# **CHEMISTRY** A European Journal



# **Accepted Article**

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To be cited as: Chem. Eur. J. 10.1002/chem.201703820

Link to VoR: http://dx.doi.org/10.1002/chem.201703820

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# Experimental Evaluation of (L)Au Electron Donor Ability in Cationic Gold Carbene Complexes

Robert G. Carden, Nathan Lam, and Ross A. Widenhoefer\*

 $[(L)Au=C=CSi(Me)_2CH_2CH_2Si(Me)_2]^+B(C_6F_5)_4^-$  [L = P('Bu)\_2o-biphenyl or NHC] relative to the *p*-substituted aryl group in the  $\alpha$ -aryl-( $\beta$ , $\beta$ disilyl)vinyl cations  $[(p-C_6H_4X)-C=CSi(Me)_2CH_2CH_2Si(Me)_2]^+ B(C_6F_5)_4^-$ Similarly, <sup>19</sup>F NMR was employed to evaluate the  $\sigma$ - and  $\pi$ -electron donor properties of the (L)Au fragments in the neutral gold fluorophenyl complexes (L)Au(C\_6H\_4F) and in the cationic (fluorophenyl)methoxycarbene complexes  $[(L)AuC(OMe)(C_6H_4F)]^+$  $SbF_6^{-}$  [L = P(t-Bu)<sub>2</sub>o-biphenyl or IPr] relative to the *p*-substituted aryl group of the protonated monofluorobenzophenones [(p-C<sub>6</sub>H<sub>4</sub>X)(C<sub>6</sub>H<sub>4</sub>F)COH]<sup>+</sup> OTf<sup>-</sup>. The results of these studies indicate that relative to *p*-substituted aryl groups, the gold (L)Au fragments [L = P(t-Bu)<sub>2</sub>o-biphenyl or NHC] are significantly more inductively electron releasing and are comparable  $\pi$ -donors and for this reason, the extent of (L)Au  $\rightarrow$  C1 electron donation in gold carbene complexes appears to exceed that provided by a p-(dimethyamino)phenyl group. Furthermore, the  $[L = P(Bu)_2 o$ biphenyl]Au fragment is a nominally stronger electron donor than is the (IPr)Au fragment while both are significantly more inductively electron releasing than are the (PPh<sub>3</sub>)Au and [P(OMe)<sub>3</sub>]Au fragments.

#### Introduction

Cationic gold carbene complexes have been widely invoked as intermediates in a diverse range of gold(I)-catalyzed reactions, most notably envne cycloisomerizations and alkene cyclopropanation.<sup>[1,2]</sup> Although the intermediacy of gold carbenes in these transformations is supported by a wealth of experimental and computational data, there is still much debate regarding the nature of the gold-carbon bond, specifically the extent of  $d \rightarrow p$  back bonding and, more generally, the extent of electron donation from the (L)Au fragment to the electrondeficient C1 carbon atom.<sup>[2]</sup> For example, Fürstner concluded that stabilization of the  $\gamma,\gamma$ -dialkoxy allylic cation by the gold phosphine fragment in complexes 1 was "marginal" on the basis of C2-C3 rotational barriers (Figure 1).<sup>[3]</sup> However, DFT analysis of complexes 2 by Toste and Goddard suggested that stabilization of a tertiary allylic carbocation by a (Me<sub>3</sub>P)Au group

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is similar to that provided by a methoxy group.<sup>[4]</sup> Straub attributed the relatively short Au-C(Mes)<sub>2</sub> bond of the structurally characterized bis(mesityl)carbene complex 3 to the "significant, but not predominant double bond character Au=CMes2".[5] Similarly, structural analysis of the aold cyclopropyl(methoxy)carbene complex 4 suggested that the extent of (L)Au  $\rightarrow$  C electron donation was similar to that provided by a cyclopropyl group.<sup>[6]</sup> Conversely, Fürstner concluded that "there is only little back donation of electron density from gold to the carbene center" in the structurally characterized bis(anisyl)carbene complex 5.[7]





Embedded within the debate regarding the extent of (L)Au  $\rightarrow$  C electron donation in gold carbene complexes is the role of the supporting ligand in modulating the electron donor ability of the (L)Au fragment.<sup>[1,2]</sup> In particular, the computationally-derived bonding model for gold carbene complexes proposed by Toste and Goddard invokes an L–Au–C bonding network consisting of a three-center, four-electron  $\sigma$ -hyperbond and two orthogonal  $\pi$ -bonds involving donation of electron density from filled metal 5d orbitals to  $\pi$ -acceptor orbitals on the ligand and carbene carbon atom (Figure 2).<sup>[4]</sup> Owing to the nature of these orbitals and the competition for electron density, the better the sigma donor is L, the weaker is the sigma component of the Au–C1 bond, and similarly, the more  $\pi$ -acidic is L, the weaker is the Au  $\rightarrow$  C1 back donation.<sup>[4]</sup>





10.1002/chem.201703820

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The pronounced effect of the supporting ligand on the catalytic behavior of gold(I) carbene complexes is well documented,<sup>[8]</sup> including notable differences between Nheterocyclic carbene (NHC) ligands and dialkyl(o-biphenyl) phosphine ligands, which are among the most important supporting ligands employed in gold(I) catalysis and which are both considered to be strong  $\sigma$ -donors and weak  $\pi$ -acceptor ligands.<sup>[8]</sup> For example, Echavarren has shown that the product ratio formed in the cycloaddition/arylation of enyne 6 with indole catalyzed by [(L)AuNCMe]+ SbF6- complexes changed from 80:20 favoring product **7a** when  $L = P(t-Bu)_2o$ -biphenyl (**P1**) to 75:25 favoring product **7b** when L = IPr (Scheme 1).<sup>[9]</sup> Similarly, Barriault documented the reversal of 6-endo/5-exo selectivity in the gold(I)-catalyzed cycloisomerization of 1,6-enyne 8 employing either IPr or o-biphenylphosphine P2 as supporting ligand (Scheme 2).<sup>[10]</sup>



Scheme 1





In contrast to the analysis of ligand effects in gold(I) catalysis, experimental quantification of the effect of supporting ligand on the electron donor properties of (L)Au fragments, particularly those in cationic gold carbene complexes, is largely absent.<sup>[11]</sup> For example, Belpassi and co-workers measured the ligand-dependent activation barriers for rotation about the C–N(pyrrolidine) bond of gold NHC complexes **9** and correlated these values to the computationally derived extent of d  $\rightarrow \pi$  backbonding, although a direct comparison of alkyl phosphine and NHC ligands was not feasible (Scheme 3).<sup>[12]</sup> Hashmi investigated the ligand-dependent hydrolytic cleavage of  $\gamma$ , $\gamma$ -dialkoxyl gold carbene complexes **10** and correlated these reaction rates with the ligand-dependent LUMO energies of the carbene complex (Scheme 3).<sup>[13]</sup> The rate of hydrolysis was

found to track inversely with the  $\sigma$ -donor ability of the (L)Au fragment which increased in the order P(OR)<sub>3</sub> < PPh<sub>3</sub> < P2 < IPr. More directly, Chen has evaluated the ligand-dependent stabilization of cationic gold carbene complexes by measuring the energy barriers for the formation of gold arylidene complexes **11a** and **11b** via collision-induced dissociation (CID) of the corresponding gold sulfonyl-imidazolylidene precursors in the gas phase (Scheme 4).<sup>[14]</sup> Quantitative CID threshold analysis for the formation of **11a** and **11b** indicated that the IPr ligand stabilized the carbene by 2.3 ± 2.7 kcal/mol relative to **P1**, which, despite the error in this analysis, correlated well with the value of 1.8 kcal/mol predicted by DFT calculations.<sup>[14]</sup>



Scheme 3



Scheme 4

We therefore sought to experimentally evaluate the liganddependent electron donor ability of (L)Au fragments in cationic gold carbene complexes, including an assessment of the relative contributions  $\sigma$ - and  $\pi$ -donation from the (L)Au fragment. Our previous efforts directed toward the experimental evaluation of the electron donor ability of the (L)Au fragment in cationic gold carbene complexes analyzed the charge-dependent perturbation of C-C bond lengths in the cyclopropyl group of the cyclopropyl(methoxy) carbene complex 4 relative to protonated cyclopropyl ketones (Figure 1).<sup>[6]</sup> However, this approach suffered from the large experimental error in the C-C bond lengths relative to the extent of perturbation and the necessity of obtaining suitable crystals of both the carbene complexes and oxocarbenium model compounds for analysis. To circumvent these limitations, we sought to exploit the large dispersion and charge-dependent chemical shifts of heteronuclear NMR to evaluate charge distribution and (L)Au  $\rightarrow$  C electron donation in cationic gold carbene complexes.

Here we report the <sup>29</sup>Si NMR analysis of cationic gold ( $\beta$ , $\beta$ -disilyl)vinylidene complexes and the <sup>19</sup>F NMR analysis of neutral

fluorophenyl aold complexes and cationic aold flourophenyl(methoxy)carbene complexes in combination with the spectroscopic analysis of relevant organic model compounds. These data allowed comparisons to be made between the electron donor ability of various (L)Au fragments relative to psubstituted aryl groups. The key conclusions drawn from this work are three-fold. (1) Relative to p-substituted aryl groups, the (L)Au (L = P1, NHC) fragments are more inductively electron releasing and are comparable  $\pi$ -donors. (2) The net electron donor ability of the (L)Au (L = P1, NHC) fragments is significant and exceeds that of a p-(dimethylamino)phenyl group. (3) The-(P1)Au fragment is a nominally stronger electron donor than is the (IPr)Au fragment, although both are significantly more inductively electron releasing than are gold triarylphosphine or triarylphosphite fragments.

#### **Results and Discussion**

Cationic Gold (β,β-Disilyl)vinylidene Complexes. Guided by the work of Müller,<sup>[15-19]</sup> we recently reported that lowtemperature hydride abstraction from the gold acetylide complex 12a with triphenylcarbenium tetrakis(pentafluorophenyl)borate leads to selective formation of the thermally unstable cationic gold ( $\beta$ , $\beta$ -disilyl)vinylidene complex **13a** (Scheme 5).<sup>[20,21]</sup> Key to characterization of **13a** were resonances at  $\delta$  = 206 and 112 in the <sup>13</sup>C NMR spectrum assigned to the C1 and C2 vinylidene carbon atoms, respectively (Table 1). Also noteworthy was the significant decrease in the one-bond C1-C2 coupling constant of **13a** ( ${}^{1}J_{CC}$  = 60 Hz) relative to the acetylide precursor **13a** ( ${}^{1}J_{CC}$  = 91 Hz;  $\Delta^1 J_{CC}$  = 31 Hz) consistent with the diminished scharacter of the C2 atom of 13a relative to 12a.<sup>[22]</sup> Detection of the C1 and C2 vinylidene carbon atoms was complicated by the facile interconversion ( $\Delta G^{\ddagger} = 9.7$  kcal/mol) of these atoms, presumably via the gold  $\pi$ -disilacyclohexyne intermediate **Ia**.



Table	1.	Select	<sup>13</sup> C	and	<sup>29</sup> Si	NMR	data	for	gold	(β,β-disilyl)vinylidene
complexes 13 and $\alpha$ -aryl- $\beta$ , $\beta$ -disilyl vinyl cations 15.										

Compound	α-Substituent	δ <sup>13</sup> C (C1)	δ <sup>13</sup> C (C2)	δ <sup>29</sup> Si	Δδ <sup>29</sup> Si <sup>[a]</sup>
13a	P1	206	112	33.5	+54.1
13b	IPr	203.5	111.8	35.8	+56.7
13c	IMes	202.8	112.3	34.6	+55.2
13d	SIPr	198.5	114.2	36.2	+57.0
13e	SIMes	202.8	115.2	34.5	+55.3
15a	4-C <sub>6</sub> H₄Me	183.9	83.6	56.0	+70.2
15b	4-C <sub>6</sub> H₄OPh	185.8	84.5	52.3	+66.6
15c	4-C <sub>6</sub> H₄OMe	187.2	84.0	50.2	+65.0
15d	4-C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	194.9	85.9	37.3	+52.2

[a]  $\Delta \delta^{29}$ Si refers to the chemical shift difference between  $\delta^{29}$ Si of the vinylidene complex or vinyl cation and the  $\delta^{29}$ Si of the C(sp)-bound silicon atom of the neutral acetylene precursor.

The propensity of a silicon atom to stabilize a carbenium ion in the  $\beta$ -position via hyperconjucation ( $\beta$ -effect) is well documented.<sup>[23]</sup> The  $\beta$ -SiC hyperconjugation, in turn, leads to the depletion of electron density from the silicon atom, which is evidenced by a number of spectroscopic features, most notably the deshielding of the silicon atom in the <sup>29</sup>Si NMR spectrum.<sup>[15-</sup> <sup>19,24-26]</sup> Noteworthy therefore, was a single sharp resonance at  $\delta$ = 33.5 in the <sup>29</sup>Si NMR (-80 °C) spectrum of 13a that was significantly deshielded ( $\Delta\delta$  = +54.1) relative to the <sup>29</sup>Si NMR resonance of the C(sp)-bound silicon atom of gold acetylide complex **12a** ( $\delta = -20.6$ ; Table 1) owing to  $\beta$ -SiC hyperconjugation as represented by resonance structures C and D (Figure 3). Importantly, all of the spectroscopy of 13a is consistent with a symmetric Y-shaped or rapidly equilibrating distorted Y-shaped ground state structure, both of which have been validated for  $\alpha$ -substituted- $\beta$ , $\beta$ -disilyl vinyl cations.<sup>[15-19]</sup>



Figure 3. Relevant resonance contributors for gold vinylidene complexes 13.

It has been shown that the extent of  $\beta$ -SiC hyperconjugation across a range of *β*-silyl substituted carbenium ions is not constant, but increases with the increasing electron demand of the electron-deficient carbon atom.[15,17,24-26] Notably, Müller quantified this relationship in the context of the  $\alpha\mbox{-aryl-}\beta\mbox{,}\beta\mbox{-disilyl}$ vinyl cations 14 containing a six-membered disilacycle by establishing a correlation between the <sup>29</sup>Si NMR chemical shift and the Hammett-Brown  $\sigma^{+}$  parameter of the *p*-substituent of the  $\alpha$ -aryl group (Chart I).<sup>[15]</sup> The Hammett-Brown  $\sigma^+$  parameter has been employed to good effect to characterize the electron donor/acceptor properties of substituents that can effectively delocalize positive change to the reaction center through conjugation with more negative values indicating greater stabilization of positive charge.<sup>[27]</sup> We therefore reasoned that <sup>29</sup>Si NMR chemical shifts could be similarly employed to evaluate the electron donor ability of (L)Au fragment in the cationic gold  $(\beta,\beta$ -disilyl)vinylidene complex 13a and related

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derivatives, provided that a similar correlation could be established between the electron donor ability of the  $\alpha$ -substituent and the <sup>29</sup>Si NMR chemical shift of the  $\alpha$ -aryl- $\beta$ , $\beta$ -disilyl cations **15** containing a five-membered disilacycle (Chart I).<sup>[28,29]</sup>



Chart I.  $\alpha$ -Aryl- $\beta$ , $\beta$ -disilyl cations 14 and 15.

Toward the objective of evaluating the electron donor ability of the (L)Au fragment in gold  $(\beta,\beta$ -disilyl)vinylidene complexes, we first sought to expand the scope of gold vinylidene complexes with respect to supporting ligand. To this end, we synthesized the thermally unstable gold  $(\beta,\beta$ -disilyl)vinylidene complexes [(L)Au=C=CSi(Me)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(Me)<sub>2</sub>]<sup>+</sup> B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> [L = IPr (13b), IMes (13c), SIPr (13d), SIMes (13e)] that contained an NHC ligand employing procedures similar to that employed to that used to synthesize 13a. Conversely, attempted synthesis of gold (B,B-disilyl)vinylidene complexes containing less electron donating ligands such as PPh<sub>3</sub> proved unsuccessful. The thermally unstable complexes 13b - 13e were characterized without isolation by low temperature <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy (Table 1). The <sup>13</sup>C NMR spectra of complexes 13b - 13e displayed vinylidene C1 and C2 resonances at  $\delta$  = 203 - 198 and  $\delta$  = 112 - 115, respectively (Table 1), that in contrast to those of 13a, displayed no broadening at -80 °C. This observation pointed to a higher energy barrier for C2/C1 interconversion via the corresponding  $\pi$ -disilacyclohexyne intermediates Ib-e relative to 13a. Indeed, spin saturation transfer analysis of the IPr-supported gold ( $\beta$ , $\beta$ -disilyl)vinylidene complex **13b** provided an energy barrier of  $\Delta G^{\ddagger} = 11.4 \pm 0.3$ kcal/mol for interconversion of the C1 and C2 vinylidene carbon atoms. Each of the complexes 13b - 13e displayed a single sharp resonance in the <sup>29</sup>Si NMR spectrum at -80 °C. The <sup>29</sup>Si NMR chemical shifts (5<sup>29</sup>Si) showed only slight dependence on the nature of the supporting ligand and ranged from  $\delta^{29}Si = 34.5$ for 13e (L = SIMes) to  $\delta^{29}Si = 36.2$  for 13d (L = SIPr), all of which were slightly deshielded relative to phosphine derivative **13a** ( $\delta$  = 33.5; Table 1).

α-Aryl-β,β-Disilyl Vinyl Cations. We next sought to establish a correlation between the <sup>29</sup>Si NMR chemical shift (δ <sup>29</sup>Si) and the electron donor ability of the α-substituent in the α-aryl-β,β-disilyl vinyl cations **15**. To this end, the thermally unstable vinyl cations  $[(\rho-C_6H_4X)-C=CSi(Me)_2CH_2CH_2Si(Me)_2]^+B(C_6F_5)_4^-$  [R = Me (**15a**), OPh (**15b**), OMe (**15c**), NMe<sub>2</sub> (**15d**)] were synthesized via treatment of the corresponding aryl acetylenes **16a-d** with triphenylcarbenium tetrakis(pentafluorophenyl)borate at -78 °C in CD\_2Cl\_2 and were characterized without isolation by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy at 0 °C (Scheme 6).<sup>[30]</sup> The <sup>13</sup>C

NMR spectra of cations **15a** - **15d** displayed diagnostic resonances at  $\delta$  = 184 - 195 and 84 - 86 assigned to the C1 and C2 vinyl carbon atoms, respectively (Table 1). In the <sup>29</sup>Si NMR spectra of vinyl cations **15**,  $\delta$  <sup>29</sup>Si depended strongly on the electron donor ability of the α-aryl group and ranged from  $\delta$  = 56.0 for the *p*-tolyl substituted vinyl cation **15a** to  $\delta$  = 37.3 for the *p*-(dimethylamino)phenyl substituted vinyl cation **15d**, all of which were significantly deshielded ( $\Delta\delta$  <sup>29</sup>Si = 52.2 - 70.2) relative to the C(sp)-bound silicon atom of aryl acetylene precursors **16a-d** ( $\delta$  = -14.1 - -14.9).<sup>[31]</sup> A plot of the Hammett-Brown σ<sup>+</sup> parameter versus  $\delta$  <sup>29</sup>Si was linear ( $R^2$  = 0.99),<sup>[27]</sup> which established a correlation between the <sup>29</sup>Si NMR chemical shift and the electron donor ability of the α-aryl group of vinyl cations **15** (Figure 4).







**Figure 4.** Plot of the Hammett-Brown  $\sigma^+$  parameter versus  $\delta^{29}$ Si for  $\alpha$ -aryl, $\beta$ , $\beta$ -disilyl vinyl cations **15a-15d** where  $\delta^{29}$ Si = (13.2 ± 0.9) $\sigma^+$  + (59.9 ± 0.9), R = 0.99. Dotted lines represent the extrapolation of  $\delta^{29}$ Si for gold vinylidene complexes **13** onto this curve: from top to bottom **13d**, **13b**, **13d** + **13e**, **13a**.

**Discussion of** <sup>29</sup>**Si NMR Data.** From the <sup>29</sup>Si NMR data for gold  $\beta$ , $\beta$ -disilyl vinylidene complexes **13** and  $\alpha$ -aryl- $\beta$ , $\beta$ -disilyl vinyl cations **15**, a number of conclusions can be drawn with varying levels of confidence. Firstly, the correlation between  $\sigma^+$  and  $\delta^{29}$ Si for  $\alpha$ -aryl, $\beta$ , $\beta$ -disilyl cations **15** established that the <sup>29</sup>Si NMR chemical shift is sensitive to and dependent on the electron donor ability of the  $\alpha$ -substituent. Therefore, we can reasonably conclude that the <sup>29</sup>Si NMR chemical shift of gold vinylidene complexes **13** likewise reflects with similar sensitivity the electron-donor ability of the respective (L)Au fragment.

Therefore, these data indicate that the electron donor ability of the (L)Au fragments decreases in the order (**P1**)Au > (IMes)Au  $\approx$  (SIMes)Au > (IPr)Au > (SIPr)Au, although the magnitude of the difference between the most and least electron donating fragment is small and less than the difference between a *p*-tolyl group and a *p*-phenoxyphenyl group.

Taking the  $\delta^{29}$ Si of vinylidene complexes **13** and vinyl cations 15 as a measure of the electron donor ability of the  $\alpha$ substituent leads to the somewhat unexpected conclusion that all of the (L)Au fragments investigated ( $\delta^{29}$ Si = 36.2 - 34.5) are more electron donating than is the p-(dimethylamino)phenyl group of **15d** ( $\delta^{29}$ Si = 37.3). A number of considerations support the validity of this comparison. Firstly, the spectroscopy of both gold vinylidene complexes 13 U vinyl cations 15 are consistent with Y-shaped vinyl cation structures and, as such, the structures of 13 and 15 differ only in the nature of the  $\alpha$ substituent. Secondly, although a number of factors in addition to electron density are known to affect <sup>29</sup>Si NMR chemical shifts.<sup>[27]</sup> the similar structures and identical counterions of the complexes and the identical medium for <sup>29</sup>Si NMR analysis suggests that these other factors are largely mitigated. Thirdly, because the silicon atoms of 13 and 15 are far removed from the  $\alpha$ -substituent, steric or through-space perturbation of  $\delta$  <sup>29</sup>Si by the  $\alpha$ -substituent appears unlikely.

As was noted by Müller, the  $\alpha$ -substituent of an  $\alpha$ -substituted  $\beta$ , $\beta$ -disilyl vinyl cation stabilizes the C1 carbon atom through a combination of inductive effects and resonance electron donation.<sup>[15]</sup> The strong correlation between  $\sigma^+$  and  $\delta^{29}$ Si for  $\alpha$ aryl cations 15 indicates that for these compounds, the C1 stabilization from the aryl group is predominantly that of  $\pi$ donation. This does not, however, require or imply that the electronic stabilization of the C1 atom in the gold vinylidene complexes 13 by the (L)Au fragment is also predominantly that of  $\pi$ -donation. Here it is important to note that sp carbenium ions are more sensitive to inductive effects than are sp<sup>2</sup> carbenium ions owing to the greater s character and higher electronegativity of the sp carbenium ion relative to the sp<sup>2</sup> carbenium ion.[32,33] For example, ab initio calculations suggest that whereas a single α-CH<sub>3</sub> group stabilizes an alkyl cation by ~1.3 kcal/mol more than does an  $\alpha$ -trimethylsilyl group, the  $\alpha$ trimethylsilyl group stabilizes a vinyl cation by ~8.3 kcal/mol more than does an  $\alpha$ -methyl group.<sup>[32]</sup> In the former case, the superior hyperconjugation of the C-H bonds outweighs the lower electronegativity of the silicon atom whereas in the latter case, electronegativity differences take precedence.

Given the sensitivity of an sp carbenium ion to inductive stabilization, we considered that the apparent greater electron donor ability of the (L)Au fragments in gold vinylidene complexes **13** relative to the *p*-(dimethylamino)phenyl group of vinyl cation **15d** might be due to the greater inductive electron releasing ability of the (L)Au fragments relative to the *p*-(dimethylamino)phenyl group. Here it should be noted that in his analysis of  $\beta$ -SiC hyperconjugation in  $\alpha$ -aryl, $\beta$ , $\beta$ -disilyl cations **14**, Müller established a correlation between the Hammett-Brown  $\sigma^{+}$  parameter and  $\Delta\delta$  <sup>29</sup>Si, where  $\Delta\delta$  <sup>29</sup>Si represents the difference between  $\delta$  <sup>29</sup>Si of **14** and that of the C(sp)-bound silicon atom of the corresponding neutral aryl silyl alkyne precursor.<sup>[15]</sup> Because

σ-donation from the α-aryl group would be felt in both the silyl alkyne moiety and the vinyl cation, whereas π-donation from the α-aryl group would be felt only in the vinyl cation, the Δδ <sup>29</sup>Si values presumably reflects the π-donor ability of the α-aryl group to a greater extent than does δ <sup>29</sup>Si. However, because δ <sup>29</sup>Si of the silyl alkynes was largely invariant of the nature of the α-aryl group, similarly strong correlations exists between the Hammett-Brown σ<sup>+</sup> parameter and either δ <sup>29</sup>Si or Δδ <sup>29</sup>Si for vinyl cations **14**.

As was the case for vinyl cations 14 and their neutral silyl alkyne precursors, the  $\delta$  <sup>29</sup>Si of the C(sp)-bound silicon atom of aryl silyl alkynes 16 was largely invariant of the nature of the  $\alpha$ aryl group and  $\alpha$ -aryl, $\beta$ , $\beta$ -disilyl cations **15** displayed equally good correlation between the Hammett-Brown  $\sigma^{\!\!+}$  and either  $\delta$ <sup>29</sup>Si ( $R^2 = 0.99$ ) or  $\Delta\delta$  <sup>29</sup>Si ( $R^2 = 0.99$ ; Figure 5). Likewise, the  $\delta$ <sup>29</sup>Si of the C(sp)-bound silicon atom of the gold acetylide complexes **12** differed by  $\leq 0.3$  ppm. However, the  $\delta^{29}$ Si of the C(sp)-bound silicon atom of arvl silvl alkynes 16 are deshielded by ~6 ppm relative to the  $\delta$  <sup>29</sup>Si of the C(sp)-bound silicon atom of gold acetylide complexes 12. Because there is no net  $\pi$ bonding in the Au-C bond of a gold acetvlide complex.<sup>[34]</sup> these differences in the  $\delta^{29}$ Si of aryl acetylenes 16 relative to gold acetylide complexes 12 can presumably be attributed to the greater inductive electron releasing ability of the (L)Au fragments of 12 relative to the p-substituted aryl groups of 16. It therefore follows that  $\sigma$ -donation from the (L)Au fragment likewise represents a significant component of the net (L)Au  $\rightarrow$ C1 electron donation in gold vinylidene complexes 13, as reflected by the respective  $\delta$  <sup>29</sup>Si values. In this context, comparison of the  $\Delta\delta$  <sup>29</sup>Si values for gold vinylidene complexes 13 and vinyl cations 15 is instructive (Table 1, Figure 5). In particular, the  $\Delta\delta$  <sup>29</sup>Si for vinyl cation **15d** (+52.2) is smaller than is  $\Delta\delta^{29}$ Si for any of the gold vinylidene complexes **13** ( $\geq$  +54.1), suggesting that the *p*-(dimethylamino)phenyl is a stronger  $\pi$ donor than are any of the (L)Au fragments.



**Figure 5.** Plot of the Hammett-Brown  $\sigma^+$  parameter versus  $\Delta\delta^{29}$ Si for  $\alpha$ -aryl, $\beta$ , $\beta$ -disilyl vinyl cations **15a-15d** where  $\Delta\delta^{29}$ Si = (12.6 ± 0.9) $\sigma^+$  + (73.9 ± 0.9), R = 0.99. Dotted lines represent the extrapolation of  $\delta^{29}$ Si for gold vinylidene complexes **13** onto this curve: from top to bottom **13d**, **13b**, **13d** + **13e**, **13a**.

Neutral Gold Fluorophenyl Complexes. Our analysis of the <sup>29</sup>Si NMR spectroscopy of gold vinylidene complexes 13, vinyl cations 15, and their neutral acetylenic precursors pointed to the greater inductive electron releasing ability of the (L)Au fragments vis-à-vis p-substituted aryl groups. To gain greater insight into the ligand-dependent  $\sigma$ - and  $\pi$ -donor properties of the (L)Au fragment, we sought to determine the inductive  $(\sigma_i)$ and resonance ( $\sigma_r$ ) substituent parameters of (L)Au fragments employing the <sup>19</sup>F NMR method developed by Taft.<sup>[35]</sup> The <sup>19</sup>F NMR chemical shifts of *m*- and *p*-substituted fluorobenzenes (FC<sub>6</sub>H<sub>4</sub>X) represent a sensitive probe of the electron donor/acceptor properties of the substituent X.[35] For a substituent X, the <sup>19</sup>F chemical shifts of m-FC<sub>6</sub>H<sub>4</sub>X ( $\delta_m$ ) and p- $FC_6H_4X$  ( $\delta_p$ ) relative to fluorobenzene internal standard are related empirically to the inductive ( $\sigma_i$ ) and resonance ( $\sigma_r$ ) substituent parameters according to the relationships  $\sigma_i = (\delta_m - \delta_m)$ 0.60)/-7.1 and  $\sigma_r = (\delta_p - \delta_m)/-29.5$ . The inductive parameter  $\sigma_i$  is a reflection of the through-space and inductive electron releasing/accepting properties of the substituent whereas the resonance parameter is a reflection  $\pi$ -donor/acceptor properties of the substituent. A negative  $\sigma_i$  or  $\sigma_r$  value indicates that the substituent is electron donating relative to hydrogen. This technique has been employed to determine the inductive and resonance donor/acceptor properties of hundreds of substituent groups<sup>[36]</sup> and has been extended to include numerous transition metal fragments<sup>[37]</sup> including a handful of gold(I)-ligand fragments. However absent are data for the (PR<sub>3</sub>)Au and (NHC)Au fragments germane to gold(I) catalysis.[38,39]

To determine the inductive  $(\sigma_i)$  and resonance  $(\sigma_r)$ substituent parameters for (L)Au fragments, we synthesized an eight-membered family of gold *m*- and *p*-fluorophenyl complexes (L)Au(C<sub>6</sub>H<sub>4</sub>F) [*m*-17/*p*-17; L = P1 (a), IPr (b) PPh<sub>3</sub> (c), P( ${}^{t}Bu$ )<sub>3</sub> (d)] via transmetallation of *m*- or *p*-fluorophenylboronic acid with (L)AuCl (Table 2).<sup>[40]</sup> The <sup>19</sup>F NMR chemical shifts ( $\delta_m$  and  $\delta_p$ ) and the associated inductive ( $\sigma_i$ ) and resonance parameters ( $\sigma_r$ ) of complexes 17 and values for  $L = P(OPh_3)_3$  taken from the literature are compiled in Table 2. In accord with our expectations, these data indicate that the gold fragments (P1)Au and (IPr)Au, in particular, are strongly inductively electron releasing and are modest  $\pi$ -donors. Notably, the (P1)Au and (IPr)Au fragments are much more inductively electron releasing than are the triarylphosphine and triarylphosphite fragments (Ph<sub>3</sub>P)Au and [P(OPh)<sub>3</sub>]Au and are likewise much more inductively electron releasing than is a simple aryl group. As a point of comparison, the inductive and resonance substituent parameters for a phenyl group are  $\sigma_i$  = 0.14 and  $\sigma_r$  = 0.01.  $^{[35]}$ Also worth noting is that these data reveal no detectable difference between the  $\sigma$ - and  $\pi$ -electron donor/acceptor properties of (P1)Au and (IPr)Au.

**Table 2.** <sup>19</sup>F NMR chemical shift data  $(\Delta \delta_m \text{ and } \Delta \delta_p)$  and inductive  $(\sigma_i)$  and resonance  $(\sigma_r)$  parameters for gold *m*- and *p*-fluorophenyl complexes **17**.

НО В		AuCl, Cs rOH, 50 °	2 <sup>CO3</sup> C, 24 h	(L)Au—	F //p- <b>17</b>
cmpd	L	δm <sup>[a]</sup>	δ <sub>p</sub> <sup>[a]</sup>	σι	σr
17a	P1	3.72	5.71	-0.44	-0.07
17b	IPr	3.74	5.85	-0.44	-0.07
17c	PPh <sub>3</sub>	2.43	3.51	-0.26	-0.04
17d	P <sup>t</sup> Bu <sub>3</sub>	3.65	4.51	-0.43	+0.01
[b]	P(OPh) <sub>3</sub>	2.10	2.95	-0.21	-0.02

[a]Chemical shift relative to  $C_6H_5F$ , with positive increments indicating more negative chemical shifts. [b]Taken from ref 39.

Gold Fluorophenyl(methoxy)carbene Carbene Complexes. <sup>19</sup>F NMR analysis of gold fluorophenyl complexes 17 revealed the strong inductive electron releasing ability and modest  $\pi$ -donor properties of the (L)Au (L = IPr, P1) fragments. We were concerned, however, that the relatively low electron demand of the fluorophenyl group in compounds 17 might mask both the  $\pi$ -donor potential of the (L)Au fragments and subtle differences between the  $\sigma/\pi$  electron donor properties of the (P1)Au and (IPr)Au fragments that might be revealed under the conditions of higher electron demand found in cationic carbene complexes. Toward an evaluation of the  $\sigma$ - and  $\pi$ -electron donor properties of the (P1)Au and (IPr)Au fragments in cationic gold carbene complexes, we first determined the inductive and resonance parameters for the (L)AuC(OMe) (L = P1, IPr) substituent groups of the cationic aold fluorophenyl(methoxy)carbene complexes  $[(L)AuC(OMe)(C_6H_4F)]^+$  SbF<sub>6</sub><sup>-</sup> [L = P1 (*m*/*p*-18a), IPr (*m*/*p*-18b)] via <sup>19</sup>F NMR analysis. We targeted the methoxycarbene complexes 18 for analysis because our previous analysis of the gold methoxy(cyclopropyl)carbene complex 4 established that the C1 methoxy group provided needed stabilization to the complex without masking the electron donor effects of the (L)Au fragment.<sup>[6]</sup>

The requisite flourophenyl(methoxy)carbene complexes 18 were isolated as thermally unstable yellow microcrystalline solids in 32-52% yield via metathesis of the chromium fluorophenyl(methoxy)carbene complexes  $(CO)_5 CrC(OMe)(C_6H_4F)$  (m/p-19) with a 1:1 mixture of (L)AuCl and AgSbF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane at -20 °C (Scheme 7). As was the case with the cationic gold vinylidene complexes 13, efforts to synthesize the corresponding triphenylphosphine  $(PPh_3)AuC(OMe)(C_6H_4F)$ carbene complexes proved unsuccessful. Complexes 18 were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F spectroscopy. Notably, the C1 carbene resonances of complexes 18 appeared at  $\delta$  = 282 - 290 in the <sup>13</sup>C NMR spectra, which is typical of gold Fischer carbene complexes.[41] <sup>19</sup>F NMR analysis of complexes 18 provided inductive and resonance parameters for the respective (L)AuC(OMe) substituent groups of  $\sigma_i$  = +0.60 and  $\sigma_r$  = +0.61 for L = **P1** and  $\sigma_i$  = +0.62 and  $\sigma_r$  = +0.62 for L = IPr (Table 3). The large positive values indicate

charge on the carbene C1 atom.

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that the (L)AuCOMe substituent group is highly electron withdrawing, as would be expected owing to the net positive





**Table 3.** <sup>19</sup>F NMR chemical shift data and inductive ( $\sigma_i$ ) and resonance ( $\sigma_r$ ) parameters for gold fluorophenyl(methoxy)carbene complexes **18** and protonated monofluorobenzophenones **20**-HOTf.

cmpd	substituent	$\delta_m^{[a]}$	$\delta_p^{[a]}$	σι	σr
18a	(P1)AuC(OMe)	-3.69	-21.58	+0.60	+0.61
18b	(IPr)AuC(OMe)	-3.78	-21.92	+0.62	+0.62
<b>20a</b> ●HOTf	(Ph)C(OH)	-6.55	-30.11	+1.01	+0.80
20b•HOTf	(p-C <sub>6</sub> H₄Br)C(OH)	-677	-29.58	+1.04	+0.77
20c•HOTf	(p-C <sub>6</sub> H₄Me)C(OH)	-6.22	-27.27	+0.96	+0.71
20d•HOTf	(p-C <sub>6</sub> H₄OPh)C(OH)	-5.82	-23.71	+0.90	+0.61
20e•HOTf	(p-C <sub>6</sub> H₄OMe)C(OH)	-5.85	-22.05	+0.91	+0.55

[a]Chemical shift relative to  $C_6H_5F,$  with positive increments indicating more negative chemical shifts

Protonated Monofluorobenzophenones. The substituent parameters determined for the (L)AuC(OMe) fragments of gold carbene complexes 18 reflect the electron demand of the C1 carbene atom, which is stabilized by electron donation from both the (L)Au fragment and the OMe moiety. To evaluate the contribution of the (L)Au fragment to the electronic stabilization of the C1 carbon atom of complexes 18, we determined the inductive and resonance parameters for the (p-C<sub>6</sub>H<sub>4</sub>X)COH substituent groups of the protonated monofluorobenzophenone derivatives  $[(p-C_6H_4X)(C_6H_4F)COH]^+$  OTf<sup>-</sup> (*m/p*-20•HOTf) [X = H (a), Br (b), Me (c), OPh (d), OMe (e)] via <sup>19</sup>F NMR analysis.<sup>[42,43]</sup> Although the OH group of oxocarbenium ions 20-HOTf represents an obvious deviation from the OMe group of fluorophenyl(methoxy)carbene complexes 18, Olah has previously shown there is no significant difference in the C=O bond polarization of protonated and methylated ketones,<sup>[44]</sup> and potential hydrogen bonding between OTf- and the protonated ketone becomes insignificant at high HOTf concentration such as those employed in these reactions.<sup>[45]</sup> Therefore, we reasoned that if correlations could be established between the inductive electron releasing ability and  $\pi$ -donor ability of the C1 aryl groups with the  $\sigma_i$  and  $\sigma_r$  parameters, respectively, of the (p-C<sub>6</sub>H<sub>4</sub>X)COH substituents, then meaningful comparisons could be made between the inductive electron releasing ability and  $\pi$ donor ability of the (L)Au fragments of 18 relative to psubstituted aryl groups of 20-HOTf.

The requisite protonated monofluorobenophenones 20-HOTf were generated *in situ* via protonation of the corresponding

monofluorobenzophenones (p-C<sub>6</sub>H<sub>4</sub>X)(C<sub>6</sub>H<sub>4</sub>F)CO m/p-20 with excess triflic acid (≥10 equiv) in CD<sub>2</sub>Cl<sub>2</sub> (Scheme 8).<sup>[45]</sup> Formation of oxocarbenium ions 20.HOTf was established by the significant deshielding of the oxygen-bound carbon atom ( $\Delta\delta$ ≈ 23) of 20•HOTf relative to 20 in the <sup>13</sup>C NMR spectra. Complete conversion of 20 to 20. HOTf was established by titrating 20 with HOTf until no further change in the NMR spectra was observed. The <sup>19</sup>F NMR chemical shifts ( $\delta_m$  and  $\delta_p$ ) and the associated inductive ( $\sigma_i$ ) and resonance parameters ( $\sigma_r$ ) for the (p-C<sub>6</sub>H<sub>4</sub>X)COH substituent groups of oxocarbenium ions 20-HOTf are shown in Table 3. The inductive parameters for the  $(p-C_6H_4X)(COH)$  substituents ranged from  $\sigma_i = +1.04$  for X = Br to  $\sigma_i$  = +0.90 for X = OPh, all of which are significantly more positive than are the inductive parameters for the (L)AuC(OMe) substituents ( $\sigma_i$  = +0.60 - +0.62). The resonance parameters for the  $(p-C_6H_4X)(COH)$  substituents were more sensitive to the nature of the p-C<sub>6</sub>H<sub>4</sub>X group and ranged from  $\sigma_r$  = +0.80 for X = H to  $\sigma_r$  = +0.55 for X = OMe, as compared to values of  $\sigma_r$  = +0.61 - +0.62 for the (L)AuC(OMe) substituents.



Scheme 8

Interpretation of the  $\sigma_r$  parameter for the (p-C<sub>6</sub>H<sub>4</sub>X)COH groups of **20**•HOTf and comparison to those of the (L)AuC(OMe) groups of 18 requires consideration of the structures of protonated benzophenones. It has been shown that the  $log(pK_a)$ of protonated monosubstituted benzophenone derivatives display a linear correlation with the Hammett-Brown  $\sigma^+$ parameter ( $\rho^{\Box}$  = 1.09),<sup>[46]</sup> but the reaction constant is attenuated relative to those obtained for the correlation of  $log(pK_a)$  with  $\sigma^+$ for protonated benzaldehyde ( $\rho^{\Box} = 1.86$ )<sup>[47]</sup> and acetophenone  $(\rho^{\Box} = 2.17)^{[48]}$  derivatives. These differences can be attributed in part to twisting of the aryl rings of the benzophenones to minimize the unfavorable van der Walls interactions of the ortho hydrogen atoms,<sup>[49]</sup> which attenuates the  $\pi$ -overlap between the aryl groups and the electron deficient carbonyl carbon atom. Nevertheless, the much lower  $\sigma_r$  values relative to  $\sigma_i$  for (p- $C_6H_4X$ )COH substituents and the greater sensitivity of  $\sigma_r$  ( $\Delta\sigma_r =$ 0.25) relative to  $\sigma_i$  ( $\Delta \sigma_i = 0.14$ ) suggests that the electron deficient carbonyl carbon atom of 20-HOTf is stabilized primarily via  $\pi$ -donation.

A plot of the Hammett  $\sigma$  parameter for aryl substituent X versus  $\sigma_i$  for the (*p*-C<sub>6</sub>H<sub>4</sub>X)(COH) substituent of protonated monofluorobenzophenones **20**•HOTf established a correlation between these parameters [ $\sigma_i = (0.26 \pm 0.03)\sigma + (0.99 \pm 0.01)$ ;  $R^2 = 0.96$ ] (Figure 6) that was clearly superior to the correlation between the Hammett-Brown  $\sigma^+$  parameter and  $\sigma_i$  ( $R^2 = 0.88$ ). Similarly, a plot of the Hammett-Brown  $\sigma^+$  parameter for aryl substituent X versus  $\sigma_r$  for the (*p*-C<sub>6</sub>H<sub>4</sub>X)(COH) substituents

established a modest correlation between these parameters  $[\sigma_r = (0.27 \pm 0.5)\sigma^+ + (0.77 \pm 0.02); R^2 = 0.92;$  Figure 6], whereas no correlation was observed between  $\sigma$  and  $\sigma_r$ . These correlations indicate that differences in  $\sigma_i$  of the  $(p\text{-}C_6H_4X)\text{COH}$  substituent are determined primarily by the inductive electron releasing ability of the  $p\text{-}C_6H_4X$  aryl group and, likewise, that differences in  $\sigma_r$  of the  $(p\text{-}C_6H_4X)\text{COH}$  substituent are determined primarily by the  $\pi\text{-}\text{donor}$  ability of the  $p\text{-}C_6H_4X$  aryl group.



**Figure 6.** Plots of  $\sigma$  versus  $\sigma_i$  ( $\Box$ ) and  $\sigma^+$  versus  $\sigma_r$  (O) for the (p-C<sub>6</sub>H<sub>4</sub>X)(COH) substituents of **20**-HOTf where  $\sigma_i = (0.26 \pm 0.03)\sigma + (0.99 \pm 0.01)$ ;  $\mathcal{R}^2 = 0.96$  and  $\sigma_r = (0.27 \pm 0.5)\sigma^+ + (0.77 \pm 0.02)$ ;  $\mathcal{R}^2 = 0.92$ .

Discussion of substituent constants for 18 and 20•HOTf. From the observed correlations between  $\sigma$  and  $\sigma_i$  and between  $\sigma^{+}$  and  $\sigma_{r}$  for the (p-C<sub>6</sub>H<sub>4</sub>X)COH substituents of protonated monofluorobenzophenones 20-HOTf, it follows that any significant differences in the  $\sigma_i$  and  $\sigma_r$  values of the (L)AuC(OMe) (L = P1, IPr) fragments of 18 or between the (L)AuC(OMe) and (p-C<sub>6</sub>H<sub>4</sub>X)COH substituents can be attributed to differences in the inductive electron releasing ability and  $\pi$ -donor ability, respectively, of the corresponding (L)Au and/or p-C<sub>6</sub>H<sub>4</sub>X groups. Therefore, several conclusions can be reasonably drawn from comparison of these data. Firstly, (P1)Au is a nominally greater inductive electron releasing ability and  $\pi$ -donor ability than does (IPr)Au, although the differences are less than those between a phenyl group and a p-bromophenyl group. Secondly, the significantly larger (more positive) inductive parameters of the (p-C<sub>6</sub>H<sub>4</sub>X)COH substituents ( $\sigma_i = +1.04 - 0.90$ ) relative to those of the (L)AuC(OMe) substituents ( $\sigma_i = 0.60 - 0.62$ ) further supports the contention that the (L)Au gold fragments are significantly more inductively electron releasing than are psubstituted aryl groups. Indeed, the observed correlation between  $\sigma_i$  and  $\sigma$  (Figure 6) predicts a  $\sigma_i$  value of +0.78 for the hypothetical (p-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)(COH) substituent [ $\sigma$ (NMe<sub>2</sub>) = -0.83], which suggests that the (L)AuC fragments are significantly more inductively electron releasing than is a *p*-(dimethylamino)phenyl group. Thirdly, comparison of the resonance parameters for the  $(p-C_6H_4X)COH$  and (L)AuC(OMe) substituents indicates that the  $\pi$ -donor ability of the (L)Au fragments is lower than that of a pmethoxyphenyl group but comparable to that of a p-Given the potential attenuation of  $\pi$ phenoxyphenyl group.

overlap of the aryl rings in **20**•HOTf, these comparisons suggest that the (L)Au groups are modest  $\pi$ -donors relative to *p*-substituted aryl groups.

#### Conclusions

We have analyzed the spectroscopy of cationic gold ( $\beta$ , $\beta$ disilyl)vinylidene complexes 13, neutral gold fluorophenyl complexes 17, cationic gold fluorophenyl(methoxy)carbene complexes 18, and relevant organic model compounds to evaluate the ligand-dependent electron donor ability of the (L)Au fragment in gold carbene complexes relative to p-substituted aryl groups. The first key conclusion drawn from these experiments is that the (P1)Au fragment is a nominally stronger electron donor in cationic gold carbene complexes than is the (IPr)Au fragment. For example, <sup>29</sup>Si NMR analysis of the cationic gold vinylidene complexes 13 suggests that the (P1)Au fragment is more electron donating than is (IPr)Au, although the difference is less than that between a *p*-tolyl group and a *p*-phenoxyphenyl group. Similarly, <sup>19</sup>F NMR analysis of the cationic gold fluorophenyl(methoxy)carbene complexes 18 suggests that (P1)Au is both more inductive electron releasing ability anda better  $\pi$ -donor than is (IPr)Au, although the differences are less than the differences between a phenyl group and a p-<sup>19</sup>F NMR analysis of neutral gold bromophenyl group. fluorophenyl complexes 17 revealed no detectable difference between either the inductive electron releasing ability or  $\pi$ -donor ability of the (P1)Au and (IPr)Au fragments. Although the contention that the (P1)Au fragment is more inductively electron releasing than is the (IPr)Au fragment, albeit minimally, appears to contradict the general perception of IPr as a strong donor ligand to gold,<sup>[50]</sup> both our analysis of the kinetics of gold(I)catalyzed allene racemization<sup>[51]</sup> and Belpassi's computational analysis of the electronic structure of cationic gold carbonyl complexes<sup>[52]</sup> support this conclusion.

Regarding the electron donor ability of the (L)Au fragments relative to p-substituted aryl groups, <sup>29</sup>Si NMR analysis of the gold  $(\beta,\beta$ -disilyl)vinylidene complexes **13** and the  $\alpha$ -aryl- $\beta,\beta$ disilyl vinyl cations 15 suggests that the electron donor ability of the (L)Au (L = P1, NHC) fragments exceeds that of p-(dimethyamino)phenyl group. Given the sensitivity of sp carbenium ions to inductive effects,[29,30] comparative <sup>29</sup>Si NMR analysis of the neutral gold acetylide complexes 12 and aryl acetylenes 16 suggests that  $\sigma$ -donation represents a major component of the net (L)Au  $\rightarrow$  C electron donation in gold This hypothesis was corroborated vinylidene complexes 13. through <sup>19</sup>F NMR analysis of gold fluorophenyl complexes 17 <sup>19</sup>F and comparative NMR analysis of the aold fluorophenyl(methoxy)carbene complexes 18 and the protonated monoflurobenzophenone derivatives 20-HOTf. These analyses revealed that the inductive electron releasing ability of the (L)Au (L = P1, IPr) fragments significantly exceeds that of a p-(dimethyamino)phenyl group, whereas the  $\pi$ -electron donor ability of the (L)Au fragment was equal to or less than that provided by a *p*-phenoxyphenyl group.

Taken in aggregate, a picture emerges from these studies of (L)Au (L = P1, IPr) fragments as strongly inductively electron releasing and modest  $\pi$ -donors, with very similar electron donor properties between the two fragments. These subtle differences in electron donor ability, coupled with the different steric profiles of the ligands, is apparently sufficient to lead to the sometimes disparate catalytic behavior observed for (P1)Au and (IPr)Au complexes.<sup>[8-10]</sup> The recognition of these (L)Au fragments as strongly inductively electron releasing is significant because extant discussions of (L)Au  $\rightarrow$  C electron donation in the context of cationic gold carbene complexes has focused nearly exclusively on d  $\rightarrow$  p backbonding as the mechanism for stabilization of the electron-deficient carbene carbon atom. Rather, our studies strongly suggest that  $d \rightarrow p$  backbonding represents a minor component of the total (L)Au  $\rightarrow$  C electron donation in gold carbene complexes. It therefore follows that any evaluation of the electron donor ability of (L)Au fragments in cationic gold carbene complexes that considers only  $d \rightarrow p$ backbonding likely significantly underestimates the full extent of (L)Au  $\rightarrow$  C electron donation.

Relevant to the discussion of the inductive electron releasing ability of the (L)Au fragment is the ambiguity regarding the electronegativity of gold. On the Pauling scale, gold is the most electronegative of the transition metals, with a value of 2.54 relative to 2.55 for carbon. However, other measures of electronegativity suggest that gold is considerably more electropositive than is carbon, as is suggested by our studies. For example, on the Mulliken-Jaffe scale, gold has a value of 1.87 versus 2.66 for sp<sup>2</sup> hybridized carbon and 2.28 for silicon.<sup>[53]</sup>

#### Acknowledgements

We acknowledge the NSF (CHE-1465209) for support of this research. RGC was supported through a GAANN fellowship (P200A150114).

**Keywords:** gold • vinylidenes • carbenes • Hammett analysis • sigma stabilization

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Spectroscopic analysis of cationic gold ( $\beta$ , $\beta$ -disilyl)vinylidene complexes, gold fluorophenyl complexes, cationic gold fluorophenyl(methoxy)carbene complexes, and relevant organic model compounds indicate that (L)Au fragments such as (IPr)Au and [P('Bu)<sub>2</sub>o-biphenyl)]Au are strongly inductively electron releasing and a  $\Box$  modest  $\pi$ -donors and that the net electron donor ability of these (L)Au fragments appears to exceed that provided by a *p*-(dimethylamino)phenyl group. Robert G. Carden, Nathan Lam, and Ross A. Widenhoefer\*

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Experimental Evaluation of (L)Au Electron Donor Ability in Cationic Gold Carbene Complexes