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Article

Calculation of Dramatic Differences in the Activation Energy of Phenyl Migratory Insertion in the Isomers of $[Rh(PMe_3)_2Cl(CO)(Ph)H]$: Important Effects from Both the Ligand trans to Ph and the Ligand trans to CO

Faraj Hasanayn* and Dina Abu-El-Ez

Department of Chemistry, American University of Beirut, Beirut, Lebanon

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trans,trans-$[RhL_2(Ph)(CO)HCl]$ (**2a**) and *trans,trans*-$[RhL_2(Ph)Cl(CO)H]$ (**2b**) are known to form as major products in the reaction between benzene and a photoexcited state of *trans*-$[RhL_2(CO)Cl]$ (**1**; L = PMe_3). In the presence of carbon monoxide, these species are believed to ultimately lead to catalytic photocarbonylation of benzene. At the B3LYP level of theory the calculated free energy of activation for the concerted transition state (TS) of phenyl to CO migration in **2b** (**TSb**) is 39 kcal/mol. In contrast, the barrier of insertion in the *trans,trans*-$[RhL_2(Ph)H(CO)Cl]$ isomer (**2c**) which is 7.4 kcal/mol higher in energy than **2b** is only 15 kcal/mol. The calculated geometries of the reactants and TSs indicate that the disparity in the given barriers arises from a combination of two factors. First, the orientation of H trans to the migrating Ph group in **2c** favors the TS because it weakens the Rh−Ph bond and thus makes it easier to begin migration of the phenyl group in comparison with **2b** where the phenyl is trans to the chloride. Second, the orientation of the hydride trans to CO in **2b** appears to strongly disfavor the reaction compared to **2c** where CO is trans to Cl. Specifically, the calculations give strong evidence that the Rh−H bond in **2b** is substantially weakened in **TSb**, and this should add to the increased barrier of this isomer. These propositions are supported by calculations on the reaction of the *cis*-$Rh(PMe_3)_2$ isomers of **2** and other related octahedral complexes.

Introduction

Carbonyl insertion into a metal−alkyl or metal−aryl bond is one of the most fundamental and characteristic reactions in transition metal chemistry.[1] The reaction is a necessary elementary step in important industrial catalytic transformations such as alcohol carbonylation[2] and olefin hydroformylation.[3] Insertion and its microscopic reverse (such as in aldehyde decarbonylation) are also important in the synthesis of fine chemicals using transition metal reagents.[4] Thus, an understanding of the mechanism and the factors that influence the kinetics of the CO insertion step is critical in any attempt of rational design or fine-tuning of such catalysts and reagents. Accordingly, the reaction has been the subject of numerous theoretical investigations conducted in different contexts.[5,6]

A particularly important and challenging transformation in transition metal chemistry that should involve a CO insertion step into a metal−carbon bond is the carbonylation of unactivated C−H bonds. The discovery by Eisenberg et al.[7,8]

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*To whom correspondence should be addressed. E-mail: fh19@aub.edu.lb.

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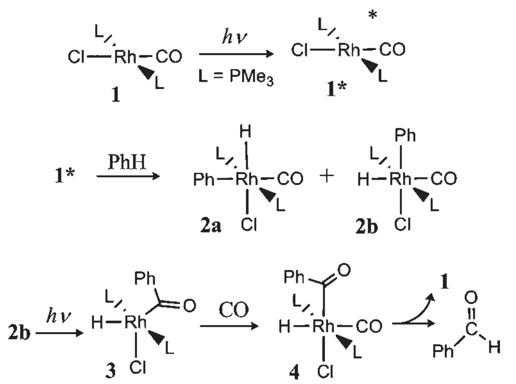
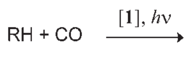
Scheme 1. Benzene Carbonylation Photocatalyzed Using **1** (from ref 10)

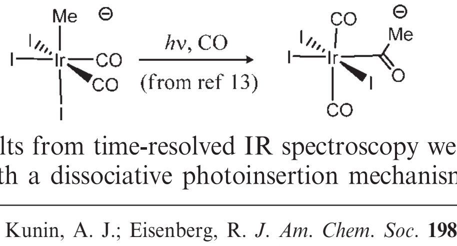


and Tanaka et al.[9] that square planar complexes related to *trans*-[Rh(PMe$_3$)$_2$(CO)Cl] (**1**) photocatalyze the carbonylation of aliphatic and aromatic hydrocarbons (eq 1) remains one of the most interesting and inspiring examples in this area.

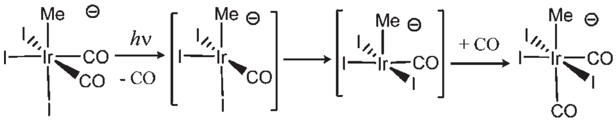

(1)

Kinetics and mechanistic experiments by Goldman and co-workers provided evidence that photocarbonylation of benzene using **1** includes two photoprocesses,[10,11] neither of which involves CO dissociation. Instead, the results were consistent with addition of a C–H bond of benzene to an excited state of **1** and the generation of the six-coordinate intermediate (**2**) shown in Scheme 1. Support for the possible involvement of **2** in this system is provided in an elegant set of NMR experiments by Field et al. in which irradiation of **1** in benzene in the absence of CO was shown to build a mixture of the two *cis*-Ph–Rh–H isomers (**2a** and **2b** in Scheme 1) that retain the initial *trans*-(PMe$_3$)$_2$ configuration of **1**.[12]

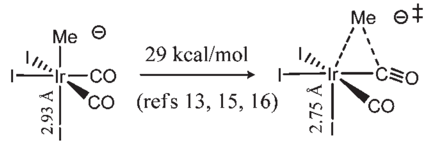
Of the two isomers observed by Field, only **2b** has the correct stereo configuration to undergo Ph to CO migratory insertion. Though unprecedented at the time, Goldman and co-workers postulated that insertion in **2b** is the step that requires the second photon in the observed 2-photon carbonylation process, but the nature of that photoprocess remained unaddressed.[10] Subsequently, Ford and co-workers reported a clear example of photoinduced CO insertion in the cis,fac isomer of [Ir(CO)$_2$I$_3$Me]$^-$ (eq 2),[13] which is implicated in the Cativa process for methanol carbonylation utilizing [Ir(CO)$_2$I$_2$]$^-$.[14]


(2)

Results from time-resolved IR spectroscopy were consistent with a dissociative photoinsertion mechanism causing cis,fac to cis,mer isomerization via a five-coordinate intermediate as shown in eq 3.[13]


(3)

In accord with prior density functional theory (DFT) predictions by Kinnunen and Laasonen (eqs 4 and 5),[15] Ford proposed that thermal insertion in *cis,mer*-[Ir(CO)$_2$I$_3$Me]$^-$ is kinetically much more facile than in the starting cis,fac isomer. Conclusive evidence for the latter proposition was ultimately presented by Haynes and co-workers who actually synthesized the cis,mer isomer and studied the kinetics of its CO insertion using stopped-flow techniques.[16]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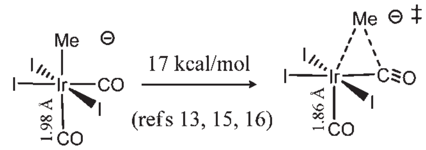
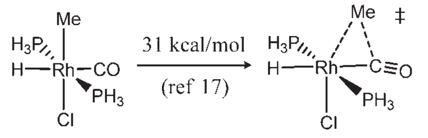
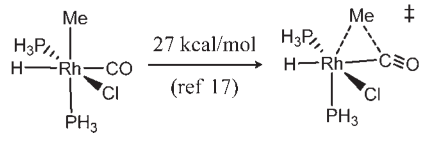

(5)

In light of the above studies on [Ir(CO)$_2$I$_3$Me]$^-$, we became interested in using electronic structure methods to explore if the activation energy of phenyl migration in [Rh(PMe$_3$)$_2$-Cl(CO)(Ph)H] (**2**) may also exhibit large dependence on the stereo configuration. A previous computational investigation of insertion in the related model [Rh(PH$_3$)$_2$Cl(CO)(Me)H] complex by Ziegler and co-workers considered only the isomer matching **2b** (eq 6) and another isomer having the two phosphines in a cis arrangement (eq 7).[17] The study found barriers that were substantial and comparable (ca. 30 kcal/mol) in the two isomers.[17]


(6)


(7)

In a recent experimental and theoretical study by Madsen and co-workers concerning the mechanism of benzaldehyde decarbonylation using [Rh(dppe)(CO)$_2$]$^+$, the migration

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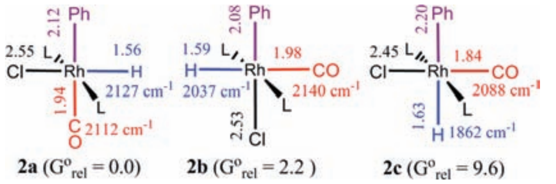

Figure 1. Geometric parameters (in Å), Rh−H and CO stretching vibrational frequencies, and relative free energy (in kcal/mol; at 298 K and 1 atm) in the *trans*-RhL$_2$ isomers of **2** (L = PMe$_3$).

barriers in the isomers of [Rh(dppe)(CO)$_2$(Ph)H]$^+$ were calculated to differ by less than 10 kcal/mol.[18]

Our DFT calculations of phenyl migration in the isomers of [Rh(PMe$_3$)$_2$(CO)Cl(Ph)H] (**2**) give activation energies that vary from 10 to 40 kcal/mol depending on the isomer. We show that these variations arise from a combination of two distinct effects, one due to the ligand trans to the migrating phenyl group and one due to the ligand trans to the carbonyl. In addition to their implications with respect to benzene photocarbonylation by **1**, these findings have significance with respect to understanding the reactivity of migratory insertion reactions in general. To facilitate the presentation of the results, we first focus on the isomers of **2** that have the two PMe$_3$ groups in a trans configuration, and we later consider the *cis*-(PMe$_3$)$_2$ isomers.

Results and Discussion

Reactants. The geometry and relative energy ($G°_{rel}$; in kcal/mol) of the three *trans*-(PMe$_3$)$_2$ isomers of **2** are compared in Figure 1.

The two octahedral isomers that were observed in the photochemical experiments by Field are calculated to have comparable energies, with the one having the phenyl group trans to Cl (**2b**) 2.2 kcal/mol higher than **2a** where the phenyl is trans to CO. On the other hand, **2c** is substantially higher in energy ($G°_{rel}$ = 9.6 kcal/mol). We note that experimentally, the addition of HCl to *trans*-[Rh(PMe$_3$)$_2$(Ph)(CO)] at low temperatures generates only **2a**,[12] which is predicted by our calculations to be the most thermodynamically stable isomer. This suggests that kinetic effects may be not relevant in this reaction.

The factors that determine $G°_{rel}$ in **2** are closely tied to the problem of the activation energy of phenyl migration of interest to the present study, so we make some effort to analyze why **2c** has a much higher energy than **2a** and **2b**. The placement of the π-donor chloride trans to the π-acceptor carbonyl in **2c** should be a favorable one, and this is indeed reflected in the Rh−Cl and Rh−CO distances, 2.45 and 1.84 Å, respectively, which are significantly shorter than in **2a** (2.55 and 1.94 Å) or **2b** (2.53 and 1.98 Å). The high energy of **2c** in this case should follow from stronger but unfavorable electronic effects arising from the trans H−Rh−Ph configuration, and this is evident in the Rh−H and Rh−Ph bond distances (1.63 and 2.20 Å, respectively) which are significantly longer than in **2a** (1.56 and 2.12 Å) or **2b** (1.59 and 2.08 Å). The hydride and the phenyl are both strong σ-donor ligands, and they presumably compete for the same metal orbitals for bonding in **2c**, thus causing mutual weakening of the Rh−H and Rh−Ph bonds that lead to a high energy of **2c**.

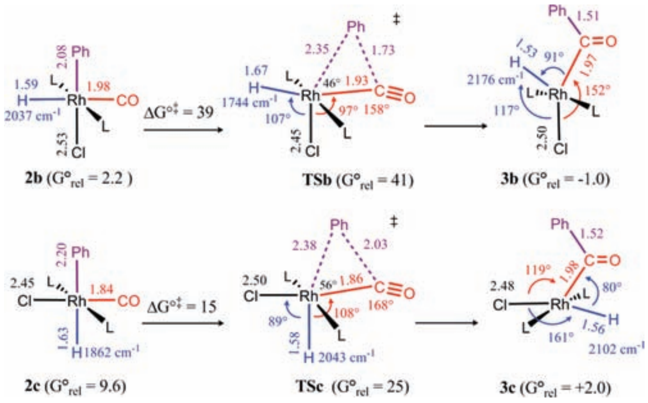

Figure 2. Geometry (in Å), free energy (in kcal/mol; at 298 K and 1 atm), and the Rh−H stretching vibrational frequency related to phenyl migration in the *trans*-RhL$_2$ isomers of **2** (L = PMe$_3$).

Significantly, the Rh−H bond distance in the given molecules, r_{Rh-H} = 1.56 (**2a**) < 1.59 (**2b**) < 1.63 Å (**2c**), shows that the lower energy isomers are associated with proportionally stronger Rh−H bonds. This is perhaps expressed more pronouncedly in the calculated Rh−H stretching vibrational frequency, ν_{Rh-H} = 2127 (**2a**) > 2037 (**2b**) > 1862 cm^{-1} (**2c**), which is much lower in the higher energy isomers. In contrast, the Rh−Cl bond is slightly shorter in the higher energy isomers, r_{Rh-Cl} = 2.55 (**2a**), 2.53 (**2b**) and 2.45 Å (**2c**), while there are no systematic relations between $G°_{rel}$ and either the Rh−Ph or the Rh−CO bond length or the CO vibrational frequency. A similar association between the Rh−H bond length (or ν_{Rh-H}) and $G°_{rel}$ holds in the set of *cis*-(PMe$_3$)$_2$ isomers (Figures 6 and 7). This suggests that when steric effects are comparable, the strength of the Rh−H bond becomes the leading factor (or at least the leading indicator) in determining the relative energy of the isomers of **2**. In turn, because H is a purely σ-donor ligand, the strength of the Rh−H bond should be particularly sensitive to the σ-properties of the ligand trans to it. Clearly, among the Ph, Cl, and CO ligands, the strong σ-donor phenyl group exerts the strongest *trans*-influence on the Rh−H bond.

Different $\Delta G^{\circ\ddagger}$ Values and Implications. The calculated structural and energy parameters of the transition states (TSs) and products of phenyl migration in **2b** and **2c** are compared in Figure 2 (**TSb** and **TSc**). The TS geometries are simple in the sense that they involve primarily displacement of the phenyl group from Rh to CO, with minimal change in the Rh−CO bond distance in either TS. The elongated Rh−Ph bond distance is comparable in the two TSs (2.35 vs 2.38 Å). However, in **TSb** the Rh−Ph bond undergoes more bending toward CO than in **TSc** (Ph−Rh−CO = 46° vs 56°) with a commensurately shorter Ph−CO bond in **TSb** (1.73 vs 2.03 Å). Finally, the metal−CO linkage is bent more in **TSb** than in **TSc** (Rh−C−O = 158° vs 168°).

The calculated standard state free energy of activation for the transformation from **2b** to **TSb** is 39 kcal/mol ($\Delta G^{\circ\ddagger}$ at 298 K and 1 atm). In contrast, $\Delta G^{\circ\ddagger}$ in the reaction of **2c** is only 15 kcal/mol. The corresponding $\Delta G^{\circ\ddagger}$ values for methyl migration in the methyl analogues of **2b** and **2c**

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[18] Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 5206.

are 34 and 8.2 kcal/mol, respectively. Changing the DFT method, the basis set or the effective core potential (ECP) on Rh in the latter reactions does not significantly change the absolute or the relative magnitude of the two barriers (Supporting Information, Table S1). All of these results converge therefore to the conclusion that the kinetics of thermal alkyl or aryl migration should be effectively forbidden in **2b** but very facile in **2c**. Even more strikingly, the isomer of **2** having a phosphine trans to each of the phenyl and the carbonyl (**2d**, eq 8) is calculated to be 2.7 kcal/mol below **2c**, and it encounters an even more reduced migratory insertion barrier of just 12 kcal/mol.

(8)

Thus, although there is evidence that **2b** is accessible as an intermediate in benzene photocarbonylation using **1** (Scheme 1), the calculations suggest that this isomer is unlikely to play any significant role in direct CO insertion. In a sense the calculated high barrier in **2b** supports Goldman et al.'s proposition that a photon is needed to affect this step.[10] Given the low energy of **TSc** and **TSd**, it becomes tempting to speculate then that isomers like **2c** or **2d** may be involved in photocarbonylation by **1**, possibly for example by being produced by photoinduced isomerization of **2a** or **2b** (Scheme 1).

In addition to carbonylation, the calculated results in Figure 2 are also directly relevant to the mechanism of thermal carbonyl deinsertion in five coordinate complexes related to $[Rh(PMe_3)_2Cl(H)(C(O)Ph)]$ (**3**). For example, *trans*-$[Rh(P^iPr_3)_2Cl(H)(C(O)Ph)]$ is synthesized from the reaction between $[Rh(P^iPr_3)_2Cl]_2$ and benzaldehyde, but it is known to undergo slow decarbonylation to give the square planar analogue of **1** and benzene.[19,20] Consistent with crystallographic data,[19] we calculate the geometry of **3** to deviate significantly from the idealized square pyramidal or trigonal bipyramidal motifs, with the Cl−Rh−acyl and Cl−Rh−H angles at 152° and 117°, respectively (**3b** in Figure 2).[21] All attempts to locate isomers of **3** that retain the trans PMe_3 arrangement always converged to **3b** or to the conformer defined by rotation of the acyl group by 180° (**3c** in Figure 2) which is 3.0 kcal/mol above **3b**. **2c** and **3c** seem to connect concertedly on the potential energy surface via **TSc**. The transformation from **2b** to **3b** is exoergic by 3.2 kcal/mol. An energy profile summarizing the relative energy of all the species considered so far is given in Figure 3.

Figure 3 shows that the activation energy from **3b** to **TSb** is 42 kcal/mol. Therefore **TSb** is again unlikely to be important in aldehyde decarbonylation by complexes related to $[Rh(P^iPr_3)_2Cl]_2$. On the other hand, the barrier from **3c** to **TSc** is 23 kcal/mol, so **TSc** can be kinetically relevant at ambient conditions. However, deinsertion via **TSc** leads to **2c** which is 7.6 kcal/mol uphill relative to **3c**, and which cannot undergo direct reductive elimination of benzene. Any role for **2c** in aldehyde decarbonylation will therefore depend on its ability to undergo rapid isomerization into the lower energy **2a** or **2b** isomers. Exploration of isomerization or alternative decarbonylation pathways is beyond the scope of the present study.[22] Instead, in the remaining parts of the study we attempt to rationalize why **TSb** has a much higher energy than **TSc**.

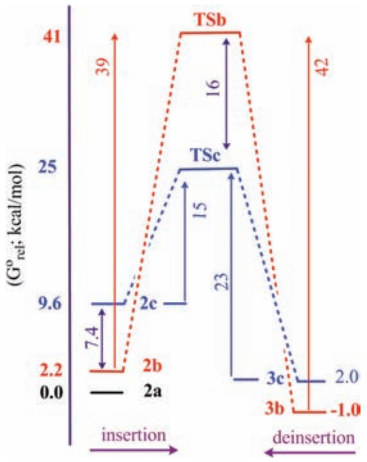

Figure 3. Free energy profile (in kcal/mol; at 298 K, 1.0 atm) for the transition states connecting the six and five coordinate *trans*-$Rh(PMe_3)_2$ isomers.

Origin of the Different Barriers. Because insertion in **2b** and **2c** entails some degree of dissociation of the Rh−Ph bond to reach the TS, their different reaction barriers should arise in part from ground state effects that pertain to differences in the strength of the Rh−Ph bond in the two reactants. The Rh−Ph bond distance in **2b** (2.08 Å) where the phenyl is trans to Cl is significantly shorter than in **2c** (2.20 Å) where it is trans to H, so a greater energy input to the activation barrier should be applied to begin dissociating this bond in **2b**. Consistently, the (vertical) energy needed to elongate this bond from its equilibrium value in **2b** to the one in **TSb** (2.35 Å) without changing any other parameter is calculated to be larger than the energy needed to stretch this bond from **2c** to **TSc** (8.3 vs 3.0 kcal/mol). Clearly however, this energy input comprises only a small fraction of the actual barrier in the two reactions (39 vs 15 kcal/mol). More importantly, if the Rh−Ph bond strength in the ground state were the only factor, the absolute energy of **TSb** ($G°_{rel}$) would be 2.1 kcal/mol lower than **TSc**. The actual energy of **TSb** is however 16 kcal/mol higher than **TSc** (Figure 3). This indicates that the barriers in the given octahedral complexes are dictated largely by transition state effects that evolve as the phenyl group is bent toward CO to begin C−C bond formation.

Since **TSb** and **TSc** are isomeric, their inherent energy difference (16 kcal/mol) can be analyzed in the same way

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[19] Wang, K.; Emge, T. G.; Goldman, A. S. *Organometallics* **1995**, *14*, 4929.

[20] Goikhman, R.; Milstein, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1119.

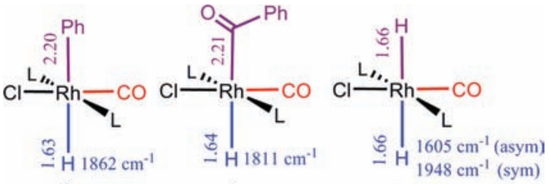
[21] For a discussion of the origin of distortion in this complex see ref 19 by Goldman and: (a) El-Idrissi, I .; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. (b) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **1992**, *11*, 729.

[22] For examples in which reductive elimination in octahedral complexes is preceded by geometry isomerization see: (a) Rosini, G. P.; Wang, K.; Patel, B.; Goldman, A. S. *Inorg. Chim. Acta* **1998**, *270*, 537. (b) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442.

adopted to analyze why the energy of **2c** is much higher than that of **2b**. In this analysis the strength of the Rh−H bond stood out as an important factor in dictating $G°_{rel}$ of the isomers. Indeed, the Rh−H bond in the high energy **TSb** is much longer than in **TSc**: 1.67 versus 1.58 Å. This implies that in the TSs the (unfavorable) influence of the migrating phenyl group on the Rh−H bond trans to it is much weaker than the trans influence of the incipient acyl group.

An assessment of the trans influence of the migrating phenyl group in the TS can be made by comparing the bond distances of the ligand trans to Ph in the reactants and TSs. In **TSb** the Rh−Cl bond is shorter than in **2b** (2.45 vs 2.53 Å), and in **TSc** the Rh−H bond is shorter than in **2c** (1.58 vs 1.63 Å; Figure 2). The shorter bonds implicate a diminished trans influence of Ph in the TSs.[23,24] Such contractions should be associated with some degree of stabilizing energy of the TS geometry depending on the nature of the ligand trans to Ph. Since the metal−H bond is highly sensitive to the σ-properties of the ligand trans to it (as is evident in the energy of the three isomers of **2** discussed before for example), it is not unreasonable for such TS stabilization energy to be more important in the reaction of **2c** over **2b**.

In contrast to the contraction of the bond trans to the migrating phenyl group, in all of the isomers considered, the bond trans to CO is calculated to be longer in the TSs than in the reactants. Thus, the Rh−H bond distance increases from 1.59 in **2b** to 1.67 Å in **TSb**, and Rh−Cl increases from 2.45 in **2c** to 2.50 Å in **TSc**. From these changes, we can infer that the incipient acyl group exerts an increased trans influence in the TS. The loss of the bonding energy implicated in the longer bonds should contribute directly to a higher energy of all the isomeric TSs. Clearly, the increase in the Rh−H bond in **2b** expressed in either absolute (0.08 Å) or percent (5%) terms is significantly greater than the increase in the Rh−Cl bond in **2c** (0.05 Å or 2%). Consistent with a very weak Rh−H bond, the Rh−H stretching vibrational frequency in **TSb** is 1744 cm^{-1}, much smaller than in any other isomer or TS of **2**. This supports without ambiguity that a greater bonding energy has been lost from the Rh−H bond in **TSb** compared to the energy lost from the Rh−Cl bond in **TSc**, and this should be an important component in the high energy of **TSb**. Note that in the five coordinate products (**3b** or **3c** in Figure 2) the trans H−Rh−acyl arrangement is avoided in the distorted geometry and the Rh−H bond is quite short (1.53 Å). This is important to take into account when the reaction is considered in the reverse (deinsertion) direction.



2c **4** **5**

Figure 4. Minimized geometries used to evaluate the trans influence of a fully formed benzoyl bond (L = PMe_3).

A weakening in the trans influence of the phenyl group in the TS geometry seems logical as the phenyl is being removed from the metal center. A contrasting increase in the trans influence of the incipient acyl group on the other hand is less obvious. Such increase may at first be thought to follow from a change in the σ-character of the incipient acyl carbon as it is being transformed from a formally neutral sp carbon in CO to an anionic sp^2 one in the final benzoyl product. However, the Rh−H bond in **TSb** (1.67 Å) is actually significantly longer than in **2c** (1.63 Å) where it is trans to the strong σ-donor phenyl group. As a matter of fact, the Rh−H bond in **TSb** is even longer than in the two octahedral analogues of **2c** (**4** and **5** given in Figure 4) where it is trans to a completely formed Rh−benzoyl or Rh−H bond, 1.64 or 1.66 Å; respectively. This is surprising because in **TSb** the extent of Ph−CO bond formation is far from being complete, with the Ph−CO bond distance still long (1.73 Å) and the Rh−C−O angle bent only to 158°. This suggests that the extreme trans influence of the incipient acyl group in **TSb** should be taken in the context of the reaction center moiety in its entirety, and not just in terms of an isolated σ-donating character of the incipient carbon atom.

In summary, the reaction center of insertion in the octahedral complexes considered in the present study requires lengthening of the Rh−Ph bond and tilting of the phenyl toward CO to begin C−C bond formation. In **2b** the trans Cl−Rh−Ph configuration is good for the Rh−Ph bond, so it makes it difficult to dissociate this bond to reach **TSb**. In addition, in **2b** the trans H−Rh−CO configuration appears to be favorable in the ground state but highly unfavorable in **TSb**. The latter condition is inferred from an exceptionally long Rh−H bond in **TSb** that implicates a significant loss of bonding energy from the Rh−H bond in this TS. The extent of the combined unfavorable effects from these two components can be associated with the calculated unusually high barrier of insertion in **2b** (39 kcal/mol). When the positions of the hydride and the chloride in **2b** are swapped to obtain **2c**, the TS is stabilized in two ways. First, the mutual weakening of the trans H−Rh−Ph bonds in **2c** makes it easier to pull the Rh−Ph bond to reach **TSc**, and possibly provides opportunity for extra stabilization from a subsequent contraction of the Rh−H bond in the TS. Second, the beginning of Ph−CO bond formation appears to become less obstructed in **TSc** since the incipient acyl group is not trans to a strong σ-donor anymore. When the

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[23] Similar bond contractions were noted by Haynes in the insertion TSs of $[Ir(CO)_2I_3Me]^-$ where the Ir−I bond trans to the methyl in the cis,fac isomer decreases from 2.93 to 2.75 Å (eq 4), and the Ir−CO bond trans to the methyl in the cis,mer isomer decreases from 1.98 to 1.86 Å (eq 5). Haynes argued that the contraction in the Ir−CO bond enables CO to become a more effective π-acceptor in the TS, thus leading to a smaller reaction barrier in the cis,mer isomer (eq 5). The fact that the migrating phenyl and methyl groups are strong σ-donor ligands suggests that the systematic decrease in the Rh−H, Rh−Cl, Ir−I, and Ir−CO bonds in all of these TSs follows at least in part from creation of more favorable conditions for σ-interaction between each of these ligands and the metal as the migrating group is removed from the trans site in the TS.

[24] For examples in which π-arguments were used to account for the reactivity of insertion in other octahedral complexes: (a) Kubota, M.; McClesky, T. M.; Hayashi, R. K.; Webb, C. G. *J. Am. Chem. Soc.* **1987**, *109*, 7569. (b) Haynes, A.; Pearson, J. M.; Vickers, P. W.; Charmant, J. P. H.; Maitlis, P. M. *Inorg. Chim. Acta* **1998**, *270*, 382. (c) Bellachioma, G.; Cardaci, G.; Jablonski, C.; Macchioni, A.; Reichenbach, G. *Inorg. Chem.* **1993**, *32*, 2404. (d) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *J. Organomet. Chem.* **1997**, *540*, 7.

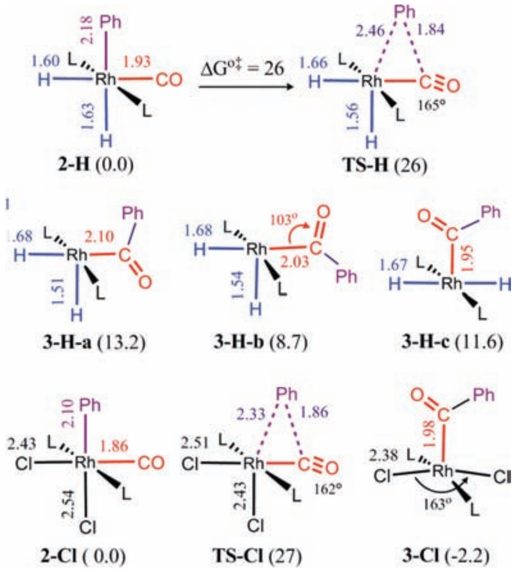

Figure 5. Migratory insertion in the dihydrido and dichloro analogues of **2**. Values in parentheses are the free energy of the TSs and products relative to the reactants (in kcal/mol; at 298 K and 1 atm; L = PMe_3).

changes in the *trans*-influence of the migrating and incipient groups that take place upon transformation from the ground state to the TS are accepted as exerting distinct effects on the barrier, it becomes possible to rationalize why the insertion barriers of two similar octahedral molecules (a pair of isomers) can differ by as much as 24 kcal/mol.

Quantifying the Individual Effects. In an attempt to separate the 24 kcal/mol difference between $\Delta G^{\circ\ddagger}$ in **2b** and **2c** quantitatively into individual *trans*-Ph and *trans*-CO ligand effects, we calculate two new reactions described in Figure 5 in which the hydride and chloride in **2** are intersubstituted. To isolate the *trans*-Ph effects we first substitute the chloride trans to Ph in **2b** by a hydride. The barrier to insertion in the resulting dihydrido complex (**2-H**) is 26 kcal/mol, 13 kcal/mol smaller than in **2b**. Conversely, when the hydride trans to Ph in **2c** is substituted by a chloride (reaction of **2-Cl** in Figure 5) the barrier increases by 12 kcal/mol.

The results from the two substitutions support the idea that a hydride trans to Ph is much more favorable for the kinetics of Ph migration than a chloride, and they agree on quantifying this effect at about 12 kcal/mol. By the same logic, the same data show that the orientation of a hydride trans to CO is destabilizing for the TS compared to the chloride by about 12 kcal/mol.

In the reaction of **2-H** in Figure 5, **TS-H** leads concertedly to the five coordinate **3-H-a** benzoyl product which has a square pyramidal geometry with the hydride in the apical position. The transformation from **2-H** to **3-H-a** is endoergic by 13.2 kcal/mol. Rotating the benzoyl group in **3-H-a** by 180° affords **3-H-b**, which is 4.5 kcal/mol lower in energy than **3-H-a**. The calculated geometry of **3-H-b** is characterized by an unusually small Rh−C−O angle (103°), which suggests that its greater stability over **3-H-a** arises from some bonding interaction between the CO bond of the benzoyl group and the metal. Finally, the isomer of **3-H** having the benzoyl group in the apical position (**3-H-c**) is 11.6 kcal/mol above **2-H**. For the reaction of **2-Cl** only one minimum could be identified for the benzoyl product, namely, **3-Cl** with a square pyramidal geometry and the benzoyl group at the apical position. The reaction from **2-Cl** to **3-Cl** is calculated to be exoergic by 2.2 kcal/mol.

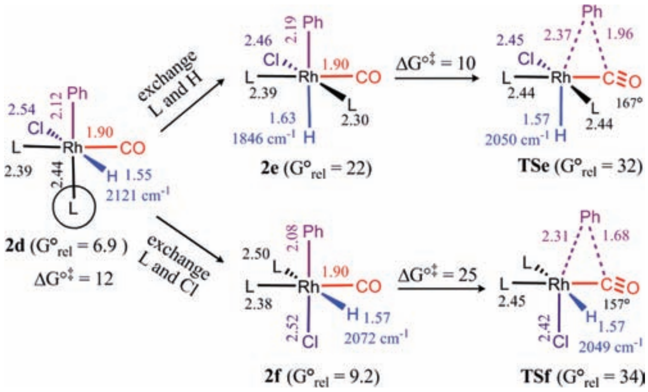

Figure 6. Evaluation of the *trans*-Ph effects of PMe_3 on the barrier of phenyl migration in the *cis*-L_2 isomers of **2**. Energies in kcal/mol; and bond distances in Å (L = PMe_3).

***cis*-(PMe_3)$_2$ Isomers.** The lowest energy *cis*-(PMe_3)$_2$ isomer of **2** that can undergo phenyl migration is **2d** which has one phosphine trans to Ph and the other trans to CO. As mentioned before (eq 8), $\Delta G^{\circ\ddagger}$ of insertion in **2d** is 12 kcal/mol. For the barrier in **2d** to be so much smaller than in either the dihydrido or the dichloro complexes considered in Figure 5 the individual *trans*-Ph and *trans*-CO effects of the phosphine (steric or electronic) must be different from those of H and Cl. The results suggest that unlike the chloride, PMe_3 does not strongly disfavor the TS when it is trans to Ph, and unlike the hydride it does not disfavor the TS when it is trans to CO. Consistently, when the phosphine trans to Ph in **2d** is exchanged with the hydride to give isomer **2e** (Figure 6), $\Delta G^{\circ\ddagger}$ decreases by only 2 kcal/mol. However, **2e** is the highest energy isomer of **2** (G°_{rel} = 22 kcal/mol) and probably the least likely to be chemically relevant. On the other hand, exchanging the phosphine trans to Ph and Cl in **2d** increases $\Delta G^{\circ\ddagger}$ by 13 kcal/mol (isomer **2f** in Figure 6).

On the basis of the data in Figure 6, the (stabilizing) relative *trans*-Ph effect of the three ligands in the *cis*-isomers may be qualitatively ranked as: H > PMe_3 ≫ Cl. This order matches the general σ-donation strength of the given three ligands. Note that in **2f** the Rh−Ph bond distance (2.08 Å) is the shortest in the series of *cis*-(PMe_3)$_2$ isomers, so as in **2b**, the larger barrier in **2f** compared to **2d** has a ground state component from the requirement of a greater energy to begin dissociation of the Rh−Ph bond in **2f**.

Finally, to evaluate the relative effects of PMe_3 on $\Delta G^{\circ\ddagger}$ when it is trans to CO, we again start with **2d** and we now exchange the PMe_3 trans to CO first with H and then with Cl (Figure 7). The first isomerization puts H trans to CO (**2g**) and increases $\Delta G^{\circ\ddagger}$ by 14 kcal/mol. The second isomerization puts Cl trans to CO (**2h**) and increases $\Delta G^{\circ\ddagger}$ by 4 kcal/mol.

The data in Figure 7 afford the following order of the (unfavorable) effects of the ligand trans to CO in the *cis*-isomers: H ≫ Cl > PMe_3. This order cannot be accounted for in a straightforward way based only σ-effects.

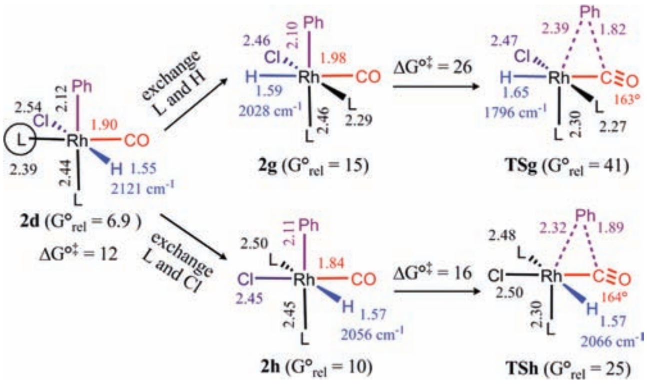

Figure 7. Evaluation of the *trans*-CO effects of PMe_3 on the barrier of phenyl migration in the *cis*-L_2 isomers of **2**. Energies in kcal/mol; and bond distances in Å (L = PMe_3).

In previous studies, both the π-properties[25] and the size[26] of the ligand trans to the incipient CO were proposed to influence the insertion barrier. Such factors can certainly be relevant to the variations in Figure 7, but we do not find it trivial to separate them convincingly in a simple way. Nonetheless, the results in Figure 7 strongly enforce the proposition that the presence of a hydride trans to CO is highly unfavorable for the TS of migratory insertion in octahedral complexes, which we regard as a particularly important finding of our study.

Conclusions

We have used electronic structure methods to study the TS of phenyl to CO migration in the octahedral isomers of $[RhL_2Cl(CO)(Ph)H]$ (**2**; L = PMe_3). This molecule has been implicated as an intermediate in benzene photocarbonylation using *trans*-$[RhL_2Cl(CO)]$. Of all the isomers that can undergo insertion, insertion in the experimentally observed *trans*, *trans*-$[RhL_2(Ph)Cl(CO)H]$ isomer (**2b**) is calculated to encounter an exceptionally high activation energy (39 kcal/mol). The barrier in the other isomers varies from 10 to 25 kcal/mol. To rationalize these huge variations we distinguish between effects involving the ligand trans to the phenyl group and effects pertaining to the ligand trans to CO. Unsurprisingly, the Rh−Ph dissociation component of the TS appears to be largely facilitated when there is a hydride trans to the phenyl group compared to Cl. Less expectedly, the calculations give strong evidence that the ligand trans to CO plays an important role in determining the reaction barrier. Comparisons of the geometries of the reactants and TSs imply that the trans influence of the CO group increases substantially in the TS, and this strongly disfavors the kinetics of migratory insertion when there is a ligand with a strong trans influence such as a hydride trans to CO.

Computational Methods

The calculations were performed at the B3LYP density functional level[27] using Gaussian 03.[28] The Hay−Wadt relativistic effective core potential (ECP) replaced the 28 core electrons of Rh.[29] The 6-31G(2d,2p) basis set was used on the main group elements.[30] For Rh, the double-ζ basis set supplied with the ECP was used along with two sets of 10f polarization functions having exponents of 1.35 and 0.45, one obtained from a study by the Frenking group,[31] and the other estimated as the third of the first exponent. The Harmonic vibrational frequencies were used without scaling to obtain the enthalpy and entropy terms at 298 K.[32] We used the reaction of methyl migration in the **2b** and **2c** isomers where the C_s point group is applicable to check the effect of the DFT functional (BPW91[33] and mPW1PW91[34]), the ECP (Stuttgart−Dresden[35] and Peterson[36]), and the basis set (cc-pVTZ)[37] on the results. The activation energies in all of these variations were very comparable. The results are summarized in Supporting Information, Table S1.

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Supporting Information Available: Cartesian Coordinates and absolute energies of the reactants, TSs, and products presented in Figure 2, and a summary table for the effects of the density functional, basis set, and ECP on the reaction barrier. This material is available free of charge via the Internet at http://pubs.acs.org.

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