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Synthetic and Computational Studies of Thiocarbonyl/σ-Organyl Coupling Reactions

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The reactions of a range of coordinatively unsaturated σ-organyl thiocarbonyl complexes with 1,4,7-
trithiacyclononane ([9]aneS3) have been investigated, leading in some but not all cases to migratory insertion of thiocarbonyl and σ-organyl ligands. Thus, under ambient conditions, the reaction of [RuR-
Cl(CS)(PPh3)]2 (R = C(CO2Me)=CHC(O)Me, C(C≡CPh)=CHPh, C6H5) with [9]aneS3 provides σ-organyl complexes [RuR(CS)(PPh3)][(9]aneS3)]. On heating, the species [Ru(C6H5)(CS)(PPh3)][(9]aneS3)]+ converts to the thiobenzoxy complex [Ru(η2-SCPh)(PPh3)][(9]aneS3)]. Similarly the silyl complex [RuCl(SiMe2OEt)-
(CS)(PPh3)]2 with [9]aneS3 provides [RuCl(SiMe2OEt)(CS)(PPh3)][(9]aneS3)]+. However, the styryl and stilbenyl complexes [RuR(η2-CPh)(CS)(PPh3)]2 (R = H, Ph) under similar conditions provide dihapto thioacetylene derivatives [Ru(η2-SCCR)(CS)(PPh3)][(9]aneS3)]+. The osmium species [Os(η2-(CH₂C₅H₅-4)(CS)-
(BTD)(PPh3)]2 (BTD = 2,1,3-benzothiadiazole), however, yields only the nonmigrated product [Os(CH₂-
C₅H₅-4)(CS)(PPh3)][(9]aneS3)]. Migratory insertion is not induced by other sulfur donor ligands, e.g., Cy₃PCS; (Cy = cyclohexyl) and Na[S₂CNMe₂], which provide the complexes [Ru(η2-CH=C(CO₂Me)-
(S₂CPCy₃)-(CS)(PPh₃)] and [Ru(η2-CH=C(CO₂Me)(S₂CNMe₂)(CS)(PPh₃)] respectively. The reactivity of different ligands (R) toward thiocarbonyl migratory insertion in [Ru(R)(CS)(PPh₃)][(9]aneS3)]+ was analyzed through density functional theory. The calculated barriers agree qualitatively with experimental observations. In order to determine the electronic effect of substituents on the migrating ligand, a series of hypothetical systems with phenyl ligands varying only in the para-substituent was considered. A general trend that electron-releasing substituents on the migrating ligand promote reaction was observed. Through symmetry-adapted fragment orbital analysis, this phenomenon is determined to correlate well with the energy of the highest occupied π-orbital of the ligand.

Introduction

Bi- and, to a lesser extent, polydentate phosphines are prevalent in many metal-mediated catalytic processes. It has long since been speculated that sulfur-based macrocycles might offer promise as co-ligands in such processes by offering a combination of multiple soft donors that mimic phosphines in combination with the robust nature of macrocycle coordination. The latter might be expected to offset the general lability of monodentate thioether binding. With very few exceptions, this potential has yet to be investigated in any detail, and little is known about how polythiacycloalkanes might effect the reactivity of organometallic co-ligands. Our own efforts to address this situation have focused on 1,4,7-trithiacyclononane ([9]aneS3) for the following reasons, each of which should predispose it to catalytic applications: (i) It is commercially available, though somewhat expensive; (ii) in serving as a facially tridentate six-coordinate electron donor, it may be considered as a cyclopentadienyl mimic; (iii) the remaining sites in its octahedral or five-coordinate complexes are, by necessity, mutually cis, and therefore preorganized for co-ligand coupling processes, e.g., insertion and migratory insertion reactions. With the exception of commercial availability, each of these points applies to the related macrocycle 3,4-benzo-[11]aneS3, the similarly rich chemistry of which has been investigated Loeb. Within the chemistry of ruthenium, [9]aneS3 has played an increasingly important role including the synthesis of organometallic complexes.

The results to be described herein relate to the key organometallic process of migratory insertion and, in particular, as it...


(8) For an early review of the coordination chemistry of carbon monosulfide see: Broadhurst, P. V. Polyhedron 1985, 4, 1801.

(9) CS is not isobaric with carbon monoxide. In an organometallic context, the isobaric isomer is carbon monosulfide.
migrate to CS with ease, including hydrides,\textsuperscript{17–21} silyls,\textsuperscript{22} boryls,\textsuperscript{23} and boranes.\textsuperscript{24} Furthermore, CS/alkyne coupling of alkenes, which might be viewed as a special case of migratory

\begin{align*}
\text{Organometallics, Vol. 27, No. 21, 2008 Green et al.}
\end{align*}

\textbf{Results and Discussion}

The \(\sigma\)-organyl/thiocarbonyl starting complexes for this study are available via two routes. The reaction of [Ru(H\textsuperscript{1}H\textsuperscript{2})Cl(CS)(PPh\textsubscript{3})\textsubscript{2}] with diphenylmercury provides the coordinatively unsaturated \(\sigma\)-aryl complex [Ru(C\textsubscript{6}H\textsubscript{5})Cl(CS)(PPh\textsubscript{3})\textsubscript{2}] by analogy with that described for the related osmium complex [Os(C\textsubscript{6}H\textsubscript{6}Me\textsubscript{4}Cl(CS)(PPh\textsubscript{3})\textsubscript{2}].\textsuperscript{16a} The series of coordinatively unsaturated \(\sigma\)-vinyl complexes (Scheme 2) arises from the facile hydrotreatment of alkenes by the same hydrido, while the 18-electron complex [Os(CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{2}OCl(CS)(BTD)(PPh\textsubscript{3})\textsubscript{2}] (BTD = 2,1,3-benzothiadiazole)\textsuperscript{32b} by virtue of the labile BTD ligand, is synthetically equivalent to a 16-electron species.

\textbf{Vinyl Complexes.} Four representative examples were chosen to illustrate various features: monosubstituted, disubstituted, \(\alpha\)-carboxymethoxy, and \(\alpha\)-alkynyl substituted. The metallacyclic complex [Ru(C\textsubscript{6}H\textsubscript{6}CO\textsubscript{2}Me)\textsubscript{C\textsubscript{6}H\textsubscript{6}CO\textsubscript{2}Me]Cl(CS)(PPh\textsubscript{3})\textsubscript{2}] is coordinatively saturated as a result of the \(\beta\)-ester group; however this coordination appears to be hemilabile.

The coordination with [9]aneS\textsubscript{3} in the presence of a salt of a noncoordinating anion (ClO\textsubscript{4} \textsuperscript{–} or PF\textsubscript{6} \textsuperscript{–}) results in the formation of the octahedral vinyl complex [Ru(C(CO\textsubscript{2}Me)\textsubscript{3}C\textsubscript{6}H\textsubscript{6}CO\textsubscript{2}Me]Cl(CS)(PPh\textsubscript{3})([9]aneS\textsubscript{3})PF\textsubscript{6} (I•PF\textsubscript{6}) via opening of the metallacycle and substitution of the chloride and one phosphine ligand (Scheme 3). The facial coordination of the macrocycle follows from the \(\text{H}^1\) NMR data associated with the ligand. In an octahedral complex of the form [ML\textsuperscript{3}•LL\textsuperscript{3}•[9]aneS\textsubscript{3}], the chirality at the metal center renders each of the 12 macrocyclic protons chemically distinct. We have in one instance shown that NOESY and COSY techniques allow the identification of each of these resonances,\textsuperscript{24,25} however detailed analyses were not attempted in the present study. The gross formulation of the cation follows from positive ion FAB-mass spectrometry, which reveals an abundant molecular ion in addition to fragmentations due to loss of vinyl and phosphine ligands. A further feature of complexes of [9]aneS\textsubscript{3} is the appearance of fragmentations attributable to ethylene elimination from the macrocycle. A singlet resonance is observed in the \(\text{31P}^1\text{H}\) NMR spectrum that further confirms tridentate coordination of the macrocycle.

\begin{align*}
\text{Crossley, I. R.; Hill, A. F.; Willis, A. C. Organometallics 2007, 26, 3891.}
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\text{Hill, A. F.; Schulz, M.; Willis, A. C. Organometallics 2005, 24–207.}
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\text{Brothers, P. J.; Roper, W. R. J. Organomet. Chem. 1983, 258, 73.}
\end{align*}
Scheme 2. Synthesis of Starting Thiocarbonyl Complexes (L = PPh₃): (i) MeO₂CC≡CCO₂Me; (ii) R²CR=C=CR; (iii) HgPh₂; (iv) SiHClMe₂; (v) EtOH

Clear evidence that migratory insertion has not ensued is provided by the appearance of an intense absorption at 1290 cm⁻¹ due to the terminal thiocarbonyl ligand.

A similar result is obtained for the α-alkynyl-substituted vinyl complex [Ru(C≡CPh)=CHPh][Cl(CS)(PPh₃)]₂, which provides the salt [Ru(C≡CPh)=CHPh][Cl(CS)(PPh₃)][9]aneS₃]PF₆ (2·PF₆) in high yield (83%). Spectroscopic data for this salt are immediately comparable to those for (1·PF₆) and are unremarkable other than to confirm that once again migratory insertion has not occurred (νCS = 1294 cm⁻¹, δC(CS) = 297.2 (d), JCP = 19.7 Hz). The possibility that the α-alkynyl group coordinates to the metal center¹ may be ruled out on the basis of both infrared (νC≡C = 2157 cm⁻¹) and ¹³C NMR data (δC≡C = 101.5, 98.6 ppm). The macrocyclic ligand gives rise to four singlet resonances (37.2, 35.2, 34.1, 30.4 ppm), one broadened singlet (34.3 ppm), and a doublet (33.8 ppm, JCP = 5.3 Hz), these latter two resonances arising from the two methylene carbons bound to the sulfur trans to the phosphine ligand. The simple vinyl complexes [Ru(C≡CPh)Cl(CS)(PPh₃)]₂ (R = H, Ph) both react with [9]aneS₃ to provide salts with similar FAB-MS data to the previous examples, confirming the gross composition. The remaining data however indicate that the products involve migratory insertion of the vinyl and thiocarbonyl ligands (Scheme 3), to provide the thioyl salts [Ru(q²-SCCR=C(H)H)[PF₆][(9]aneS₃)]⁺ (R = H, 3·ClO₄; R = Ph, 4·ClO₄). The bidentate thioyl (metallathiirene) group is an intense visible chromophore, and hence these salts are deep purple. We have so far been unsuccessful in obtaining crystallographic confirmation of the thioyl formulations; however this follows unambiguously from the following spectroscopic data: Immediate indication that the thiocarbonyl component is no longer terminal in nature follows from the absence of a characteristic intense νCS absorption in the infrared spectrum of either derivative. In the case of 4·ClO₄, for which carbon-13 NMR data are available, the thiocarbonyl resonance is observed as a doublet at 312.8 ppm (JCP = 9.7 Hz) in a region typical of metallathiirenes.¹¹,³² For the thioiynamoyl example (3·ClO₄), only one of the vinylic protons (H₆) was observed in the ¹H NMR spectrum due to the second being obscured by phenyl resonances. This signal, which appears at 7.64 ppm, in shift of the H₆ nucleus. The absence of coupling to phosphorus and the change in the H₆ resonance to higher field (8.65 ppm, dt, JHH = 14.1, JHP = 2.9 Hz in the alkenyl precursor) indicate that the

Scheme 3. Reaction of 1,4,7-Trithiacyclononane with Ruthenium Thiocarbonyl Alkenyl Complexes (L = PPh₃): (i) [9]aneS₃, NH₄PF₆, or NaClO₄

Scheme 4. Reactions of 1,4,7-Trithiacyclononane with Ruthenium Thiocarbonyl Styril and Stilbenyl Complexes (L = PPh₃): (i) [9]aneS₃, LiClO₄
CH=CHPh moiety is no longer directly bonded to the ruthenium center. We have also reported the preparation of the osmium species [Os(CH=CHC6H4Me-4)Cl(CS)(BTD)(PPh3)2], which reacts with carbon monoxide to yield the thiacarbonyl complex [Os(η2-SCCH=CHC6H4Me-4)(CO)(PPh3)]32b. However, treatment of [Os(CH=CHC6H4Me-4)Cl(CS)(BTD)(PPh3)2] with [9]aneS3 in the presence of NH4PF6 provides the nonmigrated product [Os(CH=C6H4Me-4)(CS)(PPh3)][9]aneS3PF6 (5·PF6) in 69% yield. This complex gives rise to an intense νCS absorption at 1298 cm⁻¹, and the remainder of the data compare well with those of the carbonyl analogue [Os(CH=CHC6H4Me-4)(CO)(PPh3)][9]aneS3PF632b.

Aryl and Silyl Complexes. Given that the vinyl complexes discussed above led to different products upon reaction with [9]aneS3, we have briefly investigated the reactions of the complexes [Ru(C6H5)Cl(CS)(PPh3)2]29 and [Ru(SiMe2OEt)-Cl(CS)(PPh3)2]32c with [9]aneS3. While both of these species react with carbon monoxide to provide thioacetyl complexes, the latter example described by Roper22 is remarkable in that silyl π-basicity is increased by retrodation into

\[ \sigma^* \] orbitals. A π-basic component to the bonding of [9]aneS3 complexes would certainly be in concert with the observed ability of this ligand to induce migratory insertion, given that migratory insertion is generally favored by any factor that reduces retrodonation to the (thio)carbonyl ligand. We have addressed this qualitative interpretation in two ways. Experimentally, we have investigated the reactions of the model σ-aryltiothiocarbonyl precursors with sulfur chelates that have π-basic character in the expectation that migratory insertion would not be favored. Second (vide infra) we have computationally interrogated the electronic nature of species on the migratory insertion reaction coordinate.

Reactions with π-Basic Sulfur Chelates. In contrast to [9]aneS3 which is primarily a σ-σ-bonded with at best a modest degree of π-π-interaction,36 dithiocarbamates are strongly π-basic.37 The reaction of [Ru(CH=CHPh)(Cl)(CS)(PPh3)]2 with Na[S2CNMe2] was investigated and found to provide the nonmigrated vinyl complex [Ru(CH=CHPh)(S2CNMe2)(CS)(PPh3)]9, as indicated by the appearance of an intense thiocarbonyl absorption (Nujol: 1251 cm⁻¹) and also by the double-triplet multiplicity of the low-field \[ ^1H \] NMR resonance (\( \delta_H = 8.00 \) ppm, \( J_{HH} = 17.2, J_{HF} = 2.3 \) Hz) due to the α-proton of the vinyl group that remains bound to ruthenium (Scheme 6).

In a similar manner, the reaction of [Ru(CH=CH2)-Cl(CS)(PPh3)]2 with tricyclohexylphosphino dithiocarbamate (Cy3PCS2) was investigated and found, in the presence of NH4PF6, to provide the salt [Ru(CH=CH2)(SCPCy3) (CS)(PPh3)]PF6 (10·PF6). We have previously described the analogous carbonyl salt [Ru(CH=C6H4Me-4)(SCPCy3)(CO)(PPh3)]Cl and also noted that the hydride-thiocarbonyl complex [RuHCl(CS)(PPh3)] is not converted to a thioformyl derivative by Cy3PCS2, but rather provides the complex [RuH2(CPCy3)(CS)(PPh3)]Cl, while [RuH2(CO)(PPh3)] provides a mixture of the two complexes [RuH2(S2CPCy3)(CO)(PPh3)]3+ and [Ru(S2CPCy3)(CO)(PPh3)]3+.

Scheme 5. Reaction of 1,4,7-Trimethylocyclononane with Ruthenium Aryl and Silyl Compounds (L = PPh3): (i) [9]aneS3, NH4PF6; (ii) heat (R = Ph only)

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Thus, neither dithiocarbamate nor phosphonio dithiocarboxylate ligands induce migratory insertive coupling of vinyl and thiocarbonyl ligands, consistent with the above arguments that $\pi$-donor ligands disfavor such processes.

**Computational Studies.** The variation in propensity of the migratory insertion reactions for vinyl, aryl, and silyl ligands with coordinated CS described above and summarized in Table 1 calls for more insight, which we expected might follow from computational studies. The key points of interest along the reaction coordinate (Scheme 7) are the 16-electron precursors (Pa–f), which with [9]aneS$_3$ convert to the pseudo-octahedral cationic “half-sandwich” complexes 1 (isolable for R = Ph, C(C≡CPh)=CHPh, C(CO$_2$Me)=CHCO$_2$Me, SiMe$_2$OEt), which in some but not all cases either spontaneously (R = CH==CHPh, CPh==CHPh) or with heating (R = Ph) evolve to the thiacyclcs 3 presumably via a three-center-two-electron bonded reactive intermediate 2. Thus at room temperature, [9]aneS$_3$ displaces chloride and a phosphine from precursors [Ru(R)Cl(CS)(PPh$_3$)$_2$] (Pa–f) to yield 3a,b and 1c–f. Upon reflux in THF (bp = 66 °C), 1c presumably rearranges via 2e to 3c. Heating under reflux in THF of 1f does not yield 3f. By modeling 2, 2TS (the transition state between 1 and 2) and 3, several questions may be answered: Can formation of 3a,b occur stepwise through 1a,b at room temperature? Why does 1c need heat to react? Why does 1f not react further on heating, and why do 1d,e not proceed to 3d,e at room temperature and will heat induce reaction?

The Gibbs’ free energy of 1TS relative to 1 can be interpreted as the reaction barrier (Figure 1). 1TSa,b are only +62.52 and +60.64 kJ/mol relative to their respective reactants, and reaction is expected to occur easily. 1TSc–e give reasonable reaction barriers (95.17, 84.12, and 101.24 kJ/mol) for a heated reaction. (Note: alternative structures for 1TSd with the alkynyl moiety syn to the phosphine are precluded by the cone angle of PPh$_3$, and another alternative with the phenyl rings in-plane with each other results in a higher barrier). Systems a–e are exergonic, and equilibrium favors formation of product if the reaction barrier is surmountable. 1TSa–e structures (Figure 2) match well with previously reported transition states for CO insertion.

**Table 1.** Experimental Reactivity of an Array of Ligands Towards Migratory Insertion with Coordinated CS

<table>
<thead>
<tr>
<th>R</th>
<th>reactive conditions</th>
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<tbody>
<tr>
<td>a</td>
<td>CH==CHPh</td>
</tr>
<tr>
<td>b</td>
<td>CPh==CHPh</td>
</tr>
<tr>
<td>c</td>
<td>Ph</td>
</tr>
<tr>
<td>d</td>
<td>C(C≡CPh)==CHPh</td>
</tr>
<tr>
<td>e</td>
<td>C(CO$_2$Me)==CHCO$_2$Me</td>
</tr>
<tr>
<td>f</td>
<td>SiMe$_2$OEt</td>
</tr>
</tbody>
</table>

Table 2. Migrated and Nonmigrated [9]aneS$_3$ (*not observed*)

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<thead>
<tr>
<th>R</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH==CHPh</td>
<td>1a* 3a</td>
</tr>
<tr>
<td>CPh==CHPh</td>
<td>1b* 3b</td>
</tr>
<tr>
<td>Ph</td>
<td>1c 3c</td>
</tr>
<tr>
<td>C(C≡CPh)==CHPh</td>
<td>1d 3d*</td>
</tr>
<tr>
<td>C(CO$_2$Me)==CHCO$_2$Me</td>
<td>1e 3e*</td>
</tr>
<tr>
<td>SiMe$_2$OEt</td>
<td>1f 3f</td>
</tr>
</tbody>
</table>

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<tr>
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<td>f</td>
<td>SiMe$_2$OEt</td>
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Figure 1. Relative reaction profiles for systems a–e. Intermediates 2a–e are not shown for clarity, and ensuing transition states toward 3a–e, while not found, are not expected to affect the overall reaction barrier.
The overall reaction 1f to 3f is endergonic ($\Delta G = +32.98$ kJ mol$^{-1}$). This difference from the other systems can be rationalized as being due to the weakness of the Si–C bond and the lack of $\pi$-conjugation in the product. Even if the reaction barrier were very low (unlikely, given the presumed five-coordinate nature of silicon on 1TSi), thermodynamics would prohibit a significant yield of 3f. Thus, no attempt was made to find 1TSi or 2f.

Previous carbonylation studies have observed that electron-withdrawing (EW) substituents on the migrating ligand inhibit reaction or that electron-donating (ED) ones promote it.$^{8-11}$ Such trends are difficult to observe in $a$–$e$ because of the widely varying steric profiles of the ligands. To determine the electronic effect of substituents on thiocarbonyl insertion, a series of hypothetical systems $g$–$k$ and $m$, employing sterically consistent, para-substituted phenyls, have been modeled and compared with $c$ (Table 3). Indeed, EW substituents do increase $\Delta E_{1TSr}$. inhibiting reaction. Does this effect stem from stabilization of 1 or from destabilization of 1TS? To find out, the structures are partitioned into ligand and metal fragments. Single-point calculations are run on the fragments of systems $c$ and $g$–$j$. By comparing the energies of the sum of the fragments versus the energy of the whole system, ligand binding energies (LBEs) may be determined (Scheme 8).

Surprisingly, it is found that EW substituents correlate with weaker bonding in 1 (Table 3). The electrostatic contribution to bonding favors a negative charge on the $\alpha$-carbon (next to the positively charged metal), which EW substituents inhibit. Further, gross populations of the symmetry-adapted fragment orbitals (SFOS) reveal that $\pi$-back-bonding is minimal, presumably due to the formal $+$1 charge of the ruthenium, the competitively $\pi$-acidic thiocarbonyl ligand, and the low-symmetry environment (Table 4). This result discounts the possibility that EW-substituted ligands are inert due to a greater $\mathrm{M} \cdots \mathrm{R}$ bond strength. Instead, the inhibitory effect of EW substituents lies in 1TS. The difference in Hirshfeld charge$^{44}$ between the metal fragment and the ligand decreases by 0.39–0.45 going from 1 to 1TS. Approximately 0.2 electron is transferred from the ligand to the metal fragment (Table 5).
According to the SFO populations (Table 4), charge transfer occurs primarily from the highest occupied π orbital (HOPO) of the ligand to the metal fragment’s singly occupied fragment orbital (SOFO). This occurs less readily with EW substituents and more easily with ED substituents. As the energy of the SOFO of the metal fragment does not vary much between systems, the energy of the ligand HOPO inversely correlates with reaction barrier (Figure 3).

In 3, SFO population analysis shows significant π-donation from the aryl substituent to the CS unit, evidenced by the partial population of the thiocarbonyl fragment orbitals. Also, the ligand SOMO, previously forming a polar Ru−C σ-bond, loses electron density in forming a more covalent SC−R σ-bond. This explains why reaction with ED-substituted ligands is more exothermic than with EW-substituted ligands (and allows j, containing a π-donating, σ-withdrawing fluoride substituent, to be slightly more exothermic than e). Conversely, the reverse migration reaction faces a smaller barrier with EW-substituted ligands. This agrees with previously reported electronic substituent effects in decarbonylation reactions. An elegant demonstration of this was provided by Roper and Wright and involves the σ-aryl complexes shown in Scheme 9. In solution, the 4-tolyl derivative is in equilibrium with the corresponding benzoyl isomer. However protonation of the amino groups, to the 4-amino derivative results in exclusive formation of the benzoyl isomer. However protonation of the amino groups, which removes its π-donor capacity, results in migration of the aryl ligand back to ruthenium. It was previously inferred that the electron-donating nature of the 4-amino substituent weakened the Ru−C bond of the σ-aryl isomer, thereby favoring migratory insertion. The above results however would suggest that it is stabilization of the electrophilic benzoyl carbon that is the more determining factor.

The inverse correlation between HOPO energy and reaction barrier does not cleanly apply to the substituted vinyl systems a,b,d,e due to varying steric effects and (in b,d,e) the presence of multiple high-lying π orbitals. However, because steric forces vary less among a,b,d,e than in 1TSa,b,d,e, the net thermodynamic driving force can still be rationalized as the result of the electron-donating ability of the ligands. Again, SFO population analysis finds that most of the electron donation occurs from the HOPO and SOFO of the ligand fragments. 3b has the highest ligand SOFO and is the most thermodynamically favorable product. 3a, due to the low steric profile of the ligand, is able to form a shorter SC−R bond to compensate for its relatively low-lying HOPO and SOFO. 3d is correctly more favorable than 3e, which has the lowest-lying HOPO and SOFO of all (Figure 4).

Concluding Remarks

It could be argued that the results described herein do not necessarily translate in toto to the more general manifold of migratory insertion. Nevertheless, we have tried both experimentally and computationally to separate the variables that are contributing factors, and some of these inferences will be more generally applicable. First, the computational studies indicate that while the π-basicty of the migrating group may in some part contribute to a destabilization of the ground-state precursor through a compromise in the covalent versus ionic character of the 4-amino derivative results in exclusive formation of the benzoyl isomer. However protonation of the amino groups, which removes its π-donor capacity, results in migration of the aryl ligand back to ruthenium. It was previously inferred that the electron-donating nature of the 4-amino substituent weakened the Ru−C bond of the σ-aryl isomer, thereby favoring migratory insertion. The above results however would suggest that it is stabilization of the electrophilic benzoyl carbon that is the more determining factor.

The inverse correlation between HOPO energy and reaction barrier does not cleanly apply to the substituted vinyl systems a,b,d,e due to varying steric effects and (in b,d,e) the presence of multiple high-lying π orbitals. However, because steric forces vary less among a,b,d,e than in 1TSa,b,d,e, the net thermodynamic driving force can still be rationalized as the result of the electron-donating ability of the ligands. Again, SFO population analysis finds that most of the electron donation occurs from the HOPO and SOFO of the ligand fragments. 3b has the highest ligand SOFO and is the most thermodynamically favorable product. 3a, due to the low steric profile of the ligand, is able to form a shorter SC−R bond to compensate for its relatively low-lying HOPO and SOFO. 3d is correctly more favorable than 3e, which has the lowest-lying HOPO and SOFO of all (Figure 4).

Concluding Remarks

It could be argued that the results described herein do not necessarily translate in toto to the more general manifold of migratory insertion. Nevertheless, we have tried both experimentally and computationally to separate the variables that are contributing factors, and some of these inferences will be more generally applicable. First, the computational studies indicate that while the π-basicty of the migrating group may in some part contribute to a destabilization of the ground-state precursor through a compromise in the covalent versus ionic character of the 4-amino derivative results in exclusive formation of the benzoyl isomer. However protonation of the amino groups, which removes its π-donor capacity, results in migration of the aryl ligand back to ruthenium. It was previously inferred that the electron-donating nature of the 4-amino substituent weakened the Ru−C bond of the σ-aryl isomer, thereby favoring migratory insertion. The above results however would suggest that it is stabilization of the electrophilic benzoyl carbon that is the more determining factor.

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Concluding Remarks

It could be argued that the results described herein do not necessarily translate in toto to the more general manifold of migratory insertion. Nevertheless, we have tried both experimentally and computationally to separate the variables that are contributing factors, and some of these inferences will be more generally applicable. First, the computational studies indicate that while the π-basicty of the migrating group may in some part contribute to a destabilization of the ground-state precursor through a compromise in the covalent versus ionic character of
the metal—carbon bond, it is the mesomeric stabilization of the resulting thioacyl ("metallathiirene") product that appears to dominate the energetics. This interpretation is of course biased by the cationic nature of both precursors and products, and perhaps by the possible \(\pi\)-acid role of the [9]aneS3 ligand, to which we have previously alluded. For this reason the reactions of suitable precursors with \(\pi\)-basic sulfur chelates were investigated, including one example that generates a cationic product that does not enter into migratory insertion (C=C=PC2).

In the present system, vinyl ligands appear more prone to migratory insertion than simple aryls (or silyls), and this result is consistent with the general observations of Maitlis.47 We have previously shown that vinyl ligands are capable of irreversibly entering into migratory insertion (C=C=PC2), \(\eta^2\) vinyl ligands (e.g., C6H5CH=CH2), and SACS at London Metropolitan University. In the case of organosilicon derivatives, however, the metal—vinyl bond strength, but also by reducing the mesomeric stabilization of the resulting metallathiirene.

**Experimental Section**

**General Procedures.** All operations were carried out under aerobic conditions. All solvents were used as received. Multinuclear NMR spectra were recorded in CDCl3 (unless otherwise stated) at 25 °C on a Jeol JNM EX270 NMR spectrometer. Infrared spectra were recorded as both dichloromethane solutions and Nujol mulls using Perkin-Elmer 1720-X or Mattson Series 1 FT-IR spectrometers. Characteristic “fingerprint” bands for PPh3 are omitted. FAB-mass spectrometry was carried out using an Autospec Q instrument with 3-nitrobenzyl alcohol (nba) as a matrix. The elimination of ethylene was a recurrent feature in the mass spectra, as has been noted previously for complexes of [9]aneS3.36 Quoted yields take into account dichloromethane, which was in the majority of cases not removed until crystallization was complete. The resulting yellow crystals were filtered off, washed with ethanol (10 mL) and dried. Yield: 150 mg (77%). IR (Nujol): 1585, 1530, 1527, 1329, 1277, 1263 cm\(^{-1}\). FAB-MS m/z (% abundance): 791 (100) [M]+, 702 (3) [M – C6H5]+, 469 (6) [M – PPh3]+, 441 (18) [M – C6H5 – PPh3]+, 407 (6) [M – C(9)aneS3]+. Microanalytical data were obtained for the corresponding and more crystalline perchlorate salt ([C1(C6H5)CHPh]+ 2CH2Cl2) prepared in an identical manner (LiClO4 in place of NH4PF6). Spectroscopic data associated with the cation are however identical to those for I+PF6. Anal. Found: C, 43.6; H, 3.9. Calcd for C63H50ClO4PF6×2CH2Cl2: C, 43.3; H, 4.0. Dichloromethane of solvation confirmed by \(^1\)H NMR integration.

**Preparation of [Ru(C=C=PCl)]PF6·2PF6.** A solution of [Ru(C=C=PCl)]PF6×[C(9)aneS3]PF6 (270 mg, 0.297 mmol) in dichloromethane (30 mL) and ethanol (10 mL) was treated with [9]aneS3 (60 mg, 0.333 mmol) and a solution of KPF6 (110 mg, 0.598 mmol) in water (1 mL) and ethanol (10 mL) and then stirred for 30 h. All solvent was then removed and the crude product dissolved in dichloromethane and filtered through diatomaceous earth to remove KCl. Ethanol was then added, and crystals were obtained by slow rotary evaporation. The off-white product was filtered off, washed with ethanol (10 mL) and petroleum ether (10 mL), and dried under vacuum. Yield: 230 mg (83%). IR (Nujol): 2157, 1722, 1713, 1575, 1531, 1527, 1294 cm\(^{-1}\). NMR \(^1\)H: \(\delta\) 1.90 – 2.10, 2.30 – 2.50, 2.80 – 3.45 (m, 3 × 12, H, CH2), 6.88 (s, 1 H, C=CH), 7.10 – 7.65 (m, 25 H, PC6H5+ + PC, ppm). \(^{31}\)P{\(^1\)H} (DMSO-\(d_6\)): 197.7, 192.3 (d, PC, 2JCP = 5.3 Hz) ppm. 31P{1H}: 197.7, 192.3 ppm. FAB-MS m/z (% abundance): 791 (100) [M]+, 702 (3) [M – C6H5]+, 469 (6) [M – PPh3]+, 441 (18) [M – C6H5 – PPh3]+, 407 (6) [M – C(9)aneS3]+. Microanalytical data were obtained for the corresponding and more crystalline perchlorate salt ([C1(C6H5)CHPh]+ 2CH2Cl2) prepared in an identical manner (LiClO4 in place of NH4PF6). Spectroscopic data associated with the cation are however identical to those for I+PF6. Anal. Found: C, 43.6; H, 3.9. Calcd for C63H50ClO4PF6×2CH2Cl2: C, 43.3; H, 4.0. Dichloromethane of solvation confirmed by \(^1\)H NMR integration.

**Preparation of [Ru(C=C=PCl)]PF6×[C(9)aneS3]ClO4·3PF6.** [Ru(C=C=PCl)]PF6×[C(9)aneS3]ClO4·3PF6 (200 mg, 0.247 mmol) and [9]aneS3 (50 mg, 0.277 mmol) were dissolved in dichloromethane (40 mL). This solution was then treated with NH4PF6 (110 mg, 0.675 mmol) in a mixture of water (20 mL) and ethanol (40 mL) and the mixture stirred overnight. Ethanol (40 mL) was added and the volume reduced until crystallization was complete. The resulting yellow crystals were washed with petroleum ether (20 mL) and dried under vacuum. The spectroscopically pure crude product can be recrystallized from dichloromethane and ethanol. Yield: 180 mg (87%). IR (CHCl3): 1710 \(\nu_{C=O}\), 1567 \(\nu_{C=O}\) or \(\nu_{C=C}\) cm\(^{-1}\). IR (Nujol): 1722, 1713 \(\nu_{C=O}\), 1567 \(\nu_{C=O}\), 1319, 1290 \(\nu_{CS}\), 1204, 1155, 947, 907, 855, 852, 833, 820 cm\(^{-1}\). NMR \(\delta\) 2.09, 2.27, 2.83, 3.10 – 3.35, 3.36 (m, 5 × 12, H, CH2), 3.52, 3.79 (s × 2, 3 H × 2, OCH3), 2.58 (1 H, C=CH), 7.30 – 7.85 (m, 15 H, C6H5). \(^{31}\)P{\(^1\)H} (DMSO-\(d_6\)): 37.2 ppm. FAB-MS m/z (% abundance): 731 (100) [M]+, 702 (3) [M – C6H5]+, 469 (6) [M – PPh3]+, 441 (18) [M – C6H5 – PPh3]+, 407 (6) [M – C(9)aneS3]+. Microanalytical data were obtained for the corresponding and more crystalline perchlorate salt ([C1(C6H5)CHPh]+ 2CH2Cl2) prepared in an identical manner (LiClO4 in place of NH4PF6). Spectroscopic data associated with the cation are however identical to those for I+PF6. Anal. Found: C, 43.6; H, 3.9. Calcd for C63H50ClO4PF6×2CH2Cl2: C, 43.3; H, 4.0. Dichloromethane of solvation confirmed by \(^1\)H NMR integration.

**Preparation of [Ru(C=C=PCl)]PF6×[C(9)aneS3]ClO4·3PF6.** [Ru(C=C=PCl)]PF6×[C(9)aneS3]ClO4·3PF6 (200 mg, 0.247 mmol) and [9]aneS3 (50 mg, 0.277 mmol) were dissolved in dichloromethane (15 mL), and a solution of LiClO4 (200 mg, 1.880 mmol) in water (1 mL) and ethanol (15 mL) was then added. The solution was stirred for 1 h, after which a purple precipitate that had formed was filtered off and washed with ethanol (10 mL) and petroleum ether (10 mL) and dried. Yield: 150 mg (77%). IR (Nujol): 1585, 1530, 1330, 1279, 1241, 1196, 1089 (ClO4), 969, 929, 918, 905, 823, 816, 803 cm\(^{-1}\). NMR \(\delta\) 6.10, 1.01, 1.43, 2.21, 2.57, 2.84, 3.10 (m × 6, 12 H, SCH2), 7.27 – 7.55 (m, 22 H, PC6H5+ + PC, ppm). \(^{31}\)P{\(^1\)H} (DMSO-\(d_6\)): 37.3 ppm. FAB-MS m/z (% abundance): 691 (86) [M]+, 663 (60) [M – C6H5]+, 516 (8) [M – C6H5 – SCCH=C=PH3]+, 428 (6) [M – PPh3]+, 401 (23) [M – C6H5 – PPh3]+. Analytical Found: C, 48.5; H, 4.1. Calcd for C63H50ClO4PF6×2CH2Cl2: C, 48.3; H, 4.2.
Preparation of \([\text{Ru}(\eta^2-\text{SCCH}_3\text{H})\text{PPPh}_3](\text{PPh}_3)_2\text{PF}_6\) (7-PPPh)

\([\text{Ru}(\text{SiMe}_2\text{OEt})\text{CS}](\text{PPh}_3)_2\) (200 mg, 0.247 mmol) and \([\text{Ru}(\text{Ph})\text{CS}](\text{PPh}_3)_2\) (50 mg, 0.277 mmol) were dissolved in a mixture of dichloromethane (25 mL) and ethanol (10 mL). KPF$_6$ (100 mg, 0.543 mmol) was added as an anolytic solution (10 mL). The red reaction mixture was stirred for 20 h and all solvent removed from the colorless solution. The crude product was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth. All sovent was washed with diethylyl ether (10 mL) and hexane (10 mL) and dried. Yield: 171 mg (83%). IR (Nujol): 1709, 1408, 1275 ν$_C$(C=S) (1269 for 7-PPPh) 1423, 1064, 930, 840 (PF$_6$) cm$^{-1}$. NMR \(\delta\) H: δ 0.02, 0.40 (s × 2, 2 × 3 H, C(C$_6$H$_5$)$_3$), 1.11 (t, 3 H, CH$_2$C$_6$H$_5$), 6.93 (2H, 4H, C$_6$H$_5$)$_2$, 9.21, 2.32, 2.54, 2.63, 2.78, 3.01, 3.19, 3.43 (4 × m × 7, 12 H, S, H, CH$_2$), 4.05 (q, 2 H, OCH, J$_{OH}$ = 7.04 Hz, 7.4, 7.6 (m, 15 H, C$_6$H$_5$)$_2$). 31P (H) δ: 36.2 ppm. FAB-MS m/z (% abundance): 691 (100) [M]+, 663 (8) [M – C$_6$H$_5$]+, 588 (3) [M – SiMe$_2$OEt]+, 560 (5) [M – C$_6$H$_5$ – SiMe$_2$OEt]+. IR (Nujol): 1709, 1246, 1247 (79%). Satisfactory micromerical analysis. Anal. Found: C: 57.3; H: 4.4. Calcd for C$_{118}$H$_{140}$F$_{14}$P$_4$S$_3$: C, 57.3; H, 4.4.

Preparation of \([\text{Ru}(\text{Ph})\text{C}(\text{CS})(\text{PPh}_3)_2\text{PF}_6\) (8-PPPh)

\([\text{Ru}(\text{Ph})\text{C}(\text{CS})(\text{PPh}_3)_2\text{PF}_6\) (60 mg, 0.074 mmol) was dissolved in tetrahydrofuran (10 mL) and stirred at reflux for 4 h. All solvent was evaporated and the crude product triturated ultrasonicly in hexane (20 mL). The dark red-brown product was filtered, washed with hexane (20 mL), and dried. Yield: 52 mg (87%). IR (Nujol): 1585, 1301, 1170, 977, 934, 905, 838 ν$_C$(C=S) cm$^{-1}$.

Preparation of \([\text{Ru}[\text{C}(\text{CS})(\text{PPh}_3)_2\text{PF}_6\) (9)

A solution of \([\text{Ru}([\text{CH}]=\text{C}(\text{HS})(\text{CS})(\text{PPh}_3)_2\text{PF}_6\) (160 mg, 0.198 mmol) in dichloromethane (20 mL) was treated with a solution of sodium dimethylthiocarbamate (500 mg, 3.491 mmol) in water (2 mL) and ethanol (10 mL), prompting an immediate color change (red solution to a yellow one). The solution was stirred for 2 min, after which ethanol (40 mL) was added to precipitate yellow crystals from the green solution. These were filtered and washed with ethanol (10 mL) and petroleum ether (10 mL). Yield: 139 mg (79%). Stability: Good as solid but less than 1 h in solution. IR (Nujol): 1914, 1597, 1585, 1575, 1545, 1512, 1504, 1480, 1432, 1384, 1281, 1215 ν$_C$(C=S) 1141, 1053, 966, 798 cm$^{-1}$. NMR \(\delta\) H: δ 2.64, 2.64 (s × 2, 2 × 3 H, C(C$_6$H$_5$)$_3$), 11.4 (d, 1 H, CPh), J$_{OH}$ = 16.8 Hz, 6.28, 7.00 (d × 2, 4 H, C$_6$H$_5$), 6.79, 7.57 (m × 7, 12 H, S, H, CH$_2$), 7.3, 7.2 (m × 7, 12 H, S, H, CH$_2$), 7.11 (m × 7, 12 H, S, H, CH$_2$). FAB-MS m/z (% abundance): 665 (29) [M]+, 637 (24) [M – C$_6$H$_5$]+, 323 (13) [M – C$_6$H$_5$ – C$_2$H$_4$]+, 263 (26) [M – C$_6$H$_5$ – Ph]+. Anal. Found: C, 45.9; H, 3.9. Calcd for C$_{118}$H$_{140}$F$_{14}$P$_4$S$_3$: C, 46.0; H, 4.0.

Preparation of \([\text{Ru}([\text{CH}]=\text{C}(\text{Ph})(\text{CS})(\text{PPh}_3)_2\text{PF}_6\) (9)

A solution of \([\text{Ru}([\text{CH}]=\text{C}(\text{Ph})(\text{CS})(\text{PPh}_3)_2\text{PF}_6\) (160 mg, 0.198 mmol) in dichloromethane (20 mL) was treated with a solution of sodium dimethylthiocarbamate (500 mg, 3.491 mmol) in water (2 mL) and ethanol (10 mL), prompting an immediate color change (red solution to a yellow one). The solution was stirred for 2 min, after which ethanol (40 mL) was added to precipitate yellow crystals from the green solution. These were filtered and washed with ethanol (10 mL) and petroleum ether (10 mL). Yield: 139 mg (79%).
Preparation of [Ru(CH═CH2)(κ2-S2PCy3)(CS)(PPh3)2]PF6 (10·PF6). [Ru(CH═CH2)Cl(CS)(PPh3)2] (200 mg, 0.273 mmol) was dissolved in dichloromethane (10 mL), and S2PCy3 (107 mg, 0.300 mmol) was added, resulting in an immediate deep red color. Ethanol (5 mL) was added along with NH4PF6 (90 mg, 0.552 mmol) in water (1 mL) and ethanol (5 mL). The solution was stirred for 2 h and the solvent volume then reduced (rotary evaporator) until precipitation of a purple solid was observed. This was filtered off and washed with ethanol (10 mL) and petroleum ether (20 mL) and dried. Yield: 242 mg (74%). IR (Nujol): 1716, 1586, 1551, 1267 νCS, 1237, 967, 919, 840 (PF6) cm⁻¹. NMR 1H: δ 0.09–2.15 (m, 33 H, Cy), 4.26 (dt, 1 H, H′_Cy = 17.8, H″_Cy = 2.1 Hz), 5.39 (dt, 1 H, H′_Cy, J_HCy-H″_Cy = 10.4, J_HCy-H″_Cy = 2.5 Hz), 7.32–7.55 (m, 30 H, PCy3), 7.65 (ddd, 1 H, H‴_Cy, J_HCy-H‴_Cy = 11.8, J_HCy-H‴_Cy = 6.7, J_HCy-H‴_Cy = 1.5 Hz) ppm. 31P{1H}δ: δ 36.7, 31.8 ppm. FAB-MS m/z (% abundance): 1053 (21) [M]+, 791 (72) [M – PPh3]+, 763 (4) [M – vinyl – PPh3]+, 697 (3) [M – S2PCy3+], 433 (5) [M – S2PCy3 – PPh3]+. Anal. Found: C, 55.5; H, 5.9. Calcd for C35H26F6P4Ru1·CH2Cl2: C, 55.2; H, 5.3.

Computational Details. Models used PPh3 in place of PPh3. Because ligands must rotate 90° from 1 to 1TS so that the π-system is aligned toward the CS, full phosphines would incur higher reaction barriers, particularly for 1TSb,d, which bear =CHPπ moieties syn to the phosphine. In this respect, we have previously identified C–H···π interactions between arylphosphine and vinyl ligands. Calculations were performed using density functional methods of the Amsterdam Density Functional (ADF v2006.01) with the generalized gradient approximation and the local density approximation of Vosko, Wilk, and Nusair, with Becke88 and Perdew86 electron exchange and correlation corrections. The basis sets used were uncontracted triple-ζ Slater-type orbitals (STOs) with polarization functions, labeled TZP in ADF. Scalar relativistic effects were included with the ZORA formalism. The cores of atoms were frozen: C, N, O, and F up to the 1s level, P and S up to the 2p level, and Ru up to the 3d level. Minima 1a–f and 3a–f have been verified by full frequency calculations. Although some possessed an imaginary eigenvector in the Hessian, these were visually confirmed to correspond with very flat motions on the potential energy surface; reoptimization at higher convergence criteria could resolve these, but would not significantly lower any energies. 1g–m and 3g–m were derived from 1c and 3c and underwent full geometry optimization. Guess structures for 1TSa–e were found by reoptimizing 1 while fixing the R–CS distance at decreasing intervals; the maxima along these linear transits were used in transition-state searches. Guess structures for 1TSg–m were derived from 1TSc, and the substituents were optimized prior to initiating transition-state searches. All transition states possessed an imaginary frequency vibration corresponding with formation of the R–CS bond. Some also possessed a second, lower-energy imaginary frequency. Intermediates 2a–e were determined by geometry optimization of the extremes of the corresponding imaginary frequency vibrations of 1TSa–e, but all possessed their own imaginary frequency vibration, suggesting a nearly barrierless isomerization to 3. As such, transition states from 2 to 3 were not found, and 1TS is assumed to determine the overall reaction barrier.

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Supporting Information Available: Full symmetry-adapted fragment orbital gross populations and all Cartesian coordinate files (xyz) for the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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