studies where all of these three processes have been studied at the same level of theory to allow direct comparison.[27] Several recent computational studies comparing either H−H and C−H activation or C−H and C−C activation provide trends similar to those described here. For example, the oxidative addition of H_2 to $IrCl(PH_3)_2$ is 100 kJ/mol more favorable than that of CH_4,[28] while with $(\eta^5\text{-}C_5H_5)Rh(CO)$, H_2 oxidative addition is preferred by 61 kJ/mol.[29] In the latter case both processes proceed without an activation barrier, relative to the isolated reactants. The reactions of CH_4 and C_2H_6 with $Pt(PH_3)_2$ have been computed to have similar energetics ($\Delta E_{oxadd} = +39.3$ and +31.8 kJ/mol, respectively),[30] while the C−H bond activation reaction of acetylene with $Pd(PH_3)_2$ ($\Delta E_{oxadd} = +46.8$ kJ/mol) is considerably more accessible than the equivalent C−C bond activation reaction of propyne ($\Delta E_{oxadd} = +91.6$ kJ/mol).[31] In both these studies, activation barriers are considerably lower for the C−H activation process.[32] The thermodynamic trend favoring H_2 oxidative addition has been rationalized in terms of product bond strengths, with the formation of two strong M−H bonds being preferable to the formation of one or two relatively weak

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[27] Apart from early work on the group 10 metal atoms[34a] we are aware of only one previous study where these three reactions have been compared using a consistent methodology, namely, the GVB//RHF work of Low and Goddard on the reactivity of $Pt(PH_3)_2$ and $PtCl_2(PH_3)_2$. The conclusions from that study are very similar to our own. Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

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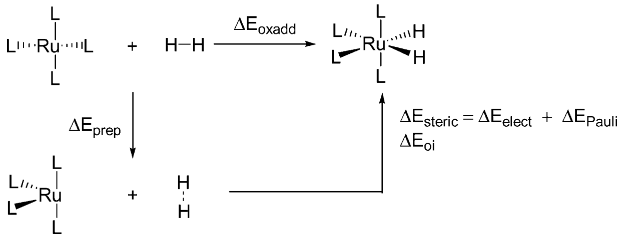
Table 4. Binding Energies (kJ/mol) and CO Stretching Frequencies (cm^{-1}) of Ru(CO)(L)(PH$_3$)$_2$ and Ru(H)$_2$(CO)(L)(PH$_3$)$_2$ Systems (L = PH$_3$, IH, IMe)

metal species	L	binding energy	ν_{CO}
Ru(CO)(L)(PH$_3$)$_2$	PH$_3$	144.3	1934.6
	IH	250.1	1885.2
	IMe	247.2	1903.5
Ru(H)$_2$(CO)(L)(PH$_3$)$_2$	PH$_3$	155.8	1976.5
	IH	258.0	1940.3
	IMe	240.1	1944.3

M−CH$_3$ bonds in the reactions of CH$_4$ and C$_2$H$_6$.[33] The more favorable kinetics for H$_2$ oxidative addition can be understood in terms of the spherical nature of the hydrogen atom, which facilitates an efficient M···H interaction.[34] For electron-rich Ru(0) systems an end-on approach of H$_2$ can be stabilized early in the reaction profile by donation into the H$_2$ σ_u* orbital.[14] In contrast, the directionality of the CH$_3$ sp^3 hybrid orbital renders it much less accessible and necessitates considerable distortion during the approach of CH$_4$, a situation that is exacerbated for the C−C bond activation of C$_2$H$_6$. Our computed structures and trends in energetics are all consistent with these ideas.

The primary focus of the present paper is to compare the relative effects of simple phosphine and NHC ligands on bond activation processes, and overall, we have found IH to be very similar to PH$_3$ in this regard. To check that no major electronic factor was being omitted by the use of the simple IH model ligand, we have extended our study to IMe. However, this rendered the energetics of oxidative addition somewhat less favorable and structural analysis suggests this is primarily a steric effect. The apparent equivalence of the PH$_3$ and IH ligands was a surprise to us, as a number of studies have indicated that NHC ligands both bind more strongly to transition metals[2a,d,10a] and are more electron donating than phosphines,[2a,4k,35] properties attributed to the strongly nucleophilic carbene carbon lone pair. More electron donating ligands would normally be expected to promote the types of oxidative addition reactions studied here. To be sure that our calculations are correctly reproducing the fundamental characteristics of NHC ligands, we have computed the Ru−L binding energies and CO stretching frequencies of the 16e Ru(CO)(L)(PH$_3$)$_2$ and 18e Ru(H)$_2$(CO)(L)(PH$_3$)$_2$ families (L = PH$_3$, IH, and IMe, Table 4). The Ru−IR binding energies are computed to be between 84 and 106 kJ/mol stronger than equivalent Ru−PH$_3$ bonds.[36] In addition, a computed lowering of 30−50 cm^{-1} in the CO stretching frequency upon PH$_3$/IR substitution indicates that the Ru center does indeed become more electron-rich when NHC ligands are present.[37] Therefore our calculations present a contradiction: for these Ru(0) systems enhancing the electron density at the metal center does not appear to promote bond activation processes.[38]

Scheme 4



To resolve this problem, we have analyzed the H$_2$ oxidative addition reaction using the energy decomposition scheme implemented within the ADF program. In this approach, based on the generalized transition state methodology,[39] $\Delta E_{\rm oxadd}$ is separated into a number of terms (Scheme 4): $\Delta E_{\rm prep}$, the energy required to distort the reactants to the geometries found in the product; $\Delta E_{\rm steric}$, comprised of $\Delta E_{\rm elect}$, the electrostatic interaction between the fragments, and $\Delta E_{\rm Pauli}$, the destabilizing energy arising from interactions between occupied fragment orbitals; and $\Delta E_{\rm oi}$, the stabilizing orbital interaction energy that results upon inclusion of unoccupied orbitals on each fragment. $\Delta E_{\rm oi}$ can itself be broken up in terms of symmetry.

We shall first consider the interaction of H$_2$ with a general C_{2v} {ML$_4$} fragment. The key frontier orbitals of the C_{2v} {ML$_4$} fragment are well-known,[40] and central to concerted oxidative addition processes are a high-lying occupied b$_2$ orbital and a low-lying vacant a$_1$ orbital (Scheme 5). During the reaction σ-donation occurs from the H$_2$ σ_g orbital into the {ML$_4$} a$_1$ acceptor orbital, an interaction in which {ML$_4$} acts as a Lewis acid. This is reinforced by π-back-donation from the {ML$_4$} occupied b$_2$ orbital into H$_2$ σ_u*, with {ML$_4$} now acting as a Lewis base. In C_{2v} symmetry the $\Delta E_{\rm oi}$ term of the energy decomposition scheme will allow these two processes to be quantified separately. Unfortunately, for Ru(CO)(IH)$_{3-n}$(PH$_3$)$_n$ species C_s symmetry is the maximum available, and only then when $n = 0$ or 2. In this case H$_2$ → {ML$_4$} σ-donation and {ML$_4$} → H$_2$ π-back-donation will both occur in a′ symmetry and so can no longer be distinguished. We have therefore chosen to compare the reactions of the closely related species

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(32) Intramolecular C−H and C(sp^2)−C(sp^3) bond activations have also been compared in a computational study. This showed C−H activation to be preferred kinetically but the C−C activation product to be more stable thermodynamically. Rybtchinski, B.; Oevers, S.; Montag, M.; Vigalok, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 9064.

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(36) Our results compare with the first absolute values for transition metal−NHC bond strengths of 180 ± 13 and 163 ± 13 kJ/mol for Ni(CO)$_2$(IAd) and Ni(CO)$_2$(I^{t}Bu), respectively (IAd = 1,3-diadamantylimidazol-2-ylidene and I^{t}Bu = 1,3-di-*tert*-butylimidazol-2-ylidene). Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490.

(37) Experimentally determined IR frequencies support the shift to lower frequency upon substitution of phosphine for NHC ligands: Ru(H)$_2$(CO)(PPh$_3$)$_3$, 1940 cm^{-1}; Ru(H)$_2$(CO)(IMes)(PPh$_3$)$_2$, 1937 cm^{-1}; Ru(H)$_2$(CO)(IMes)$_2$(PPh$_3$), 1880 cm^{-1}; Ru(H)$_2$(CO)(IEt$_2$Me$_2$)(PPh$_3$)$_2$, 1913 cm^{-1}; Ru(H)$_2$(CO)(IEt$_2$Me$_2$)$_2$(PPh$_3$), 1874 cm^{-1} (IEt$_2$Me$_2$ = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene). Douglas, S. R.; Paine, B. M.; Whittlesey, M. K., unpublished results.

(38) We have also investigated the substitution of PH$_3$ with the more electron-donating PMe$_3$ ligand. As with the PH$_3$/IH comparison, the energetics of H$_2$ oxidative addition barely change. For the Ru(H)$_2$(CO)(PMe$_3$)$_{3-n}$(PH$_3$)$_n$ series $\Delta E_{\rm oxadd} = -123.5$, -122.2, and -120.7 kJ/mol for $n = 1$, 2, and 3, respectively. In other studies the substitution of PH$_3$ by PMe$_3$ has been shown to cause a distinct increase in $\Delta E_{\rm oxadd}$ for H$_2$ oxidative addition. Clot, E.; Eisenstein, O. *J. Phys. Chem. A* **1998**, *102*, 3592. See also ref 28.

(39) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

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Scheme 5

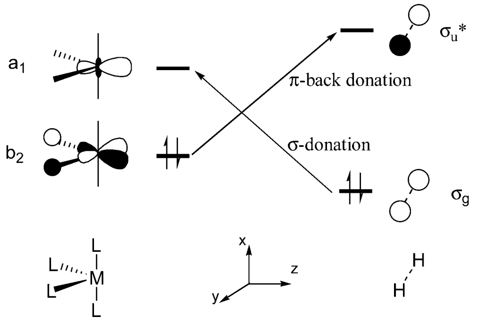

Table 5. Energy Decomposition Analysis (eV) for the Oxidative Addition of H_2 to $Ru(CO)_2(L)_2$ Species (L = PH_3 and IH)

energy term	L = PH_3	L = IH
ΔE_{prep} (H_2)	+4.98	+4.89
ΔE_{prep} ($Ru(CO)_2L_2$)	+1.13	+0.92
total ΔE_{prep}	+6.11	+5.81
ΔE_{elect}	−8.73	−8.24
ΔE_{Pauli}	+8.60	+7.91
ΔE_{Steric}	−0.13	−0.33
$\Delta E_{oi}(a_1)$	−2.20	−1.63
$\Delta E_{oi}(b_2)$	−4.99	−5.12
total ΔE_{oi}	−7.23	−6.78
ΔE_{oxadd}	+1.20	+1.19

$Ru(CO)_2(PH_3)_2$ and $Ru(CO)_2(IH)_2$ with H_2. C_{2v} symmetry can now be maintained throughout with H_2 adding in the OC−Ru−CO plane.

An important initial result is to show that the change of model system does not affect our basic finding that PH_3/IH substitution has a minimal effect on reaction energetics. This is indeed the case with ΔE_{oxadd} = −115.8 kJ/mol with $Ru(CO)_2(PH_3)_2$ and −115.0 kJ/mol with $Ru(CO)_2(IH)_2$.[41] The results of the energy decomposition analysis for these reactions are given in Table 5 and show that the major difference between the two systems occurs for ΔE_{oi}. Upon PH_3/IH substitution, π-back-donation from the $\{ML_4\}$-based b_2 orbital increases to the extent of 0.13 eV. More significant, however, is the effect of the IH ligands on the σ-donation into the $\{ML_4\}$-based a_1 acceptor orbital, which results in a 0.57 eV weaker interaction in $Ru(H)_2(CO)_2(IH)_2$. Overall, the total value for ΔE_{oi} is less favorable in the IH system by 0.45 eV.

Both these changes in the orbital interaction terms can be understood by considering the energies and compositions of the key b_2 donor and a_1 acceptor orbitals of the two $\{Ru(CO)_2(L)_2\}$ fragments, and details of these are shown in Table 6. For $\{Ru(CO)_2(PH_3)_2\}$ these two orbitals are very close in energy, while for $\{Ru(CO)_2(IH)_2\}$ both orbitals are strongly destabilized, with this effect being far greater for the a_1 acceptor orbital. The b_2−a_1 splitting therefore increases from 0.04 eV in $\{Ru(CO)_2(PH_3)_2\}$ to 0.45 eV in $\{Ru(CO)_2(IH)_2\}$. The composition of the a_1 acceptor orbital is also more affected by the introduction of IH ligands. This orbital takes on more metal character, and in particular the degree of metal s/p character increases markedly over the degree of d character. In contrast only subtle variations are seen in the composition of the b_2 donor orbitals. Overall, the destabilization of both the $\{ML_4\}$ b_2 and a_1 orbitals in $\{Ru(CO)_2(IH)_2\}$ is consistent with the metal center being more electron-rich than that in $\{Ru(CO)_2(PH_3)_2\}$. However, the major effect is not to make the metal fragment a better Lewis base (although this does occur to some extent) but rather to make it a considerably weaker Lewis acid. This latter difference dominates the ΔE_{oi} term and accounts for the lower value computed for the $Ru(H)_2(CO)_2(IH)_2$ system.[42] The changes in ΔE_{oi} tend to disfavor H_2 oxidative addition to $Ru(CO)_2(IH)_2$ relative to $Ru(CO)_2(PH_3)_2$, although, overall, ΔE_{oxadd} is approximately the same for the two systems. This result arises from the cumulative effects of small differences in ΔE_{steric} and ΔE_{prep}, which are more favorable in the $Ru(H)_2(CO)_2(IH)_2$ system.

Table 6. Orbital Energies (eV) and Percent Composition for the Key Frontier Molecular Orbitals of $Ru(CO)(L)(PH_3)_2$ Fragments (L = PH_3 and IH)[a]

L	orbital	energy	% composition
PH_3	$11a_1$	−3.90	Ru 60.1 (s: 6.1, p_z: 20.7, d_{z^2}: 13.9, $d_{x^2-y^2}$: 18.2) CO: 12.5 L: 26.9
	$7b_2$	−3.94	Ru 63.8 (p_y: 22.7, d_{yz}: 40.8) CO: 20.6 L: 15.9
IH	$18a_1$	−2.58	Ru: 69.8 (s: 11.6, p_z: 33.9, d_{z^2}: 13.9, $d_{x^2-y^2}$: 10.2) CO: 17.4 L: 11.4
	$9b_2$	−3.03	Ru 62.2 (p_y: 23.5, d_{yz}: 38.5) CO: 21.4 L: 16.9

[a] See Scheme 5 for molecule orientation.

Conclusions

In this paper we have used density functional calculations to compare the effects of phosphine and N-heterocyclic carbene ligands on the oxidative addition reactions of H_2, CH_4, and C_2H_6 to $Ru(CO)(IR)_{3-n}(PH_3)_n$ species (R = H = 1,3-imidazol-2-ylidene and R = Me = 1,3-dimethylimidazol-2-ylidene). Our results show that exchanging one or two PH_3 for IH results in minimal changes in the energetics of these reactions. The replacement of IH by IMe disfavors oxidative addition both kinetically and thermodynamically, a result that can be linked to the greater size of the IMe ligand. Computed Ru−PH_3 and Ru−IR bond strengths and CO stretching frequencies indicate that the presence of N-heterocyclic carbene ligands does create a more electron-rich metal center. These apparently counterintuitive findings, whereby a more electron-rich metal center does not promote oxidative addition, have been rationalized by fragment calculations. These show that while NHC ligands enhance the Lewis basicity of the metal reactants, a more significant result is a reduction in their Lewis acidity, and this latter effect dominates the orbital interactions with substrates such as H_2. More generally our results suggest that creating a more electron-rich transition metal center may not *necessarily* promote bond activation processes and that the effects

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(41) The energetics of these reactions change by less than 0.5 kJ/mol when recomputed without any symmetry constraints.

(42) We have also performed the fragment analysis on the optimized structures of $Ru(H)_2(CO)(PH_3)_3$ and $Ru(H)_2(CO)(IH)_2(PH_3)$. As was seen for the $Ru(H)_2(CO)_2(PH_3)_2$/$Ru(H)_2(CO)_2(IH)_2$ comparison, ΔE_{oi} is greater when more PH_3 ligands are present, in this case by 0.41 eV.

of the coordination environment on *both* the donor and acceptor capabilities of the metal species must be taken into account.

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Supporting Information Available: Tables of Cartesian coordinates and energies for all stationary points and unique imaginary eigenvalues for all transition states. This material is available free of charge via the Internal at http://pubs.acs.org.

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