ORGANOMETALLICS

Computational Discovery of Stable Transition-Metal Vinylidene Complexes

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Supporting Information

ABSTRACT: Experimental results have long suggested that catalyst optimization is an inherently multivariate process, requiring the screening of reaction conditions (temperature, pressure, solvents, precursors, etc.), catalyst structure (metal and ligands), and substrate scope. With a view to demonstrating the feasibility and utility of multivariate computational screening of organometallic catalysts, we have investigated the structural and electronic properties of a library of transition-metal-coordinated alkyne and vinylidene tautomers in different coordination environments. By varying the substituents on the organic moiety of 60 alkyne/vinylidene pairs we were able to capture and quantify the key structural and electronic effects on tautomer preference. For a carefully selected subset of substituents, the effects of metal and ancillary ligands were then explored. We have been able to formulate a protocol for assessing the stabilization of vinylidenes in transition-metal complexes, suggesting that the d⁶ square-based-pyramidal metal



fragment $[RuCl_2(PR_3^2)(=C=CHR^1)]$, combined with electron-withdrawing substituents R^1 and electron-rich groups R^2 , would provide the ideal conditions favoring the vinylidene form thermodynamically.

INTRODUCTION

The syntheses of novel organic compounds and natural products increasingly rely on transformations catalyzed by transition-metal complexes to access elaborate and valuable structural motifs.¹ Key transformations lead to the formation of carbon–carbon and carbon–heteroatom single and multiple bonds through atom-economical² and highly selective addition and cyclization reactions. Metal coordination of substrates facilitates their activation, while suitable ancillary ligands on the metal center can be used to fine tune the activity and selectivity of catalysts.³

The Nobel Prize winning, metal-catalyzed metathesis $(2005)^4$ and cross-coupling $(2010)^5$ reactions are widely used, and their ongoing development is underpinned by catalyst screening⁶ and detailed mechanistic studies.⁷ For less well understood transformations, catalyst development can be more difficult; in such cases, computational studies can be used to test and refine mechanistic proposals^{7a,8} and to explore the thermodynamic and kinetic consequences of modifications to both catalyst and substrate on the mechanism and performance of catalysis.⁹

Such computational studies of reaction mechanisms continue to pose notable challenges, as capturing mechanistic manifolds and accommodating the structural and conformational variability of complexes with sufficient accuracy to reproduce and then predict experimental observations require extensive and accurate computational studies.¹⁰ However, high-throughput computation combined with rigorous statistical data analysis can be used to screen catalyst designs efficiently (see for example ref 6b), potentially accelerating the discovery and ultimately the (rational) design of novel catalysts on the basis of computational prediction.¹⁰ To date, such computational studies have focused on a single variable, usually the ligand,9 but catalyst optimization is inherently multivariate.¹¹ While reaction conditions are perhaps best varied experimentally, the interplay among metal, substrate, and ancillary ligands in determining the properties of organometallic complexes can be captured computationally; with a view to demonstrating the utility of multivariate computational screening, we have evaluated the effect of these three variables on the tautomerization (Scheme 1) between alkynes and their vinylidene analogues.

The energy balance between alkynes and vinylidenes was selected for this study, as alkynes have been demonstrated to bind to nearly all transition metals, whereas there are relatively fewer examples of stable vinylidene complexes. In addition, while the reactivity of organometallic η^2 -coordinated alkyne complexes can resemble that of alkenes, e.g. in metathesis,¹ the reactivity of vinylidene complexes is different from that of either

Received: January 31, 2014 Published: March 18, 2014 Scheme 1. Alkyne/Vinylidene Tautomerization and Difference in Reactivity on Nucleophilic Attack



the free or coordinated alkyne,¹² which has been exploited in carbon–carbon and carbon–heteroatom bond formation.¹³ The binding of both alkynes and vinylidenes to an electrophilic metal center increases their reactivity toward nucleophiles, with nucleophilic attack of alkynes giving Markovnikov addition,¹⁴ whereas vinylidenes give rise to net anti-Markovnikov products (Scheme 1).^{13c,15}

This behavior may be rationalized on the basis of the MO overlap diagrams for the respective metal-coordinated tautomers (see the Supporting Information, Figure S1). In the case of an alkyne, the LUMO is centered on the ligand π^* -orbital and nucleophilic attack may be assisted by slippage of the metal.¹⁶ For a vinylidene, the LUMO is primarily localized on the α -carbon, thus promoting nucleophilic attack at this site.¹⁷

A number of recent developments have widened the synthetic scope of these tautomeric pairs. In 2008 Ishii and co-workers demonstrated that half-sandwich ruthenium complexes promote the formation of disubstituted vinylidene complexes from internal alkynes (Scheme 2).¹⁸ The migration



of keto substituents within alkynes PhC \equiv CCOR (R = Me, Ph) to form vinylidene complexes M \equiv C=CPh(COR) has also been observed, a process which proceeds via an η^1 -O \equiv CR-bound intermediate.¹⁹

Transition-metal vinylidene complexes have been invoked in a number of gold-catalyzed reactions of terminal alkynes (Scheme 3).²⁰ To date, no gold vinylidene complexes have been directly observed, although a gold(I) complex with a related allenylidene ligand has been reported,²¹ as have other group 10^{22} and group 11^{23} species. In these cases the allenylidene ligand is supported by strong π -donor substituents and may be better described as a substituted propargyl cation.²¹

In view of the potential synthetic utility of controlled activation of alkyne and vinylidene tautomeric pairs from readily available alkyne precursors, a quantitative understanding of the different factors which control the tautomer preference can provide important insights into (1) the regiochemical outcome of nucleophilic attack, (2) the availability of disubstituted vinylidene complexes, and (3) how vinylidene complexes may be supported by late-transition-metal centers. Scheme 3. Summary of Gold-Catalyzed Reactions of Terminal Alkynes Where Gold Vinylidene Intermediates Have Been Postulated



Computational studies to date suggest that the mechanism of interconversion may vary with coordination environment,^{12a,c,24} making a large-scale mechanistic study of the rearrangement kinetics for multiple tautomeric pairs in different environments computationally challenging. However, determining the thermodynamic tautomer preference is less expensive computationally and could provide insights which will allow synthetic efforts to be targeted, as well as providing a quantitative guide for complex/catalyst screening and optimization, similar to the ligand knowledge bases previously developed in Bristol.²⁵

Here we have investigated the structural and electronic properties of a library of alkyne and vinylidene tautomer pairs coordinated to a variety of transition-metal complexes computationally, with density functional theory (DFT). Our goal was to explore how substituents on the organic moiety and changes to the coordination environment afforded by different transition-metal complexes and ligands would attenuate the thermodynamic energy balance between the two tautomeric forms. We note that kinetic effects, not considered here, will also affect whether the vinylidene tautomer can be accessed experimentally; in addition, the alkynyl hydride form may be accessible for monosubstituted pairs in some coordination environments,²⁶ potentially complicating computational prediction further. We also discuss how high-throughput multivariate computation can be used to propose strategies for the stabilization of the vinylidene tautomer by coordination of transition-metal complexes.

RESULTS AND DISCUSSION

Experimental Survey. An examination of the available experimental data for transition-metal vinylidene complexes indicates that both the metal and the substituent on the vinylidene affect the nature of their interaction. Table 1

Table 1. Selected ¹³ C NMR Data for Vinylidene Comp	lexes
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Complex	δα	δβ	Ref.
[Cr(CO) ₅ =C=	399.3	121.3	28
$[Mn(\eta^{5}-C_{3}H_{4}Me)(CO)_{2}(=C=CPh_{2})]$	381.4	116.9	12b
$[Ru(\eta^{5}-C_{5}H_{5})(PMe_{3})_{2}(=C=CHPh)]^{+}$	347.9	103.4	12b
$[RuCl_2(PCy_3)_2(=C=CHPh)]$	342.1	109.6	29
[RhCl(P ⁱ Pr ₃) ₂ (=C=CHPh)]	295.2	111.7	12b
$[IrCl(P^{i}Pr_{3})_{2}(=C=CHPh)]$	261.9	110.7	12b

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Figure 1. Correlation between the changes in chemical shift of the *a*-C and the relevant Hammett substituent parameter³⁰ from systematic studies of transition-metal compounds: $[(p-cymen)Ru(\mu-Cl)_3RuCl(=C=CHAr)(PCy_3)]$ (1, where $Ar = C_6H_5$ (1a), C_6H_4 -4-OMe (1b), C_6H_4 -4-Me (1c), C_6H_4 -4-Cl (1d), C_6H_4 -4-CF₃ (1e), C_6H_3 -3,5-CF₃ (1f));³¹ $[Ru(\eta^5-C_9H_7)(PPh_3)_2(=C=CHR)]^+$ (2, where R = H (2a), C_6H_4 -4-OMe (2b), C_6H_4 -4-Me (2c), C_6H_4 -4-Ph (2d), C_6H_4 -4-F (2e), C_6H_4 -4-Cl (2f), C_6H_4 -4-I (2g), C_6H_4 -4-MeCO (2h), C_6H_4 -4-NO₂ (2j));^{24d} trans- $[Ru(\kappa^2-O_2CR^1)(\kappa^1-O_2CR^1)(PPh_3)_2(=C=CHAr^2)]$ (5, where $R^1 =$ Me and Ar^2 with $R^3 = H$ (5a), 4-NMe₂ (5b), 4-OMe (5c), 4-Me (5d), 4-F (5e), 4-CF₃ (5f), 3-Me (5g); 6, where $Ar^2 =$ Ph and Ar^1 with $R^2 = H$ (6b), 4-NMe₂ (6c), 4-OMe (6d), 4-Me (6e), 4-F (6f), 3-F (6g), 3-Me (6h)) (Scheme 4). Trendline: $R^2 = 0.998$ (1), 0.745 (2), 0.942 (5), 0.820 (6).

contains selected ¹³C NMR data for a number of representative vinylidene complexes from groups 6–9. Although care must be taken in the interpretation of the absolute chemical shift of metal-bound carbon atoms,^{12b,27} it is clear that the wide variation (a range of 137.4 ppm in the examples below) in the chemical shift of the metal-bound carbon atom indicates that the nature of the metal complex is profoundly affecting the interaction with the vinylidene ligand.

The substituent on the vinylidene also appears to affect the nature of the interaction between metal and ligand, which can be probed via the chemical shift of the carbon atom bound to the metal. Delaude has shown that in a series of compounds $[(p-cymene)Ru(\mu-Cl)_3RuCl(=C=CHAr)(PCy_3)]$ (Ar = C_6H_4 -R, **1b**-f; Figure 1) it is possible to correlate the Hammett substituent parameter³⁰ with the chemical shift of the α -carbon atom in comparison to compound **1a** (Ar = C_6H_5).³¹ In addition, data reported by Bassetti^{24d} show a similar correlation for complexes based on $[Ru(\eta^5-C_9H_7)-(PPh_3)_2(=C=CHAr)]^+$ (Ar = C_6H_4 -R, **2b**-j; Figure 1), in this case relative to compound **2a**, $[Ru(\eta^5-C_9H_7)(PPh_3)_2(=C=CH_2)]^+$.

In order to investigate this correlation further, we have prepared a series of compounds based on *trans*-[Ru(κ^2 -O₂CR¹)(κ^1 -O₂CR¹)(PPh₃)₂(=C=CHR²)] (5) by reaction of the carboxylate complexes *cis*-[Ru(κ^2 -O₂CR¹)₂(PPh₃)₂], (3) with appropriate alkynes HC=CR² (4) (Scheme 4, see the Supporting Information for experimental details).^{8b,32} The ¹³C chemical shifts of the α -carbon atom for complexes *trans*-[Ru(κ^2 -O₂CMe)(κ^1 -O₂CMe)(PPh₃)₂(=C=CHR²)] (5b-f) relative to the parent phenyl complex 5a exhibit the same trend as the data reported by Delaude and Bassetti (Figure 1), showing a negative correlation with the Hammett parameter.



Legend: (1) CH_2Cl_2 , room temperature.

However, in the cases where the electronic demand of the carboxylate complexes is systematically altered (**6b**-**h**), the *opposite* trend in ¹³C NMR chemical shifts is observed, giving a positive correlation. In addition, the chemical shift of the metal-bound carbon in *trans*-[Ru(κ^2 -O₂CMe)(κ^1 -O₂CMe)(PⁱPr₃)₂(= C=CHPh)] (**5a**^{iPr}), prepared from the reaction of *cis*-[Ru(κ^2 -O₂CMe)₂(PⁱPr₃)₂] with HC₂Ph, lies 2.8 ppm to higher field than the corresponding resonance in **5a**.³³

Assuming that the chemical shift of the α -carbon of the vinylidene ligands is broadly indicative of the nature of the interaction between the metal and the ligand, a number of trends are evident. Notably, it appears that metal complexes

which contain more electron-withdrawing substituents exhibit lower field chemical shifts in comparison to those that are electron rich (compare, for example, chromium and iridium vinylidene complexes (Table 1), and the positive slope of the Hammett plot for compounds 6b-g). The opposite trend is observed when electron-withdrawing groups are present within the vinylidene ligand (note the negative slope of the Hammett plot for compounds 1 and 2 and the difference in $\Delta\delta$ between 5a and 5a^{iPr}).

These experimental data confirm that metal—ligand interactions may be affected by both metal fragment and substituents on the vinylidene ligand and these interactions are, presumably, also affecting the difference in energy between vinylidene and alkyne tautomers.

Design of Computational Database. As outlined above, this work describes a large-scale computational study of the factors controlling the difference in energy between tautomers; interconversion pathways and barriers were not considered but also affect experimental access to tautomers. The general requirements for such a study, with a view to achieving both interpretation and prediction of ligand effects, have been discussed extensively elsewhere^{25b} and can be summarized in brief as follows: the chosen computational approach (see the Supporting Information for details) should perform consistently across the complexes studied; quantitative agreement with e.g. binding energies is less important than the correct order of variable effects, at least when undertaking statistical analysis (Table S1 in the Supporting Information summarizes an evaluation of functional effects on tautomer energy differences). In addition, the substitution patterns studied should seek to capture as wide a chemical range as possible, thus ensuring that chemical space is sampled well. Likewise, transition-metal complexes should be chosen with a view to maximizing transferability to varied chemistry and the parameters used for analysis should be responsive to complex modifications.

These criteria still apply, but in the present work additional considerations arise. Rather than considering the effect of alkynes and vinylidenes as ligands, i.e. focusing on the modification of the properties of transition-metal centers, the tautomeric pairs considered here are of greater interest as substrates in further transformation and the motivation for the screening of multiple substituents has changed: here the structure and form of the substrate itself are of greater interest than the effect of its coordination on the rest of a complex. This affects which structural and energetic parameters are most responsive to modifications and hence useful in statistical analysis. In addition, treating vinylidenes and alkynes as a pair highlights substituent effects on the energetic balance between them, as well as structural effects arising from substituents and coordination environment (see the Supporting Information for a more detailed discussion). Finally, π -coordinated ligands have not previously been included in ligand knowledge bases and have necessitated minor modifications to both calculation protocols and the data extracted; these have been summarized in the Supporting Information.

In their uncoordinated form, alkynes are between 140 and 260 kJ mol⁻¹ more stable than the corresponding vinylidenes, but a careful choice of substituents, transition metal, and ancillary ligands can be used to favor the vinylidene tautomer on coordination. With a view to separating these effects, the present database consists of three branches, capturing the

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effects of substituents, metal centers, and ligands iteratively (Figure 2).



Figure 2. Schematic illustrating the exploration of different variables in the present database.

Substituent Effects. Substituent effects have been probed by calculating property descriptors for 32 monosubstituted and 28 disubstituted tautomer pairs of alkynes and vinylidenes (Scheme 5; see the Supporting Information, Table S2, for

Scheme 5. Alkyne and Vinylidene Tautomer Pairs



detailed numbering); in all subsequent discussion, the binding modes of substrates will be denoted by "a" and "v", respectively, to denote the different tautomers.

For monosubstituted ligands, a broad range of alkyl substituents allows the consideration of steric effects, while aryl groups with different para substituents facilitate the consideration of electronic effects free of steric variation, suitable for comparison with experimental data^{18a,d,24d} and in particular Hammett parameters.^{24d} In addition, a range of ester³⁴ and keto^{19a} groups, as well as representative iodine,³⁵ silicon,³⁶ tin,³⁷ and sulfur³⁸ substituents, for which migration from an alkyne precursor to the vinylidene tautomer have been reported, have been included. The tautomers have been considered both as free ligands and in a range of representative coordination environments (see the Supporting Information for further information on computational approaches and settings used).

Two of the complexes (Au-1 and Ru-1-H; Scheme 6) used for descriptor calculations have been described previously for the ligand knowledge base for carbenes and other C-donor ligands (LKB-C),^{25a} but the third complex considered in that work, [PdCl₃L]⁻ (Pd; Scheme 7) gave a strong predicted preference for the η^2 -alkyne tautomer for most substituents, of less interest in the present study. Scheme 6. Metal Complexes Considered in Substituent Effect Branch



Scheme 7. Metal Complexes Explored in Metal Effect Branch for Pairs 2, 15, 36, 42, 45, and 60^a



^aSee Table S2 in the Supporting Information for substituent numbering.

For the substituent screen, this has been replaced by a square-planar rhodium complex, *trans*- $[RhCl(PMe_3)_2L]$ (**Rh**), which provides a similar coordination geometry and allows the extraction of *trans* influences but has been found to support the vinylidene form.

Experimentally, the vinylidene tautomers have been observed for complexes related to the fragments $[RuCl_2(PR_3)_2]$ (**Ru-1-R**; R = H, Me)³⁹ and $[RhCl(PMe_3)_2]$ (**Rh**),^{26b,36a,40} albeit with larger substituents on the phosphine ligands. In contrast, η^2 alkyne complexes have been observed for the gold fragment [AuCl] (Au-1).⁴¹ Scheme 6 shows the metal complexes considered in this branch, and a summary of the parameters extracted from these calculations may be found in Table S3 (Supporting Information); these include C=C/C≡C and M− C bond lengths, tautomer energy differences, bond energies, and structural parameters for the metal fragments.

The energy differences between vinylidene and alkyne pairs have been calculated for the complexes considered in the substituent effect branch of the database. For each of the metal complexes considered, these energy differences span considerable ranges (between 67.8 and 103.5 kJ mol⁻¹; Table S4 (Supporting Information)) and are reasonably highly correlated (Figure 3; correlation coefficients R = 0.842 (Au1/Ru-1-H), 0.824 (Au1/Rh), 0.923 (Ru-1-H/Rh)).

These results suggest that substituent effects are broadly consistent across different coordination environments and that



Figure 3. Scatter plot of tautomer energy differences ($\Delta E_{v,av}$ kJ mol⁻¹) for metal complexes considered in the substituent effect branch. Trendline: $R^2 = 0.709$ (**Ru-1-H**), 0.679 (**Rh**).

more electron withdrawing groups generally make the vinylidene tautomer more favorable, as does monosubstitution. In addition, for the late-transition-metal fragment Au-1, most substituents favor the η^2 -alkyne, while the vinylidene form is clearly favored for Ru-1-H throughout. Substrates complexed to the Rh fragment are closer to the energetic borderline, and both tautomers may be energetically accessible, provided a suitable selection of substituents can be accessed. This is consistent with the observation that both tautomers may be observed when coordinated to trans-[RhCl($P^{i}Pr_{3}$)₂] fragments.^{26b} Substituents 60 (F/F) give rise to the only tautomeric pair which favors the vinylidene form for all metal complexes (Table S4, Supporting Information),⁴² and for the other monosubstituted halides (pairs 26-29) only the Au-1 complex is predicted to favor the η^2 -alkyne form, while the other complexes are also found to stabilize the vinylidene tautomer. The substituents also affect the geometries of each substrate, showing high correlations between the $C=C/C\equiv C$ bond lengths of tautomer pairs, and these effects are transmitted to the metal fragment, affecting fragment geometries, such as metal-ligand bond lengths and angles (see Table S5 (Supporting Information) for details).

While the analysis of bivariate correlations and scatter plots can help to explore substituent effects for individual descriptors, consideration of the whole database is more difficult and multivariate approaches need to be employed. Principal component analysis (PCA) is a statistical projection method⁴³ which can be used to process a multivariate and correlated data set to fewer orthogonal, i.e. uncorrelated, variables (principal components, PCs). The resulting PCs are linear combinations of the original variables, derived to maximize the variance/ information content in the first few PCs. This gives rise to a set of principal component scores for each tautomeric pair, which can be plotted to produce "maps" of chemical space where the proximity of scores indicates similarity.

Here we have performed PCA of the correlation matrix on the 35 variables in Table S3 (Supporting Information). While these 35 initial descriptors will give rise to the same number of derived variables (PCs), the first few are sufficient to capture most of the information content/variation, and Figure 4 shows such a map for the first two PCs, in this case already capturing about 67% of the variation in the data set, while Table S6 (Supporting Information) collects descriptor loadings and Table S7 (Supporting Information) includes the principal



Figure 4. Principal component score plot (PC1 and PC2) for all tautomeric pairs (Table 1), capturing 67% of variation in the data. Pairs selected for exploration of metal and ligand effects are shown in red squares.

component scores for each tautomeric pair. The Supporting Information includes a larger version of the PCA map discussed here (Figure S2) with all ligand numbers as shown in Table S2, as well as further details of the PCA.

This map of chemical space confirms expected chemical similarities, e.g. for the alkyl- and aryl-substituted pairs (black and blue colors in Figure 4), PC scores cluster, but also highlights outliers, such as pairs 60 (F/F) and 39 (CF₃/CF₃), both with very electron-withdrawing substituents, pairs 31 and 58 (H/SnMe₃ and Ph/SnMe₃; see discussion below), and to a lesser extent the diester-substituted systems 40 and 41 (CO₂Me/CO₂Me, CO₂Et/CO₂Et).

The fact that the tin-containing complexes appear as outliers prompted us to explore their properties in more detail. In both pairs 31 and 58 the vinylidene complexes have very short C=Cdistances and the optimized geometries show a distortion around the β carbon (cf. other alkyl substituents). The difference in behavior highlighted by PCA is supported by experimental data. For complexes based on the $[Mn(\eta^{5}$ - $C_5H_4R^1$ ($R_2^2PCH_2CH_2PR_2^2$) (=C=C R^3R^4) framework, the 13 C NMR spectra for the carbon atoms exhibit resonances at δ 320-330 when a tin substituent is present, whereas when alkyland aryl-containing groups are present, this resonance is at δ >340.^{37b} In addition, the crystal structure of $[Mn(\eta^5-C_5H_5)-$ (Me₂PCH₂CH₂PMe₂)(=C=C(SnMe₃)Ph)] shows a significant distortion at the β -carbon atom, with the $C_{\alpha} = C_{\beta} - Sn$ angle (115.2(4)°) much smaller than $C_{\alpha} = C_{\beta} - Ph$ (123.8(5)°). This indicates that the tin atom is closer to the metal-bound carbon, which, taken in conjunction with the conclusion from Ozawa^{36c} that the addition of SiMe₃ groups increases the stability of the vinylidene complexes through $(\sigma - \pi)p$ hyperconjugation, may be related to the β -silicon effect.

The symbols chosen also illustrate differences between mono- and disubstitution; monosubstituted pairs generally have lower/more negative scores on PC2 than the related disubstituted pairs (e.g., 17 and 47, 25 and 55). This becomes more pronounced on consideration of the third PC (Figure S3, Supporting Information); pairs appear in bands across PC2, suggesting that the main difference between these two subsets has been captured.

Inspection of trends across the map in terms of likely substituent electronic effects suggests that tautomeric pairs with more electron withdrawing substituents appear at lower/more negative values of PC1. As indicated above, PC2 expresses a difference between mono- and disubstitution, in line with the greater relative stabilization of vinylidenes in the monosubstituted pairs. Figure 5 highlights the effect on tautomer energy preference for ΔE_{v-a} (**Ru-1-H**).



Figure 5. Principal component score plot (PC1 and PC2), with continuous coloration according to $\Delta E_{v-a}(\mathbf{Ru-1-H})$ (kJ mol⁻¹). More negative values are displayed in shades of red and yellow and less negative ones in shades of green and blue.

Analysis of experimental data, individual descriptors, and the data set as a whole thus confirms the importance of substituent effects, with more electron withdrawing substituents making the vinylidene tautomer relatively more favorable.

The coordinated metal center also plays a substantial role in determining the energy difference between tautomers, with the **Au-1** fragment showing a high energy threshold for vinylidene



Figure 6. Calculated tautomer energy differences, ΔE_{v-a} (kJ mol⁻¹), for different metal complexes (see Scheme 7 for details): (a) results for pair 15 (H/Ph); (b) mean energy differences ΔE_{v-a} (kJ mol⁻¹) and their standard deviations for all six substrate pairs considered (2, 15, 36, 42, 45, 60; see the Supporting Information for full data).

stabilization while this tautomer becomes accessible for the **Rh** and **Ru-1-H** fragments. For the rhodium complex **Rh**, the tautomer energy differences are not large and substituent effects are sufficient to change the calculated preference, with monosubstituted pairs favoring the vinylidene form while most of the disubstituted substrates are expected to favor the alkyne.

Metal Effects. While modification of the substituents in tautomeric pairs can be used to access a broad range of substrate properties, the transition-metal center itself appears to determine the relative threshold for vinylidene stabilization in each tautomeric pair (Figure 3). In order to explore this more extensively, a subset of six substrate pairs was selected, chosen to capture the substituent effects discussed above and to reflect key experimental data. The pairs selected are highlighted on the substituent map (Figure 4, red squares); they access different areas of chemical space and are representative of both mono-and disubstituted pairs.

The effect of changing from an alkyl to an aryl substituent in the monosubstituted substrate is captured by including 2 (H/ Me) and 15 (H/Ph) and comparison of 15 with 42 (Ph/Ph) allows consideration of mono- vs disubstitution effects. Since keto- and ester-substituted pairs are sensitive to conformational noise, especially for the disubstituted pairs (see computational details in the Supporting Information), 36 (Me/CO₂Me) was chosen as a simple example; spontaneous conversion from alkyne to vinylidene was observed experimentally for the related pair 40 (CO₂Me/CO₂Me).^{18a} In addition, 45 (Ph/ C(O)Ph) was included both because spontaneous migration from alkyne to vinylidene was observed for these substituents in a RuCp(PPh₃)₂ fragment^{19,44} and because we wanted to explore the effect of keto substitution. Finally, pair 60 (F/F) is the only example for which the vinylidene has been preferred in all metal complexes considered so far.

For these pairs, a wider range of metal fragments, shown in Scheme 7, were considered to probe the effects of the transition-metal group (e.g., **Cr/Mo**, **Pd/Pt**, **Ag/Au-1**) and period (e.g., **Mn/Ru-2-CO**) on the predicted tautomer energy preferences. Of the fragments employed here, well-defined vinylidene complexes are known for $[Cr(CO)_5]$ (**Cr**)⁴⁵ and $[Mn(\eta^5-C_5H_5)(CO)_2]$ (**Mn**),⁴⁶ as well as complexes related to **Rh** and **Ru-1-H**, as discussed above. In contrast, **Au-1** is known to support η^2 -alkynes (discussed above), and so is $[PdCl_3]^-$ (**Pd**).⁴⁷ The fragment $[AuN((C_3F_7)C(Dipp)N_2)]$,⁴⁸ related to

Au-3, is also known to support alkyne ligands bound in an η^2 fashion; however, considering the number of times that η^2 -alkyne complexes have been proposed as intermediates in gold-catalyzed reactions, there is still a paucity of isolated examples of this type of compound.^{41,48,49} The carbene fragment [AuIMes]⁺ (**Au-2**) has been included here as a further gold(I) complex representative of common catalyst precursors and is likely to favor the η^2 -alkyne tautomer.

The tautomer energy preferences ΔE_{v-a} for the 6 pairs selected have been calculated in the 11 complexes shown in Scheme 7; no further structural or energetic data have been considered in this part of the study.

Metal effect results for the representative substituents are summarized in Figure 6, and full data tables have been included in the Supporting Information. Figure 6a shows the results for substrate pair 15 (H/Ph) and Figure 6b shows mean energy differences and their standard deviations for the subset of six substrate pairs considered here. The standard deviations shown in Figure 6b are large, primarily a consequence of including pair 60 (F/F), which strongly favors the vinylidene form in all metal complexes.

In line with experimental observations, these results confirm that group 7–9 transition metals in low oxidation states are most likely to stabilize the vinylidene tautomer, with later transition metals increasingly favoring the alkyne form. Periodic trends can be observed, and these are discussed in greater detail in the Interpretation below.

Ligand Effects. Ligands represent the third possible variable for the stabilization of the vinylidene tautomer in different coordination environments. To evaluate whether tautomer energy differences could be fine-tuned by the choice of ancillary ligands on different transition-metal centers, ligand effects within selected ruthenium complexes have been explored further. Using the same subset of substituents as for the metal branch, i.e. 2, 15, 36, 42, 45, and 60, the electronic properties of coordinated ligands in the $[RuCl_2(PR_3)_2]$ (Ru-1-**R**) and $[Ru(\eta^5-C_5H_5)(L^1)_2]^+$ (**Ru-2-L**) fragments have been varied systematically (Scheme 8). Experimentally, a vinylidene complex has been isolated for $[Ru(\eta^5-C_5H_5)(PMe_3)_2]^+$ (Ru-2- PMe_3).⁵⁰ Again, only the effect on the tautomer energy difference has been considered; these results have been summarized in Figure 7, with full data tables included in the Supporting Information.

Scheme 8. Ligands Explored for Pairs 2, 15, 36, 42, 45, and 60 in Ligand Effect Branch for Ruthenium Complexes



Figure 7. Ligand effects on calculated tautomer energy differences, $\Delta E_{\rm v.a}$ (kJ mol⁻¹), for different ruthenium complexes (Scheme 8) and substrate pairs 2, 15, 36, 42, 45, and 60 (see the Supporting Information for data tables).

For the ruthenium complex family Ru-2-L, the tautomer energy differences show increasing stabilization of the vinylidene tautomer (more negative ΔE_{v-a}) as the ancillary ligands become more electron rich. While the carbonyl-substituted Ru-2-CO favors the alkyne tautomer for all substituents except 60 (F/F), the electron-poor phosphines in Ru-2-PF₃ and Ru-2-PH₃ show improved stabilization of the vinylidene. The most electron rich phosphine in this series, Ru-2-PMe₃, achieves the switch to make the vinylidene the favored form for all pairs considered here. Likewise, while the vinylidene is favored for Ru-1-H with all substituents, this preference grows when replacing PH₃ with PMe₃ in Ru-1-Me. Considerable modification/fine tuning of tautomer energy preferences can thus be achieved by altering the ancillary ligands coordinated to the transition-metal center, again in good agreement with the experimental observations discussed above.

Interpretation. These data sets illustrate that the vinylidene tautomer is favored by the presence of electron-withdrawing substituents on the alkyne substrate and can be further supported by the presence of electron-donating ancillary ligands on the metal; meanwhile, the coordinated metal center determines the magnitude and sign of the tautomer energy preference. These results may be rationalized on the basis of the MO overlap diagrams (Figure S1, Supporting Information), which illustrate that the interaction between the metal and vinylidene ligand is likely to be strengthened by increased π back-bonding.^{51,52} The presence of electron-withdrawing groups on the vinylidene and/or electron-rich ligands coordinated to the metal center will promote metal to ligand back-donation and hence stabilize the vinylidene tautomer. This is particularly important, as vinylidenes are believed to be better π acceptors than the corresponding alkynes.^{46a}

As illustrated by the PCA maps, mono- and disubstituted substrates occupy different regions of chemical space; the increased stabilization of the vinylidene form relative to the alkyne in monosubstituted substrates is likely to contribute to this differentiation. Inspection of a subset of sterically similar substituents (small alkyl and *para*-substituted aryl) shows a reasonably high linear correlation between tautomer energy differences for mono- and disubstitution with these groups, suggesting that the observed differences may indeed be attributed mainly to steric differences. This is further supported by similar substrate dissociation energies (BE) for mono- and disubstituted versions of pairs, which are reasonably highly correlated once steric effects are accounted for (see the Supporting Information for details).

The exploration of metal effects suggests that the greatest preference for the vinylidene tautomer occurs on coordination to group 8 metals, although both the manganese and rhodium complexes also significantly stabilize the vinylidene. The greatest stabilization is present in the d⁶ **Ru-1-R** complexes, which appear to offer an optimal combination of π interactions and orbital size/availability for the vinylidene form.

Although the chromium and molybdenum complexes also have a d⁶ electronic configuration, albeit in an octahedral geometry, their five carbonyl ligands are very good π acceptors, reducing the scope for π back-bonding from metal to substrates and hence relatively disfavoring the vinylidene tautomer. In molybdenum, where π back-bonding is expected to be less extensive than in the chromium case,⁵³ the alkyne tautomer becomes more favorable. When the manganese complex is compared with the isostructural **Ru-2-CO**, again in the d⁶ electronic configuration, the increase of metal charge is likely to reduce the extent of π back-bonding and thus the stabilization of the vinylidene tautomer.

The group 10 and 11 complexes Pd, Pt-2, and Ag and all gold complexes, Au-1, Au-2, and Au-3, favor the alkyne tautomer for all substituents apart from 60 (F/F), although this preference is quite small for the d¹⁰ complex Pt-2. The increase in effective nuclear charge is likely to cause a contraction of d orbitals, which may affect the efficiency of π interactions and thus potentially reduce the capability for π back-donation. While this has little effect on the alkyne, the additional stabilization from this interaction appears to be more important for the vinylidene tautomer, which becomes energetically inaccessible. The progression from second- to third-row metals in the d^8 and d^{10} electronic configurations of isostructural complexes Pd/Pt-1 and Ag/Au-1 counters the trend observed for the group 6 metals (although first- to second-row changes were considered), likely due to the contribution of relativistic effects in the third transition series,⁵⁴ which may also be affected by additional shielding from the lanthanide contraction on the extent of π interactions.

The magnitudes and ranges of substrate dissociation energies are summarized in Table S5 (Supporting Information) and appear to confirm these global observations. The alkyne binding energies are relatively lower for **Ru-1-H** and higher for **Au-1**, while vinylidene binding energies show the opposite trend. The rhodium complex **Rh**, which has a d⁸ electronic configuration in a square-planar coordination geometry, lies in between: the metal center is more electron-rich than **Ru-1-H** but, unlike **Au-1**, an empty d orbital may still be accessible for ligand to metal π donation, albeit high in energy. This appears to be reflected in the binding energies (Table S5)—the rhodium–alkyne bond dissociation energies are similar in range and magnitude to those for gold–alkyne complexes, whereas

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rhodium-vinylidene binding resembles the ruthenium-vinylidene interactions more closely.

Consideration of the data shown in Figures 3, 6, and 7 also reveals an important additional facet of these results: the ordering of the relative stability of the vinylidene complexes in comparison to that of the alkyne is intrinsically related to the substituent and is essentially independent of the metal center. The metal simply moves this sequence to either higher or lower energy; hence, the correct choice of metal can ensure that the vinylidene (or alkyne) tautomer is thermodynamically favored. Indeed, on the basis of these results we can predict that complexes based on the $[RuCl_2(PR_3)_2]$ fragment will have the greatest preference for the vinylidene form; this can be further supported by selecting electron-withdrawing substituents and electron-donating ancillary ligands PR₃.

CONCLUSION

Experimentally, it has been demonstrated that catalyst optimization is an inherently multivariate process, requiring the screening of catalyst structure (metal and ligands), substrate scope, and reaction conditions (temperature, pressure, solvents, precursors, etc.). We have demonstrated here that computational chemistry can provide a valuable tool for the in silico screening and evaluation of at least three of these variables, exploring the effects of substituents, metal, and ligands on the thermodynamic tautomer preference for metal-coordinated alkyne and vinylidene pairs.

This approach can be used to identify not only unusual substituents, such as the β -heteroatom stabilization observed for tin (and, to a lesser extent, silicon), but also groups with similar properties and to explore the range of structural and electronic effects accessible by substituent variation. Consideration of a small number of metal complexes in this initial substituent screen has allowed us to identify the interplay between substituent and metal effects, leading to the selection of a subset of tautomeric pairs for which metal and ligand effects were explored more fully. On the basis of the resulting databases we have been able to formulate a protocol for the stabilization of vinylidenes in transition-metal complexes, suggesting that the metal fragment $[RuCl_2(PR_3^2)] = C =$ CHR^{1}], combined with electron-withdrawing substituents R^{1} and electron-rich groups R², would provide the ideal conditions favoring the vinylidene form thermodynamically. Clearly, kinetic effects would play a role as well, especially since most vinylidenes are prepared from the corresponding alkyne precursor, and this aspect is not currently captured by our database. While transition states and key intermediates for tautomer interconversion could be screened computationally, several possible mechanisms might need to be considered, placing this outside the scope of the present study. We also note that for monosubstituted pairs a third tautomeric form, the alkynyl hydride, may be energetically competitive,²⁶ further complicating prediction.

Identifying the key factors needed for the stabilization and isolation of metal-coordinated vinylidenes is of considerable interest in the context of the emerging utility of dual gold catalysis, although here only pair 60 (F/F) has been predicted to favor the vinylidene form in the gold complexes considered. This approach also serves as a proof of principle for the use of computationally generated databases for evaluation of organometallic complexes. While the number of variables considered here is too small to provide a truly rational design of stable

vinylidene compounds, our observations can perhaps guide experimental searches in the right direction.

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF and .xyz files giving experimental and computational details, crystallographic data, databases evaluating substituent, metal, and ligand effects, further diagnostic statistics, plots identifying all compounds and sample input files for all complexes considered, and computed Cartesian coordinates of representative, as well as unusual, complexes discussed in this study. This material is available free of charge via the Internet at http://pubs.acs.org. The .xyz file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home. aspx) for visualization and analysis.

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Notes

The authors declare no competing financial interest.

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